Graftable Antioxidant For Peroxide Crosslinked Polyethylene: Stabilisation and Performance

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Doctor of Philosophy

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November 2014

ASTON UNIVERSITY

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SUMMARY

The overall aim of this work was to investigate antioxidant systems based on three synthesized reactive (graftable) hindered amine stabilisers (g-HAS) used in combination with either synthesized reactive (g-Ph), or conventional, hindered phenols to prevent antioxidant migration and offer effective long term stabilisation under aggressive solvent and water extractive environments, in peroxide crosslinked high density polyethylene (HDPE) targeted for use in water pipe applications (both potable and hot water). This study also addressed the question of interference of the peroxide initiated crosslinking process with grafted and conventional (non-grafted) hindered phenol antioxidants.

Pipes and laboratory thin film samples highly crosslinked by peroxides were prepared using commercial and laboratory production methods. The melt grafting of reactive HAS stabilisers on HDPE was optimized along with the polymer crosslinking using two different laboratory developed methods; **a two-step process,** where the HAS-grafting was achieved in a first step followed by polymer crosslinking**,** and a **one-step** method where both grafting and crosslinking took place in one step. The effect of the chemical composition and processing conditions of the reaction system in the two-step method were investigated using an internal batch mixer in order to optimize the extent of grating of the stabilizers. It was found that lower peroxide concentration and a higher processing temperature gave rise to an increase in the level of HAS-grafting with lower extent of HAS-homopolymer formation. In the case of the pipes which were produced using one of two commercial continuous processes, the **Engel process (PEX_{Eng})** and a **High Speed Extrusion-IR Process (PEX_{HS}),** the formulations were not optimised due to lack of time but their choice was based on both the experience (by the sponsor company) with commercial pipe production using conventional (non-graftable) antioxidants (AO), and the laboratory-optimised grafting-crosslinking methods developed in this work. **PEX_{HS} pipes** showed more homogenous AO distribution compared to the PEX_{Eng} pipes and this is almost certainly due to the lack of sheer in the Engel process.

PEX pipes (e.g. PEX_{Eng}) containing the g-HAS (used with a g-Ph or a conventional/non-graftable hindered phenol, (Irganox 1076) were found to have both high AO-retention and high long term polymer thermal stability especially under exhaustive solvent extraction environment, in contrast, similarly prepared pipes but containing conventional AOs (with similar AO functions), were shown to suffer from high AO-losses, thus, resulting in a much lower long term thermal stability, LTTS. Furthermore, the amount of AOs retained in the polymer after the commercial Pipe production processes (e.g. in PEX_{Eng}) revealed that the grafted antioxidants, e.g. the g-Ph, (DBPA) was retained to a much higher extent than the commercial hindered phenol Irganox 1076 (retention of 75% vs 50%, respectively). This suggests that the peroxide crosslinking process does not interfere (or interferes much less) with the g-AOs compared to non-graftable conventional AOs. Similarly, a very high retention of over 90% of the g-Ph was found in the PEX_{HS} pipes (e.g. Pipe X6) compared to similar pipes containing Irganox 1076 (PEX_{HS} pipe X1) with retention of only 46% after sequential solvent extraction using DCM/xylene. However, extraction with boiling water has resulted in hydrolysis of the ester groups of the grafted AOs (the g-Ph) resulting in their partial loss in the water extracts. Qualitative analysis of transformation products of g-Ph and of Irganox 1076 (and Irg 1010) obtained from PEX_{HS} pipes extracts in DCM and in boiling water and their identity were determined using HPLC-MS analysis.

Keywords: PEX, crosslinking, grafting, reactive antioxidants, long term thermal stability

Acknowledgement

I would like to express my deepest gratitude to my supervisor Professor Sahar Al-Malaika for her valuable guidance and constructive suggestions throughout this project.

I would like to thank Uponor Ltd., for their financial support for this project and I wish to acknowledge with gratitude in particular Drs David Harget, Jyri Jarvenkyla and Patrik Roseen for the numerous meetings and very valuable discussions throughout the period of this project.

It has been great pleasure to be part of the PPP-group at Aston University, I would like to acknowledge Dr Husam Sheena for advice and technical support, along with present and past members of the group. I would also like to thank Dr Michael Perry and Dr Khalid Doudin for their assistance in performing the NMR analysis.

My great friends, Dr Amanda Goodby, Dr Cezary Lewucha and Dr Daniel Nowakowski, have been wonderful company and we have had great times together, without you, this would not have been made possible: I treasure your friendship and am thankful for all the help you have given me.

Penultimately I want to send special thanks to the people who have kept my spirit up even on the bad days, for being encouraging and distracting in equal measures.

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Abbreviations

ASE	Accelerated Solvent extraction
AATP	Reactive HAS: 4-acryloyloxy 2,2,6,6-tetramethyl piperdine
AIBN	Azoisobutyronitryle ©
AO	Antioxidant
AOPP	Reactive HAS: 4-acryloylloxy 1,2,2,6,6-pentamethyl piperidine
AOTP	Reactive HAS: 1-acryloyl 4-acryloyloxy 2,2,6,6-pentamethyl piperdine
b.p	boiling point
chim 944	HAS: chimasorb 944 ©
c-AO	conventional AO
CB-A	Chain Breaking Antioxidants
CB-D	Chain Breaking Donor
DBPA	Reactive HP: 3-(3,5-tert-butyl-4-hydroxy phenyl)propyl-1-acrylate
DCM	Dichloromethane
DCP	Peroxide: Dicumyl peroxide ©
DMB	Dilute Master Batch
DTBP	Peroxide: di tert butyl cumyl peroxide ©
DTBPHY	Peroxide: 2,5-dimethyl-2,5-dimethyl2,5-di (tertiary butylperoxy)-hexyne-3©
DSC	Differential scanning Calorimetery
g-AO	Graftable antioxidant
g-PEX	Grafted crosslinked polyethylene
g-Ph	Graftable Hindered Phenol
HDPE	High density polyethylene
h-ph	Hindered phenol
HAS	Hindered amine stabilisers
Irg 1010	Irganox 1010 ©
Irg 1076	Irganox 1076 ©
Irg 1330	Irganox 1330 ©
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
LTTS	Long term thermal stability
MD	Metal deactivator
m.p	Melting point
MW	Molecular weight
OIT	Oxidation induction time
PD	Peroxide decomposer
PE	Polyethylene
PE_L	HDPE: Lupolen 5261-unstablised powder
PE_B	HDPE: BorPex 1878E-stablised powder
PEX	Crosslinked polyethylene
PEXa	Peroxide initiated crosslinked polyethylene
PEX_C	Electron beam crosslinked polyethylene
PEX_{Eng}	Peroxide crosslinked pipe produced by Engel process
PEX_{HS}	Peroxide crosslinked pipes produced by commercial high speed extrusion Infrared process
TB	Peroxide: Trigonox B©
Tin622	HAS: Tinuvin 622
Tin723	HAS: Tinuvin 622
T145	Peroxide :Trigonox 145-E85 ©

T101	Peroxide :Trigonox 101 ©
$t_{1/2}$	Half life time of peroxide
UHMWPE	Ultra high molecular weight polyethylene
UVA	UV stabilisers
XL	Crosslinked, crosslinking
NXL	Not crosslinked

Chapter 1
Introduction

Introduction

Polymers and plastics constitute an important part of our daily life having wide range of applications including food packaging, automotive, electrical and electronics, medical and pharmaceutical, constructions and pipe applications. For pipe applications, the past several decades have seen a considerable increase in the use of polyolefin pipes in different water applications. Originally, floor heating was the largest field of application, but today, polyolefin pipes are also utilized for district heating and for drinking water distribution networks. In 2004, polyethylene (PE) water pipes accounted for 33.5% of the world's plastic pipe demand and in the UK and USA, PE represents 70% of some water utilities total pipe inventory [1]. The advantages of using plastic pipes, compared with metal pipes, are numerous; including lower weight and installation costs, and greater durability particularly with respect to corrosion [2]. Plastic pipes for water applications which are often based on peroxide crosslinked polyethylene, (PEXa) must have a long-term stability, with the current requirement for service life of a hot-water polyolefin pipes being around 50 years [3, 4]. The lifetime of PEXa plastic pipes is usually predicted by using internal pressure tests [5, 6], in which the pipe is subjected to different internal stresses and the time to rupture is measured. Several researchers have reported that the degradation of PEXa pipe's occurs after the antioxidants (AO) used have been depleted [7, 8].The AO depletion can occur non-uniformly due to migration from the polymer into the water. Therefore, the quality of water passing through the polyethylene pipes can be affected by migration of components from the plastic material such as additives and degradation products thereof as well as oxidation by-products of the polymer that may cause health and safety issues [9]. Leaching of phenolic compounds related to antioxidants such as butylated hydroxytoluene (BHT) and various carbonyl compounds formed from degradation of the polyethylene used in manufacturing the pipes have been reported [10, 11]. Detailed studies of the failure of pipes in a pressure test have shown that different mechanisms contribute to their rupture, including the diffusion of oxygen, and various degradation reactions. These processes depend on the type of the polymer, the additive package used, the surrounding environment and other conditions. Therefore there is a need to develop new stabilising packages that would be much less susceptible to migration into the surrounding contact environment in order to address health and safety issues, as well as, providing higher stabilising efficiency and in a cost effective way. The work described in this thesis addresses some of the issues mentioned above by investigating the chemical grafting of antioxidants on HDPE which is peroxide crosslinked for use in pipe applications with the aim of preventing the migration of the antioxidants into the contact liquid media.

1.1 Polyethylene

Polyethylene (PE) is one of the most widely used polymer in many applications ranging from food packaging, cables, pipes, gaskets, crates to cables and coatings [12]. It is a semi-crystalline polymer produced by free radical polymerisation using either Ziegler Natta catalyst, Philips process-based catalyst or the more recent metallocene catalyst. The type of catalyst and the polymerisation conditions used give rise to different molecular structures of the polymer produced.

Low density polyethylene (LDPE) is produced by high pressure free radical polymerisation resulting in a low molecular weight branched polymer. The branching hinders the crystallisation process making LDPE partially (50-60%) crystalline solid with melt temperature of about 115°C and density in the range of 0.90-0.92 g/cm^3 [12]. LDPE's flexibility enables it to be used in films, shrink wrap, shopping and trash bags as well as in coatings of juice or milk cartons to make them water tight and heat sealable [13].

High density polyethylene (HDPE) is produced by a low pressure process, resulting in a linear structure which has little effect on its molecular organisation, hence, has generally a higher degree of crystallinity (60-90%) with density ranging between 0.94-0.97 g/cm^3 and a melt temperature above 127°C. HDPE provides stiffness, chemical resistance and barrier properties that allow it to be used in small to large container applications for liquids, its low permeability and resistance to corrosion makes it also suitable for use in pipes [13].

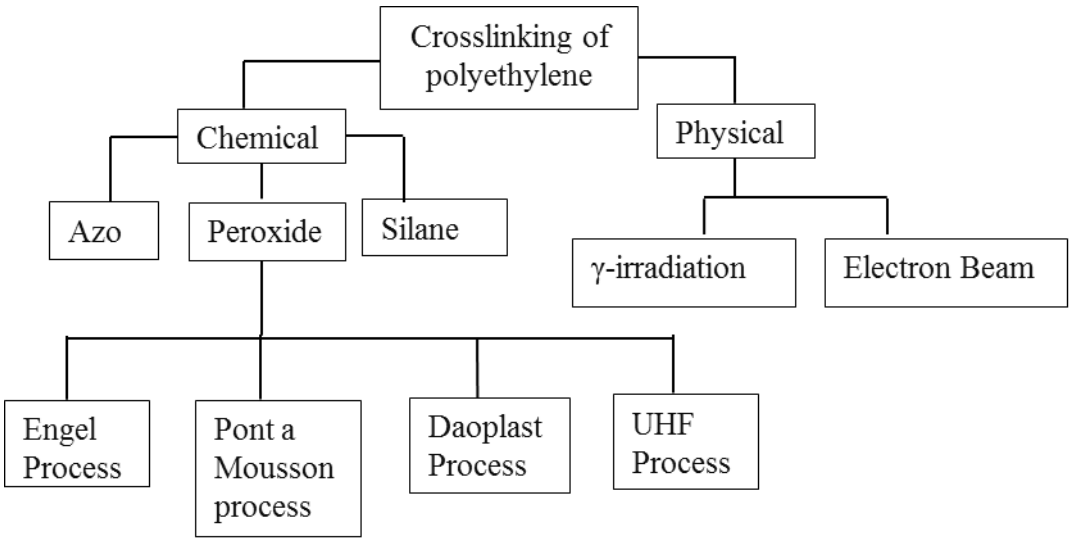
Linear low density polyethylene (LLDPE) is produced by copolymerization of ethylene with alpha-alkenes at low pressure and is essentially made up of linear chains with random short branching. These random short chain branches do not hinder the crystallisation process as much as in low density polyethylene, hence lowering the density to 0.900-0.94 g/cm^3[12]. This polymer is chemically a compromise between HDPE and LDPE [13].

Ultra high molecular weight polyethylene (UHMWPE) is structurally very similar to HDPE but with very high molecular weight. One of the main uses of the UHMWPE is as a load bearing material in orthopaedic applications because of its wear and impact resistance properties [14, 15]

1.2. Modification of polyethylene via crosslinking

The use of polyethylene in certain applications e.g. in pipes or cables, is restricted due to some undesirable inherent properties such as low melting temperature, low resistance to stress cracking and resistance to slow crack growth. In order to overcome these shortcomings, the polymer properties were improved through modification by crosslinking. Irradiation of the polymer in the solid state showed a major improvement in wear resistance and tensile properties at higher temperatures [16-18]. It was shown later that such improvement was directly associated with the formation of three dimension crosslinked network [13, 16, 19, 20]. The improved properties led to further development of new crosslinking methods classified in two categories; chemical and physical crosslinking (**See scheme 1.1**). A brief description of each method is outlined below.

Scheme 1. 1: polyethylene crosslinking methods **[21]**



(i) Chemical crosslinking

Chemical crosslinking is classified according to the initiator used as AZO, peroxide and silane crosslinking.

- **Azo –**this is a two-stage process where an AZO (-N=N-) compound is used during the extrusion of polyethylene below its decomposition temperature. Crosslinking takes place in the second step by placing the extrudate in a vulcanization tube at high temperature (240-270°C) to initiate the crosslinking process[21, 22]

- **Peroxide (PEXa) –** in this process crosslinking takes place by reactive processing, where free radicals are generated using an organic peroxide (ROOR) initiator at an elevated temperature [23-26].

- **Silane (PEXb)–** this is a two-step process , in the first step a silane molecule is grafted on to the polymer backbone followed by crosslinking via hydrolysis with the aid of a catalyst [20, 21, 26].

(ii) Physical crosslinking process (PEXc)

In this process a high-energy radiation sources such as electron beam, gamma rays or UV radiation is used to generate the free radical required to trigger off the crosslinking reaction [22, 26, 27].

Both physical and chemical processes described above have their advantages and disadvantages and the choice of the production method is dependent upon the end use product and the cost of the process [19, 24, 27, 28], See **Table 1.1**.

Table 1. 1: Comparison of PEX production methods [19, 24, 27]

Crosslinking process	Advantages	Disadvantages
Physical	• One step process • Clean system fewer additives • Room temperature for reaction	• Restriction of thickness of sample • High cost of equipment • High safety requirements
Chemical	• Homogenous crosslinking • No restriction in product thickness	• Two step process • Use of initiating chemical for crosslinking process • Higher cost of production

1.2.1 Chemical crosslinking using peroxide initiator, PEXa

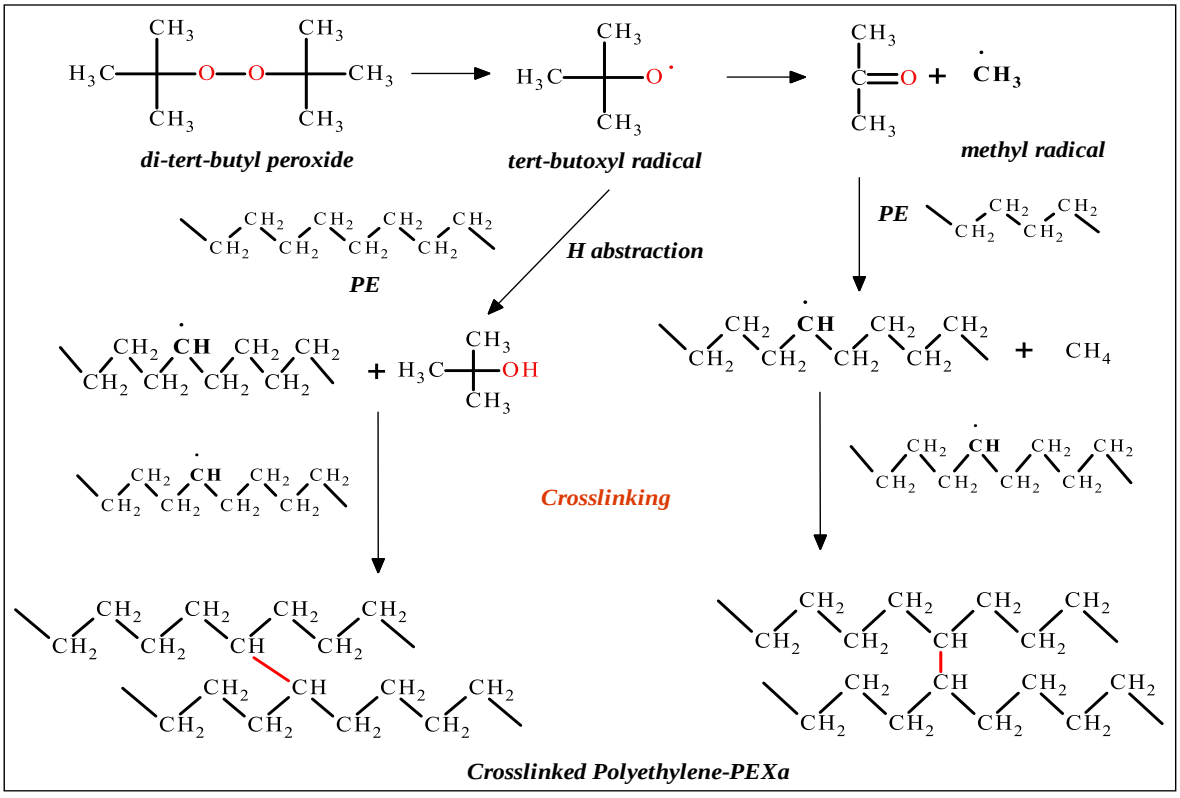
In this work only the peroxide crosslinking process was used. The decomposition of peroxides generate alkoxyl radical that would abstract a hydrogen atom from the polymer chain to generate macro radicals, which would subsequently recombine to form polymer crosslinks **(see Reaction Scheme 1.1**). Peroxide crosslinking of PE can take place in various processes as outlined below[23].

- **Daoplast process-** the polyethylene is extruded without the peroxide followed by immersion in a peroxide media under high pressure and temperature, whereby the peroxide would diffuse in to the polymer and give rise to the desired crosslinking [20, 21].
- **Engel process –** this was the first commercially available process where a mixture of polyethylene and a peroxide is fed in to a special "extruder" with a plunger action where a reciprocating piston generates pressure around 2000 bar that results in

instantaneous rise in temperature to melt the polymer. The polymer melt is then pushed through the long hot die to produce the final crosslinked polymer [29].

- **Pont a Mousson process-** low, medium or high density polyethylene can be crosslinked by this method, where a mixture of polyethylene and a peroxide are extruded and subsequently immersed in a salt bath at temperature ranging from 250-280°C [20].
- **UHF process (ultra high frequency initiation) -** in this process a mixture of polyethylene and a peroxide is extruded below the peroxide decomposition temperature followed by passing the mixture through a high IR beam radiation (at ~ 250°C temperature) where the peroxide decomposition takes place to initiate the crosslinking process [30]. In this work a similar process is used at Uponor Ltd and is referred to here as "**High Speed Extrusion Infrared**" process.

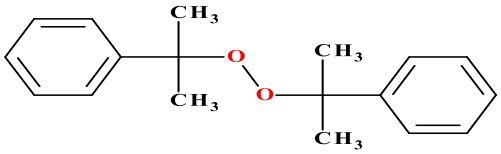
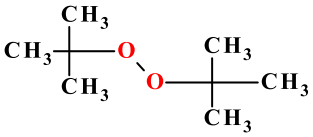
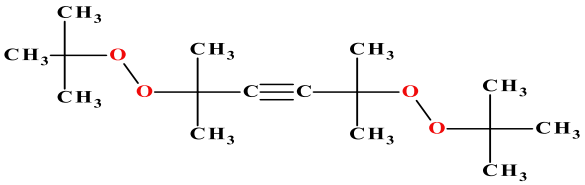
Reaction Scheme 1. 1 : Crosslinking of polyethylene initiated by peroxide



Peroxide crosslinking of polyethylene depends on the temperature used and the types of the peroxide. A suitable peroxide is selected to give a fast crosslinking reaction without scorching or premature crosslinking in the extruder [25]. Typically the extent of crosslinking is increased by increasing the peroxide concentration. Various organic peroxides are available for chemical crosslinking of PE, examples include dicumyl peroxide (DCP) , di tert

butyl cumyl peroxide (DTBP), and 2,5-dimethyl-2,5-dimethyl2,5-di (tertiary butylperoxy)-hexyne-3 (DTBHY), see **Table 1.2** for structure. DCP is one of the main peroxide used for crosslinking of LDPE [31, 32], whereas DTBP and DTBHY are used for the crosslinking of HDPE [20]. Theoretically, decomposition of one peroxide molecule into two radicals should result in the production of one crosslink [33]. However, the efficiency of the crosslinking reaction is affected by many factors including the type of peroxide [34-36] , the presence of unsaturation in PE and the presence of other additives [37]. The extent of the crosslinking reaction increases with increasing the peroxide concentration [34], the number of vinyl groups present in the polymer[32, 38, 39], the number of side chain branches and molecular weight [39]. Generally, it was shown that the peroxide crosslinking process produces homogenous crosslinked polymer when compared, for example, to the silane and irradiation crosslinked polymer [28, 40].

Table 1. 2: Examples of peroxides

Peroxides
 **DCP** (dicumyl peroxide)
 **DTBP (**di tert butyl peroxide)
 **DTBHY** (2,5-dimethyl-2,5-dimethyl2,5-di (tertiary butylperoxy)-hexyne-3)

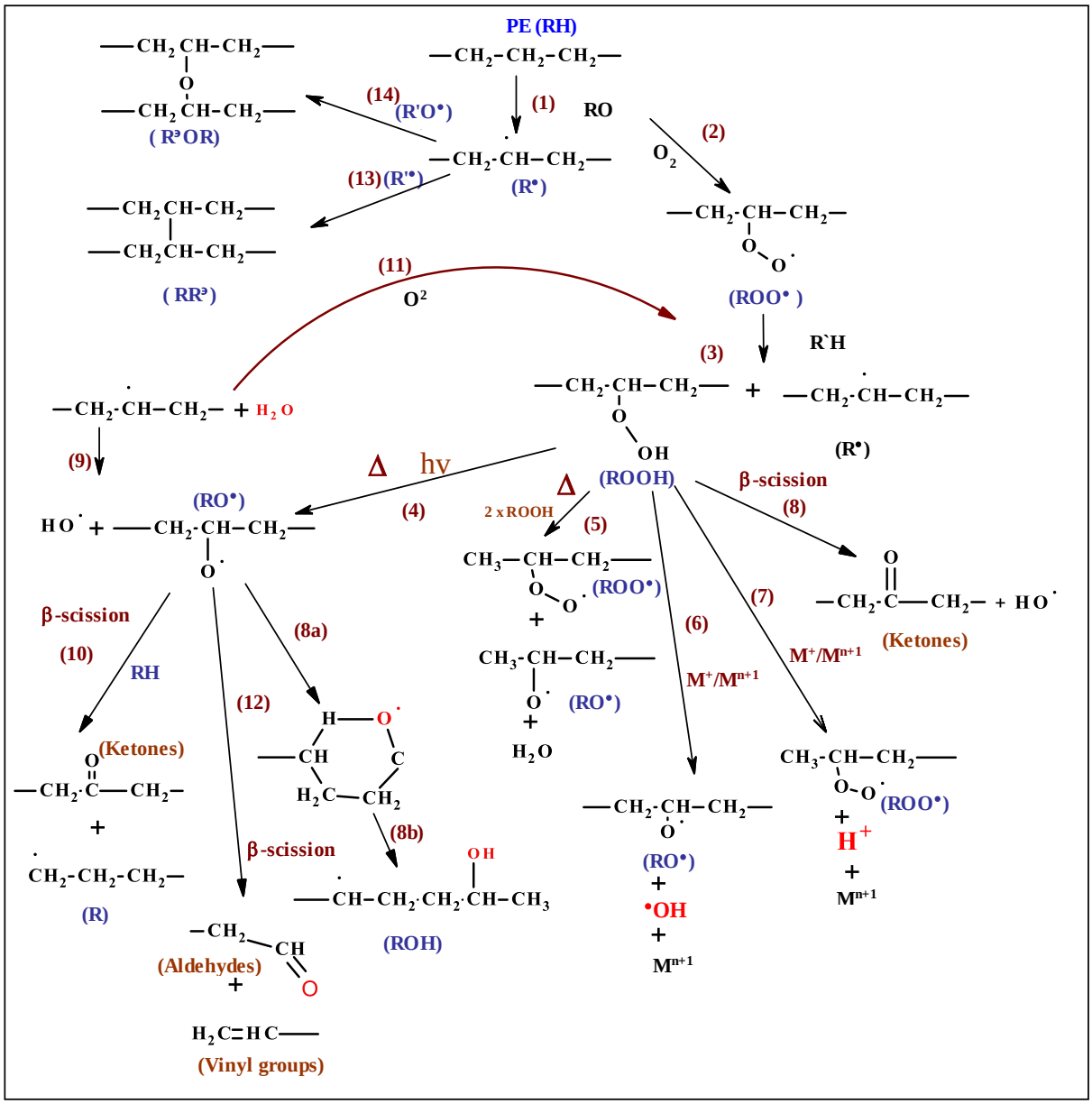
1.3 Oxidation and stabilization of polyethylene

1.3.1 Autoxidation of polyolefin

Polymers are susceptible to oxidative degradation during their life time due to the action of oxygen, heat, stress, radiation and chemical agents. Hydrocarbon polymers undergo auto-

accelerated reaction at high temperatures (e.g. during melt processing) in the presence of limited amount of air but this process becomes much faster in the presence of oxygen [41].

This process can be further accelerated in the presence of initiators or inhibited or retarded in the presence of antioxidants and stabilizers. The autoxidation process for hydrocarbons is a free radical reaction involving a set of chain reaction steps: initiation, propagation and termination [42, 43] . The initiation process is influenced by factors such as heat, light and the presence of transition metal impurities which lead to the formation of the first macro-alkyl radicals **R·** (see **Reaction Scheme 1.2, Rn1**) [44]. The propagation reaction involves a reaction of the macro alkyl radicals with an oxygen biradical to form macro alkyl peroxyl radicals **ROO·** (see **Reaction Scheme 1.2, Rn 2**). The first oxidation product is formed by abstracting a hydrogen atom from another macromolecule by inter or intramolecular hydrogen atom abstraction to form macro hydroperoxides, **Rn 3.** This is the rate determining step which involves activation energy required for breaking a C-H bond (allyl < benzyl < tertiary < secondary < primary) and is affected by the stability of the resulting macro-alkyl radical (**Rn 3**). Subsequently, the formed macro hydroperoxides undergo homolysis in the presence of heat, light (**Rn 4 & 5**) or metal ions (**Rn 6 & 7**) to produce alkoxyl, peroxyl and hydroxyl macro radicals. These in turn undergo further reactions by abstracting a hydrogen atom from another polymer chain to from new macro alkyl radicals (see **Rn 8-10** in **Reaction scheme 1.2**). These alkoxyl radical can undergo further β-scission reaction (see **Rn 10,12**) and radical formation. Termination of the oxidative process takes place through recombination and disproportion reactions of either two **ROO·**, two alkyl radicals resulting in crosslinking or coupling via reactions of **R· and ROO·** radicals.



Reaction Scheme 1. 2: Thermal Oxidation of PE [44]

As the propagation step leading to formation of a hydroperoxide is the rate determining step, under normal oxygen pressure (oxygen saturation) alkylperoxyl radicals become the dominating species i.e. [ROO$^{\bullet}$] > [R$^{\bullet}$] which would lead to termination via **Rn 14** giving rise to diperoxides, carbonyl compounds and alcohols, whereas under oxygen deficient conditions, alkyl radicals predominate i.e. [R$^{\bullet}$] >[ROO$^{\bullet}$] leading to crosslinking and disproportionation reactions [44].

1.3.2 Thermal Oxidation of Polyethylene

Polyethylene degradation may occur at any stage of its lifetime from manufacturing to the in-service final stages. For most PE applications, the stage where the degradation process occurs most rapidly is during melt processing (manufacturing), where the polymer is exposed to severe conditions of high temperature, oxygen (trapped in the polymer),shear and a small

amount of catalyst present as impurity. These factors have detrimental effect on the polymer and would result in either chain scission or crosslinking [45-48]. For example, HDPE processed above 290°C was found to undergo a decrease in its melt viscosity due to chain scission, but at lower temperatures, the melt viscosity increases as well as the molecular weight due to crosslinking becoming the dominant reaction [49]. Similarly, branched LDPE processed at temperatures lower than 350°C (between 284-315°C) was found to give predominantly crosslinking, but when processed at higher temperature (350°C) chain scission reactions dominated [50-53].

The thermo-oxidative stability of polyethylene is directly affected by the method of its production since different polymerization routes give rise to differences in the type and concentration of unsaturated groups present in the polymer as "defect" mainly vinyl, trans-vinylene and vinylidene, and also results in differences in the molecular weight and molecular weight distribution of the polymer. The presence of vinyl groups has been shown to play a major role in the crosslinking of the polymer during melt processing [54] , whereas trans-vinylene and vinylidene have been shown to play a less prominent role in the degradation process[55]. The Philips process was found to give rise to high level of unsaturation, thus PE manufactured by this method is more prone to crosslinking whereas, the Ziegler type HDPE has generally low level of double bonds leading to more preference of chain scission reactions especially at high temperatures [49, 53, 55].The difference in the degradation processes is suggested to be due to the presence of different polymerization catalytic residues in the polymer. Chromium catalyst residues from Philip type polymerization catalyzes the decomposition of hydroperoxide formed during the thermal degradation, whereas the Ziegler Natta Ti catalyst residues have influence on the formation of carbonyl and alcohol products in the degradation process[56]. Simultaneous exposure to heat and oxygen leads to the formation of volatile oxidative products such as aliphatic hydrocarbons, ketones, acids and aldehydes which may cause an off-taste, odor and discoloration in the final product [57].

It is important to point out that the diffusion of oxygen in solid state PE takes place only in the amorphous region and cannot penetrate the dense crystalline phase [46, 58]. A decrease in crystallinity would therefore result in higher extent of oxygen diffusion, giving rise to a more oxidation susceptible polymer [45]. The catalytic residues have also an important effect on the extent of oxidation reaction e.g. a small amount of Cr catalyst (in Philips- type PE) residue was found to oxidize the polymer more rapidly than in the presence of Ti- catalyst residues

from the Ziegler-type PE [59]. Furthermore, the thermal degradation in the solid state was shown to be directly proportional to the thickness of the sample [58-62].

1.4 Stabilization of Polyolefin

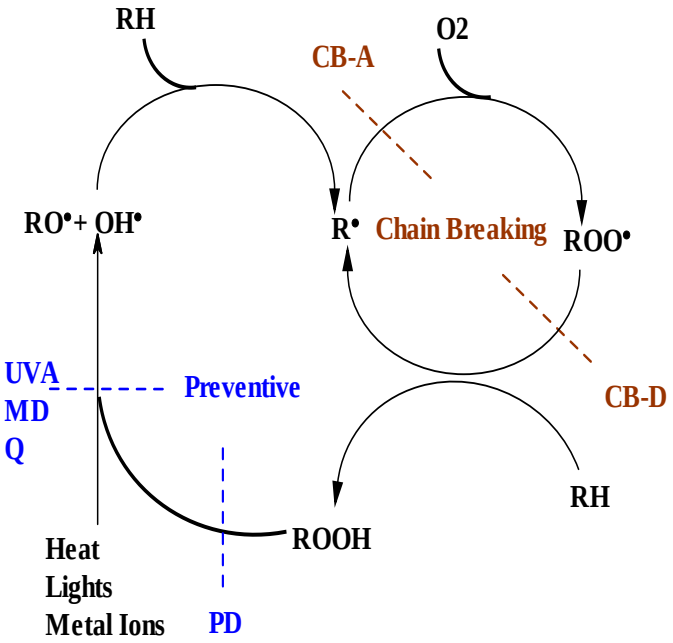
Polymer stabilization in the melt is of major importance in order to inhibit the oxidative degradation process, when the polymer is subjected to heat, shear and low levels of oxygen during fabrication. Antioxidants and stabilizers are group of compounds that are typically used at low concentration (below 1%) to inhibit or retard the oxidative degradation of polymers.

1.4.1 Antioxidants and Mechanism of antioxidants Action

Antioxidants operate mainly by two major mechanisms to inhibit polymer oxidation. Chain breaking antioxidants act by removing the propagating radicals (alkyl peroxyl and alkyl radicals), whereas, preventive antioxidants inhibit the generation of free radicals, see **Scheme 1.3**.

The chain breaking mechanism is further classified into chain breaking- Acceptor (CB-A) and Chain Breaking Donor (CB-D) processes. CB-D antioxidants act as primary antioxidant by removing the propagating radicals ROO• and R• formed during the oxidation cycle. Hindered phenols are CB-D antioxidants, they operate by reducing the Alkyl peroxyl radical ROO• to ROOH. CB-D antioxidants must be able to compete effectively with the polymer for the ROO• and should be able to produce ultimately stable molecular products. Chain breaking acceptor (CB-A) antioxidants are electron- acceptors; they operate by oxidising the alkyl radicals R• and are only effective in oxygen deficient environment [41, 63].

Phenolic antioxidants are widely used and are among the most extensively investigated stabilisers used during melt processing of polymer and in service for long term thermal stabilisation for end use applications. The function of hindered phenol antioxidants depends on their rate of reaction with $ROO^{\bullet}$ and on the reactivity of the generated antioxidant radical, e.g., phenoxyl radical from synthetic hindered phenol.



Antioxidant Mechanism and classes

Chain-Breaking Antioxidant

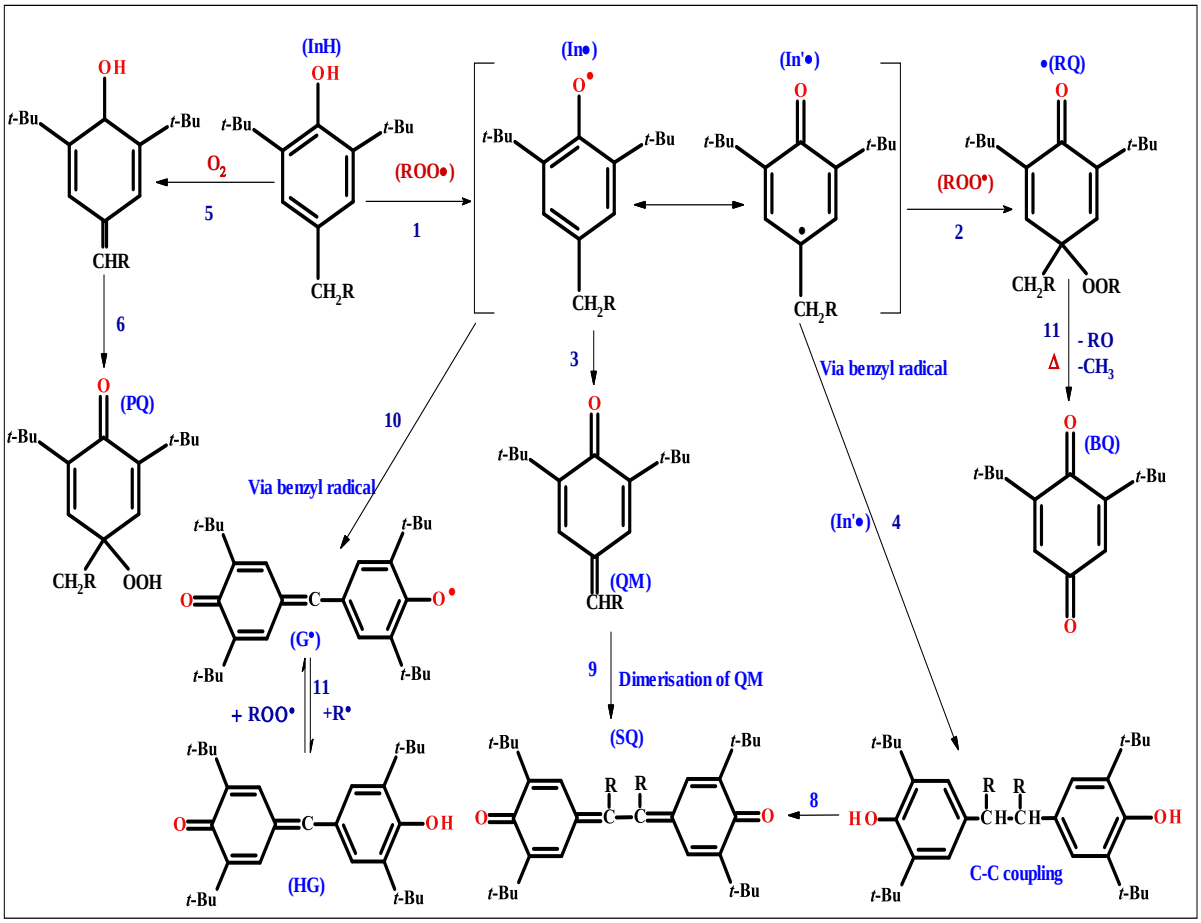
CB-	**Chain-Breaking Acceptors**
	Lactones,
	Hydroxylamines
	Hindered amine photo AO
CB-D	**Chain-Breaking Donor**
	Phenolic AOs
	aromatic amines

Preventive Antioxidants

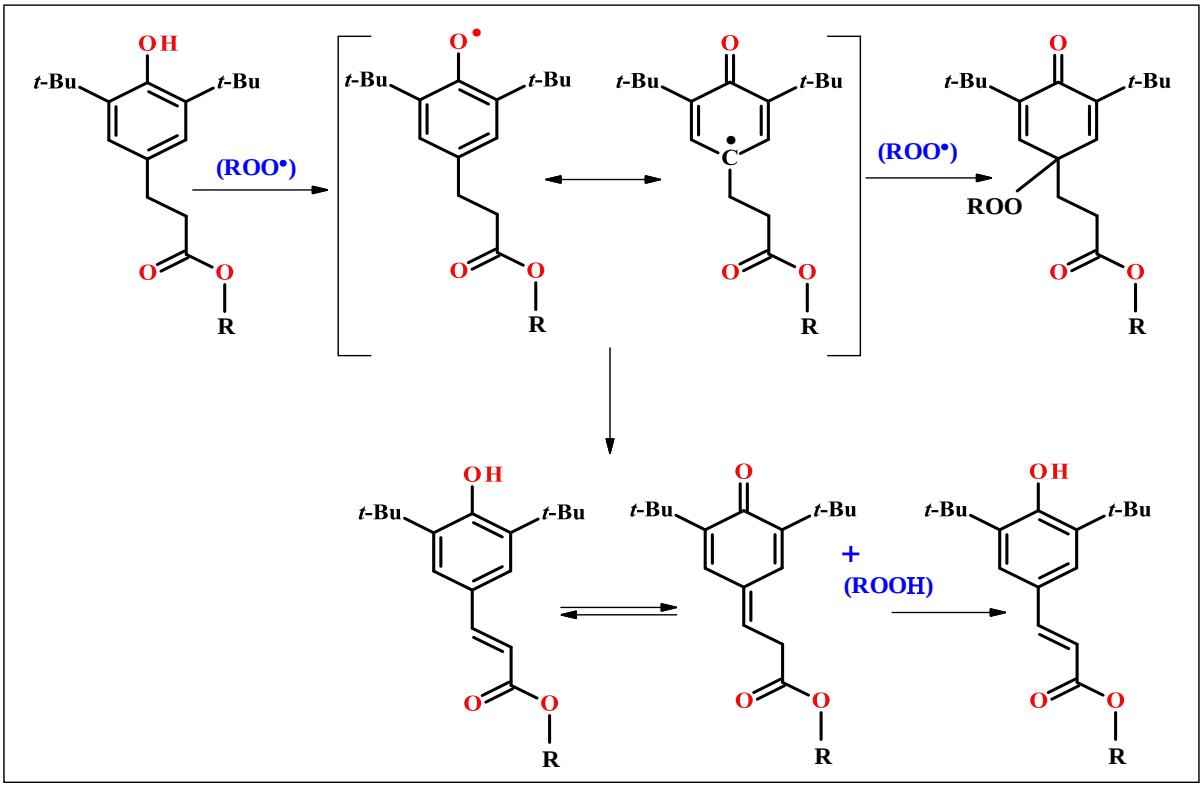
PD	**Peroxide Decomposers**
	Phosphites
	Sulphur containing AOs
	Nickel complexes
	hydroxylamines
UVA	**Ultraviolet Absorber**
	Hydroxyl benzophenones
	Hydroxyl benzotriazole
MD	**Metal Deactivator**
	poly functiobal chealating agents
Q	**Excited state Quenchers**

Reaction Scheme 1. 3: schematic representation of oxidation cycle and AO-Mechanisms[64]

Transformation products formed from hindered phenols have been shown to have a great influence on the stabilising function of the antioxidants and their role in the melt and long term thermal stabilisation of the polyolefins [65]. The most efficient commercially used phenolic antioxidants are Irganox 1076 ®, Irganox 1010 ® and Irganox 1330 ® (see **Table 1.3** for structures, pg 43). The oxidation mechanism of one of the simplest hindered phenol antioxidants , 2,6-di-tert-butylphenol (**BHT**) is given in **Reaction Scheme 1.4** which gives a good overall representation of the chemistry of hindered phenols in general [41, 65]. The main chemistry of the transformation products of phenolic antioxidant (**InH**) therefore starts with formation of stable phenoxyl radical $In^{\bullet}$ (**scheme 1.4, Rn 1)** which followed by its further transformations through disproportionation lead to quinonoid compound (**QM**) **(scheme 1.4, Rn3**). Stilbenquinone (SQ)Phenolic dimers are produced by C-C coupling of benzyl radicals formed through formal rearrangement of ($In^{\bullet'}$), (**scheme 1.4, Rn4 and 8**), and through dimerization of quinone methide (**scheme 1.4, Rn 9**). Ethylene bisphenol (**In-In**) was found to be as effective as the original antioxidant itself , whereas Peroxidienones (PQ) are pro-oxidants which is formed by direct oxidation of BHT (**scheme 1.4, Rn 6**)[66]. The dimerization process can lead to stable phenoxyl radical galvinoxyl ($G^{\bullet}$, **scheme 1.4, Rn 10**), which is an effective thermal. The antioxidant efficiency of phenolic antioxidants is enhanced by the presence of propionate group (**see Reaction Scheme 1.5**) [67].



Reaction Scheme 1. 4: Stabilisation action of CB-D antioxidant [65]

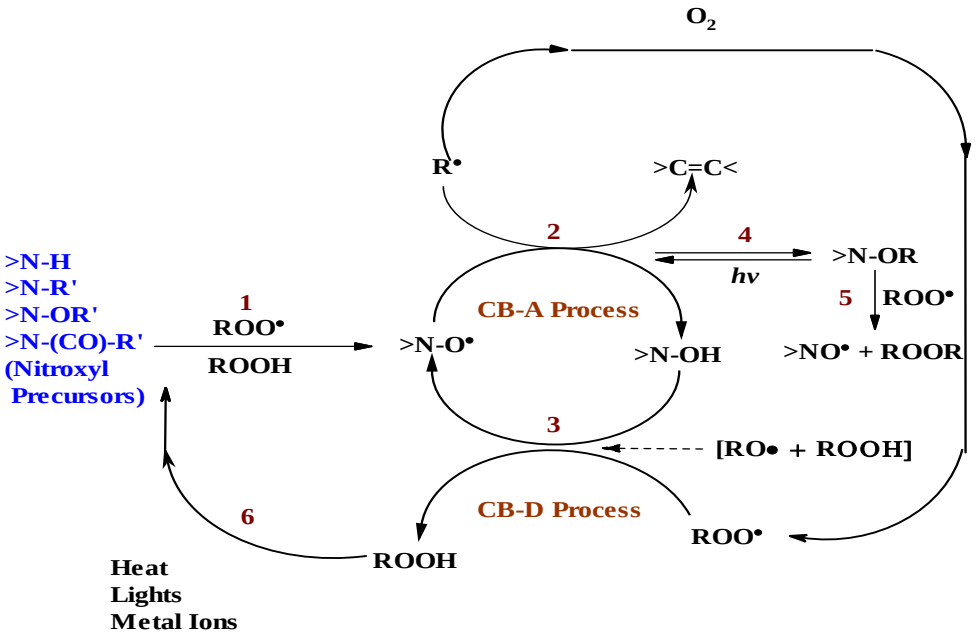


Reaction Scheme 1. 5 : Stabilisation mechanism of propionate type monophenols [67]

Furthermore, some of the thermo-oxidative degradation products formed from hindered phenols in polyolefins have a major dis-colouring effect in the polymer. The colour development is mainly attributed to the formation of quinonoid compounds e.g. **BQ, SQ, QM** [68, 69] . Discoloration of the polymer depends on the concentration and the structure of the phenolic transformation products, but the discolouring effect is generally reduced when a propionate-type phenolic antioxidant is used. This is a consequence of intramolecular rearrangement of a part of the primarily formed quinone methide, and is due to oxidative dimerization resulting in nonconjugated dimeric quinone methides, (see **scheme 1.4, Rn**) [68].

Hindered amine stabilisers operate initially through a chain breaking a step via the formation of the corresponding >NO• formed as the first important transformation product that can trap both R• (alkyl) and ROO• through a regenerative cyclical mechanism involving >NO• and NOH or/and NOR• (see **Reaction Scheme 1.6**) [63, 70].

Sterically hindered amines were shown to be efficient stabilizers against both thermal and photo oxidative degradation of polyolefins [71, 72]**.**Therefore, they are designated both as Hindered Amine Stabilizer (HAS) and Hindered Amine Light Stabilizer (HALS). The HAS compounds are mainly secondary and tertiary amines, in which their carbon atoms are fully alkylated, with most being cyclic aliphatic amines based on the structure of 2,2,6,6-tetramethyl piperdine derivatives, see **Table 1.3** for structures of some of commercial HAS stabilisers.

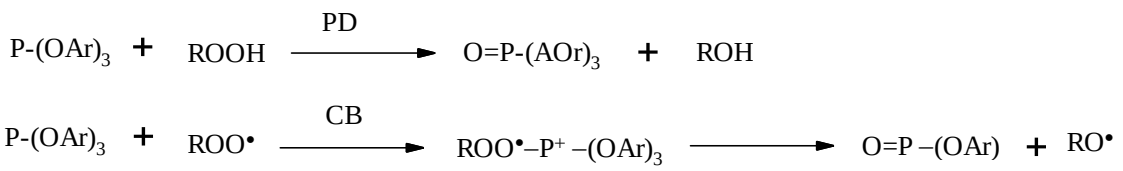


Reaction Scheme 1. 6 : Mechanism of the stabilisation action of hindered amine stabilisers via their Nitroxyl radical precursor [63, 70]

Although the activity of hindered amines as antioxidants is based on their ability to form the corresponding nitroxyl radicals; the exact mechanisms of the nitroxyl radical formation and its function have been controversial in the literature [73, 74]. The rate of reaction of nitroxyl radicals with alkyl radicals is only slightly lower than that of the reaction of alkyl radicals with oxygen [75]. The reaction of an alkyl radical with the >N-O• radical leads to the formation of hydroxylamine ether (NOR'). This reacts with a peroxyl radical (ROO•) resulting in the formation of alkyl peroxide (ROOR) and the regeneration of the nitroxyl radical , see **Reaction 5** in **scheme 1.6.**

Hindered amine light stabilisers (HAS), both low molecular weight such as Tinuvin 770 and high molecular weight polymeric HAS such as Tinuvin 622, Chimassorb 944 (see **Table 1.3** for structures) have been used as efficient light stabilisers but they were shown to be also able to act synergistically in the presence of other antioxidants giving rise to an enhanced melt and long term thermal stability (LLTS) of polymers [76-79]. When two polymeric HAS additives e.g. **Tinuvin 620 and chimasorb 944** are combined, much higher synergistic effects were observed than that when low molecular mass HAS and high molecular mass HAS were combined [78-81] . On the other hand it has been observed that no synergism can usually be achieved in combination of two low molecular mass HAS compounds possible due to antagonism in specific combinations [78].

Preventive antioxidants are referred to as secondary antioxidants, they act by interfering in the second oxidation cycle by inhibiting or preventing the generation of free radicals (see **Scheme 1.3**). Phosphite esters and sulfur containing compounds are the most important peroxide decomposers, the phosphites, for example, act by reducing hydroperoxides to alcohols and are oxidized themselves to the corresponding phosphate, see **reaction scheme 1.7**. Some phosphite esters can also act as chain breaking mechanism, depending on their structure and the oxidizing ability of the substrate as well as the reaction conditions [82]. In this work only hindered phenols and HAS stabilisers were used for the stabilisation of HDPE.



Reaction Scheme 1. 7 : Antioxidant reactions of phosphites

1.4.2 Physical Factors affecting antioxidant performance

The performance success of antioxidant packages is critically dependent on the chemical (structure and its activity) and physical factors. Physical factors, which affect the antioxidant performance are, their solubility and diffusion in the polymer and the surrounding media, volatility, and leachability in to the contact media. The loss of antioxidants from the polymer is controlled, either by the rate of their loss from the surface, or by the rate of their migration through the bulk to reach the surface, or by combination of these parameters [83]. Antioxidants are generally less soluble in polymers than in the lower molar mass liquid hydrocarbon models, although antioxidants are typically highly soluble in polymers at elevated processing temperatures, they do come out of solution upon cooling down to room temperature. It has been shown that antioxidants dissolve only in the amorphous phase and are rejected from the crystalline phase of the polymer melt on cooling [46, 84]. Solubility of the antioxidants is also influenced by their intrinsic properties (heat of fusion and melting point) and their interaction with the polymer, this intrinsic effect was shown to have a larger effect than the compatibility parameter [84]. An increase in solubility is favoured by lower heat of fusion of an antioxidant with lower melting point which enhance the antioxidant interaction in the polymer matrix (for antioxidants with groups that give favourable interaction with the polymer matrix) [84].

In the context of stabilisation of polymers, diffusion of antioxidant plays an important role in determining how easily antioxidants can be extracted out from the polymer into a contact media. Diffusion involves the movement of an individual molecule through tangled mass of polymer chains [83]. The process of diffusion and permeation are closely related, and the diffusion coefficient of antioxidants is related to the permeability of the polymer to that antioxidant and its solubility in the polymer [84]. Generally, the diffusion coefficient of antioxidants decreases with increasing the polar interactions with the polymer, or the molar mass of the antioxidants and also with increase branching in their alkyl side chains [82].In addition, the diffusion coefficient is affected by the polymer morphology, hence an increase in the density and crystallinity of a polymer implies a steady decrease in the diffusion coefficient. Further, Diffusion coefficients are also affected by the flexibility of additives hence a greater flexibility within the antioxidant structure would result in easier diffusion in the polymer than in the case of a more rigid antioxidant structures [83]. Permanency of antioxidants is, therefore, affected not only by the diffusion characteristics of the additive but also by the nature of the surroundings media and temperature. Loss of antioxidants by volatility is controlled by its diffusion to the surface, which in turn[44] depends on the

thickness of the sample [85]. The rate of evaporation of antioxidants is inversely proportional to the thickness of samples and is directly proportional to its surface area. Volatility decreases with increasing in molecular weight, hence the simplest hindered phenol (BHT) antioxidant is not used in polymers due to its high volatility [86].

Loss of antioxidant when in contact with liquid medium (leaching) from the polymer surface depends on both their diffusion coefficient and the partition coefficient between the liquid and the polymer. As in the case of volatilization, the rate of leachability of antioxidants from the surface of polymers in to a liquid contact media increases with temperature and surface area to volume ratio [82, 84, 87].

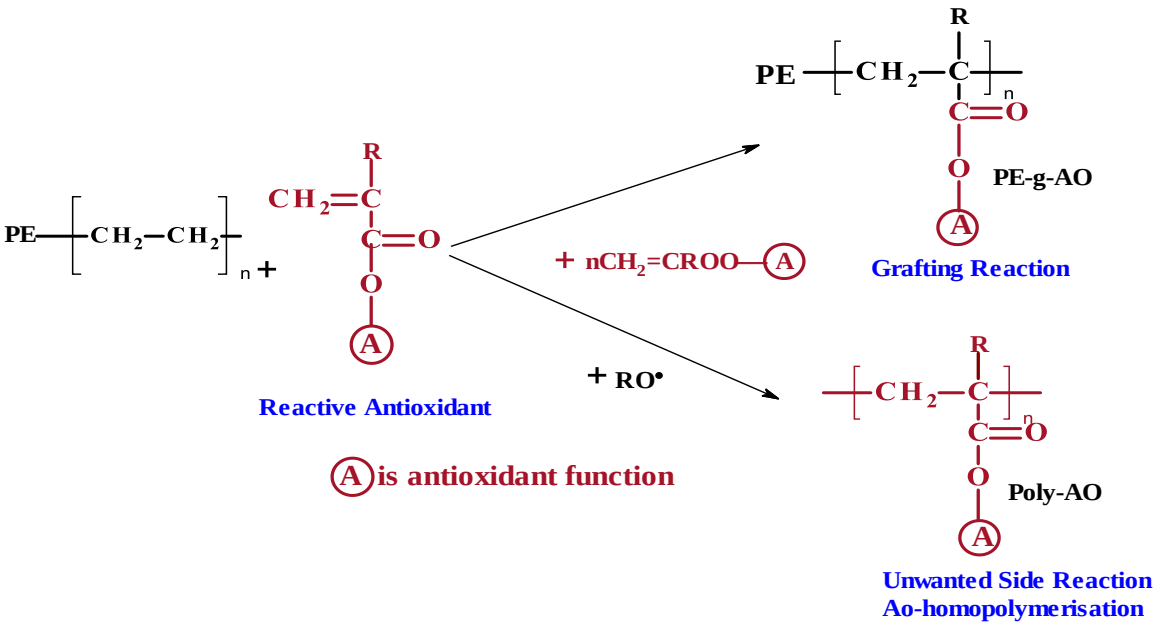
1.4.3 Reactive Antioxidants and Free Radical Grafting

There are many limitations associated with the use of antioxidants, particularly low molar mass antioxidants, especially when in contact with an extractive environment, e.g., when used in contact with food, in medical applications, and for drinking water pipes, due to ease of physical loss of the antioxidants in the contact media. Although antioxidants are licensed to be used in polymers for food applications they have to undergo strict toxicity testing regime, however, although they would have to be approved, this does not necessarily mean that the oxidation products formed during the processing would be nontoxic. Several approaches have been described in the literature to improve the substantivity of antioxidants in polymers. One approach is to use high molar mass antioxidants; however such antioxidants can still be lost when subjected to aggressive conditions [63]. Another approach is the copolymerisation of antioxidants during synthesis of the polymer but this can be an expensive process. A third approach is to use reactive antioxidants for grafting on pre-formed polymers [64, 87-98]. The grafting process has been used to give highly bound antioxidants on polymers resulting in increased polymer stability, particularly under extreme extractive conditions. Grafted antioxidants in the polymer offer enormous advantages when they are subjected to aggressive service conditions, they also do not suffer from the problem of compatibility, they are non-volatile, non- migratory and are therefore not lost to a great extent from the polymer even in the presence of highly extractive solvents.

In a melt free radical grafting system, reactive antioxidants become chemically attached to the polymer, normally in the presence of an initiator (peroxide) [82]. One of the problems associated with the process of chemical attachment of antioxidants is the competition from a number of unwanted side reactions, thus an optimum melt grafting system would depend on

the chemical composition, the reactivity of the polymer, the antioxidant, the initiator, as well as the process conditions [64, 87-96] . A wrong choice of the chemical system and/or the processing variables, which may result in alteration of the polymer characteristics e.g., molar mass, morphology and physical properties , thus not achieving the required end results of just grafting the antioxidants without affecting the overall properties of the polymer [63, 99].

In the last 30 years, the Polymer Processing Performance Research Unit has devoted much of its research to chemically attaching antioxidants and other additives to a wide range of polymers during melt processing. Typically high concentration (a masterbatch) of polymer bound antioxidant is prepared and then diluted down to a normal low antioxidant concentration [64, 87-89, 93-95, 100, 101]. Reactive antioxidants contain one or more antioxidant functions and one or more chemical functions capable of reacting with the polymer. The antioxidant moiety can be composed of any of the conventional antioxidant functions and the reactive function can be a polymerisable or non polymerisable function e.g, vinyl, allyl, amide or acryloyl groups. There are three different types of reactive antioxidants typically used for free radical melt grafting. Monofuncntional polymerisable antioxidants with one polymer-reactive function per antioxidant group such as the mono-acryloyl containing hindered phenol (DBPA) and hindered amine (AOTP) stabilisers (see **Table 1.4, pg 44** for structures). These have been shown [87, 93] to graft on PP but to low levels due to the competing antioxidants homopolymerisation reactions, See **reaction Scheme 1.8**. To overcome the problem of AO-homopolymerisation, non polymerisable monofuntional (non-reactive double bond) antioxidants were used, such as a meleated HAS antioxidant ,e.g, BPM and APM (see **Table 1.4** for structures) either of these were shown to graft to a much higher extent due to the fact that the maleate function is a non-polymerisable function, with stabilisation efficiency shown to have outperformed a “similar” conventional non graftable antioxidants [63, 94].



Reaction Scheme 1. 8 : Grafting and homopolymerisation reactions of reactive antioxidant [63]

A bifunctional reactive antioxidant (with two polymerisable functions in the same molecule), such as AATP (**see Table 1.4** for structure) has shown very high level of grafting efficiency in PP in contrast with the much lower grafting levels achieved with monofuntional HAS analogues[63, 93]. Grafting of such antioxidants was shown to occur through the intermediacy of a crosslinked structure, involving the polymer and the reactive antioxidant resulting finally in a high level of antioxidant grafting without polymer crosslinking [63, 93].

A novel reactive processing method was also developed in the Aston PPP research group where, a reactive di or polyfunctional comonomer having no antioxidant function is co-grafted with a monofuntional polymerisable antioxidant and this was shown to have overcome the major drawback associated with the low grafting level of mono-functional reactive antioxidants [100]. The grafting efficiency of a mono-functional AO by this approach was shown to improve from as low as 10-40% to an excess of 80-90%, however this strategy presents challenges because of the presence of more than one polymerisable group in the comonomer which may lead to additional undesirable competing side reactions. Overall, however, this co-grafting method was applied to a wide range of antioxidants, e.g., HAS, hindered phenols, aromatic amines and other non-antioxidant reactive monomers leading to outstanding levels of grafting and a superior performance under extractive conditions [63, 100].

1.5 Stabilisation of PEX polymers

Crosslinked polyethylene is a popular material for pipe applications including insulation for pressurized cold and hot water, heating systems and pipes for potable water use. The guarantied service life of such pipes is typically of the order of 50 years [3, 4] . The life time of pipes is usually predicted by using internal pressure test, in which the pipe is subjected to different internal stresses and the time to rupture is measured [5]. Stabilisation of pipes can be achieved by addition of antioxidants [7, 102], however, the concentration of antioxidants in the pipes has been shown to decreases with time [7]. The maximum efficiency of an antioxidant depends on its retention in the polymer during long-term use; hence the loss of antioxidants is an important issue when predicting lifetime performance of a polymer in service.

Typically, the addition of hindered phenol antioxidants has been shown to provide protection during fabrication of peroxide crosslinked (**PEXa**) pipes. However, hindered phenols as effective radical scavengers interfere with the polymer crosslinking process [10, 37, 103]. For example, the stabilisation achieved by α-tocopherol (Vitamin E), an effective biological hindered phenol radical scavenger, used in crosslinked UHMW-PE (used for medical implants) was shown to interfere with the γ-irradiation or electron radiation used for crosslinking, resulting in reduction in the extent of the crosslinking and consumption of the AO [10]. Another example is the use of Irganox 1081(see **Table 1.3** for structure) in the crosslinking process of LDPE which was shown to reduce the oxidation induction time (OIT) down to 50% at various temperatures, compared to when crosslinking was absent [104]. For crosslinked polyethylene systems (PEX), therefore, extra stabilisation is required. **PEX** polymer stabilisation, therefore can only be achieved by using a combination of hindered phenols together with secondary stabilisers [105]. Crosslinking polyethylene, results in reduced migration of antioxidants due to decreased flexibility of the polymer chains and lowering the degree of crystallinity but any increase in the temperature was found to diminish this effect [106]. During synergistic studies of hindered phenol sulfur containing AO, Santonox R (4,4’ thio bis (3-methyl-6-t-butylphenol), see **Table 1.3** for structure, it was suggested that such antioxidants may graft on to the polymer during the crosslinking process [107]. A study on the migration of Irganox 1076 from peroxide crosslinked (PEXa) pipes showed that the antioxidant was retained in the polymer after extraction in boiling water [3]

As the crystallinity of PE decreases with crosslinking, the diffusion coefficient of the antioxidants increases in a linear fashion; but at the same time, higher crosslink density acts as higher diffusion barrier and this would override the crystallinity influence [108]. It is also important to mention that an increase in crosslinking increases the amorphous region thus the polymer becomes more susceptible to oxidation [17].

The service life of plastic pipes for water applications and the factors influencing their performance have been the subject of considerable interest for some time. Gedde and co-workers have devoted much of their research for over a decade to understand and improve the stability of pipes [7]. It was also established that the pipe extrusion process plays an important role in the stabilisation of the pipes. DSC oxidation induction time measurements of extruded MDPE pipes showed that the antioxidant concentration is almost twice in the centre of the pipe wall than in the near inner and outer wall sections [109]. It was also observed that the loss of sulfur containing phenolic antioxidants anomalously was rapid at the beginning of the exposure of pipes to high temperatures (80-105°C) [109] and the oxidation of the pipes was accelerated when in contact with water due to antioxidant extraction in to the water phase [4]. Results from a study conducted for over 20 years on the durability of crosslinked polyethylene pipes extruded for hot water supplies, based on the time to failure determined in a hoop stress test at different temperatures (20-120°C), where the results of the crosslinked polyethylene pipes were compared with those of non crosslinked polyethylene pipes, had concluded, that lifetimes larger than 50 years can be reasonably expected for temperatures up to 80°C [110].

Polyethylene pipes have been widely used in networks for water conveyance, where chlorine disinfectants are commonly used to ensure potability and quality for the consumer; however, the release of chlorine produces a strong oxidative environment that would have a deleterious effect on mechanical, surface and morphological characteristics, thus drastically reducing the lifetime of the pipes by several decades [1, 111]. Chlorinated water was shown to either significantly reduce the pipe lifetime or promotes the consumption of antioxidants [111, 112]. The problem here is that only a small amount of aqueous chlorine is necessary to initiate subsequent chain reactions, capable of producing more radicals that can react with the HDPE polyolefin surface [113]. It was found that the pipes exposed to the same length of time to water, internally and externally were less affected by oxidation than the pipes exposed to air externally [7]. Extensive and visible degradation in pipes failing according to stage-III failure was confined to the so-called "oxidation spots''. The most degraded material in the

oxidation spots exhibited a significantly higher crystallinity and higher melting temperature than the material outside the oxidation spots [4]. Pipe failure mechanism dominated by chemical degradation of the polymer is referred to as stage-III failure, which occurs typically due to consumption of antioxidants by migration. The pipes exposed to different internal pressures exhibited different failure mechanisms [4, 109, 114], see **Figure 1.1**.

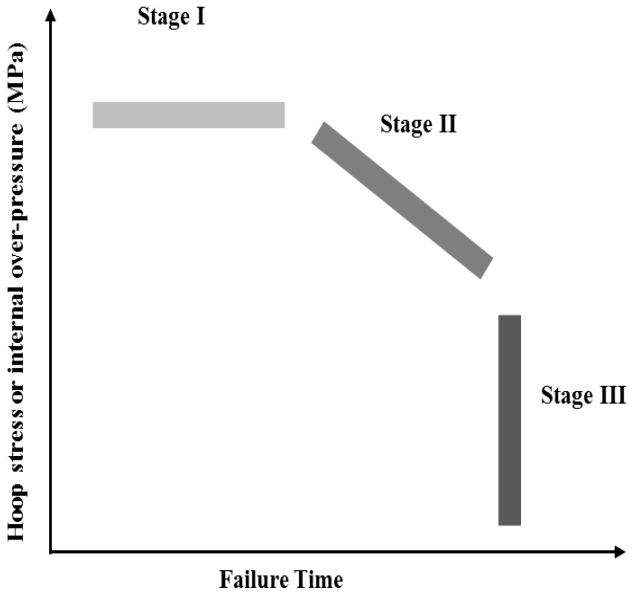
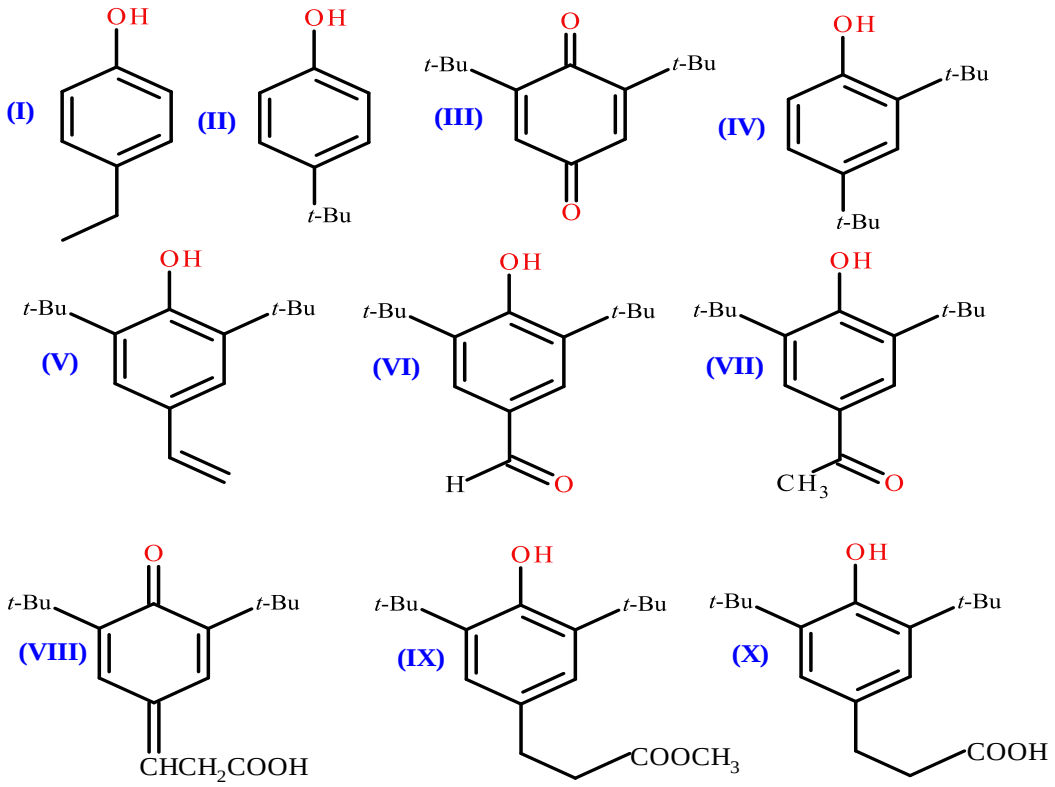


Figure 1. 1: The three failure stages (I-III stages) of typical long term fracture of crosslinked pipe under pressure [115]

Pipes made from high-density polyethylene (HDPE) have found wide-spread use in the drinking water distribution network. However, the quality of water passing through the polyethylene pipes can be affected by migration of any component from the plastic material such as additives and any oxidative degradation products. Most of the migrating compounds were shown to have a basic common structure characterised by a Phenolic ring typically substituted with hindered alkyl groups in positions 2 and 6 on the aromatic ring see **Figure 1.2** [9]. Studies on migration of organic compounds from polyethylene pipelines to drinkable water showed also migration of volatile organic components (VOC) related to decomposition products of phenolic antioxidants that are responsible for an intense odour and taste change of the water [9, 11, 116].



I) 4-ethyl phenol; **(II)** 4-tert-butyl phenol; **(III)** 2,6-di-tert-butyl-p-benzoquinone; **(IV)** 2,4-di-tert-butyl phenol; **(V)** 3,5-di-tert-butyl-4-hydroxy styrene; **(VI)** 3,5-di-tert-butyl-4-hydroxy benzaldehyde; **(VII)** 3,5-di-tert-butyl-4-hydroxy aceto phenone; **(VIII)** Cyclo hexa 1,4 dien, 1,5-bis (tert-butyl), 6-on,4-(2-carboxy-ethylidene); **(IX)** 3(3,5-di-tert-butyl-4-hydroxyphenyl) methyl propanoate; **(X)** 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoic acid

Figure 1. 2: structures and names of organic compounds identified in water samples taken out from PE and PEX polymer samples (VI, VII, VIII) [9].

The main volatile compounds migrating were found to be aliphatic hydrocarbons aldehydes, ketones and olefins. Compounds responsible for the off-odour from thermally oxidized PE were shown to be based on α-unsaturated aldehydes and ketones. Whereas most of the aroma were found to result from hexanal, 1-hepten-3-one, 1-octen-3one, octanal, 1-nonen-3one, nonal, trans-2-nonenel and diacetly [117]. Additionally, the formation of oxygenated by-products from crosslinking processes based on organic peroxide reactions during PEXa pipe production contributed towards VOC production in the water samples. MTBE (Methyl tert-butyl ether) has been found as one of the major contributors to the high values for threshold odour number (TON) in all the PEX pipes samples from examined PEX pipes [9, 11, 116]. Off-flavours from HDPE are ascribed to the presence of carbonyl compounds such as aldehydes, ketones and esters [57, 117-119] and some alkylated benzoquinones are also known to cause off-flavours in water [120] . However, the amount and type of compounds

produced, resulting from thermal oxidation of PE during the pipe processing, are observed to be affected by the time and temperature of the processing operation [57].

To enhance the lifetime and safety of PEX pipes, it is crucial; therefore to minimise, or avoid the diffusion of antioxidants from the PEX pipes to the surrounding environment, the compatibility and leachability of the antioxidants has therefore to be addressed. A good solution for this problem of antioxidant loss from PEX pipes would be to graft antioxidants on the polymer backbone thus not only the pipe lifetime [101, 121] but even more crucially increase the safety of their use in contact in potable water applications. A further study into the grafting of reactive antioxidants on PEXa pipes is the subject of the work presented in this thesis.

Table 1. 3: Examples of Commercial Antioxidants

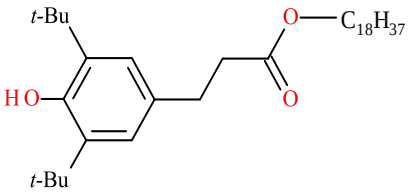
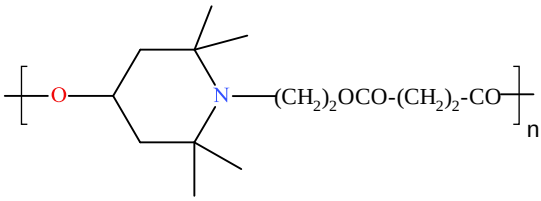
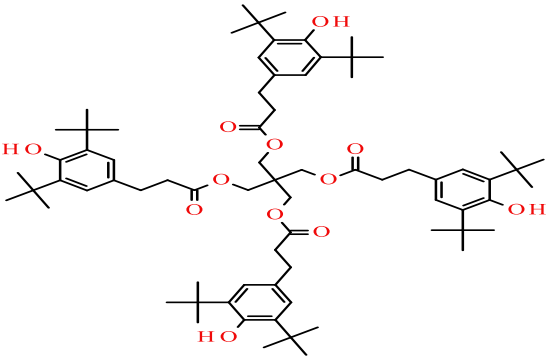
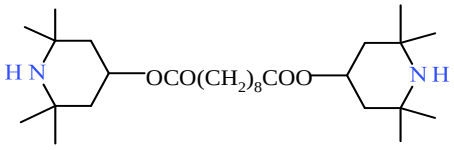
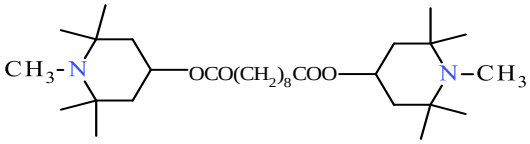
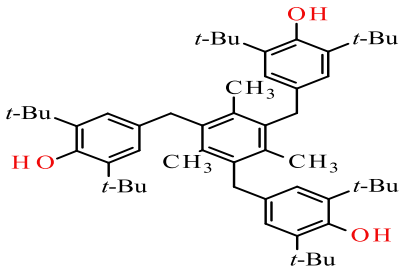
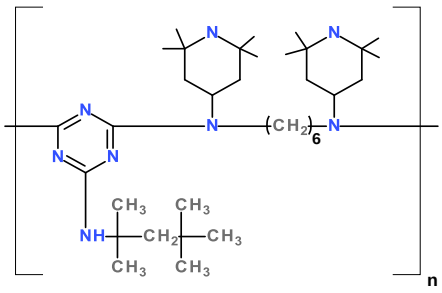
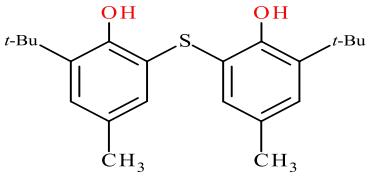
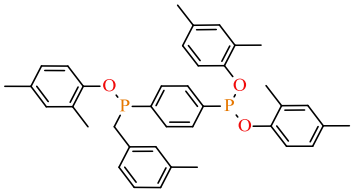
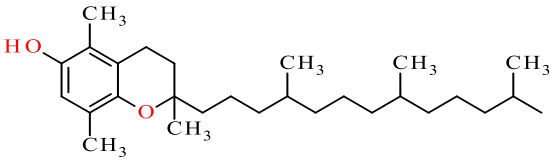
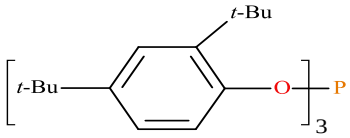
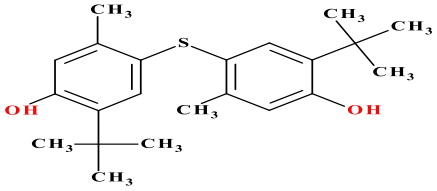
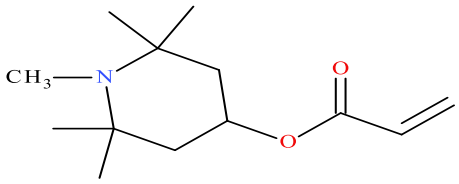
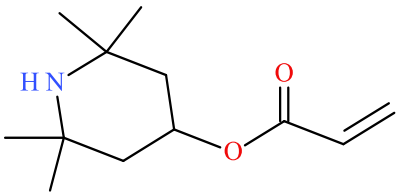
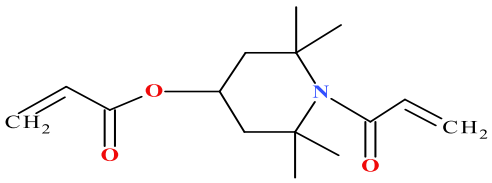
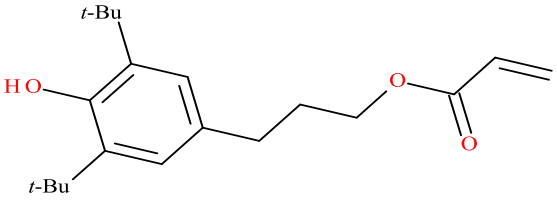
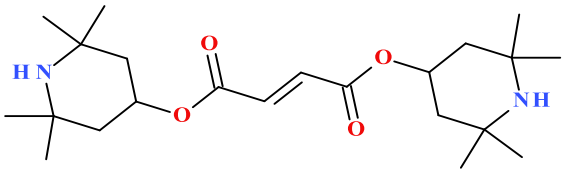
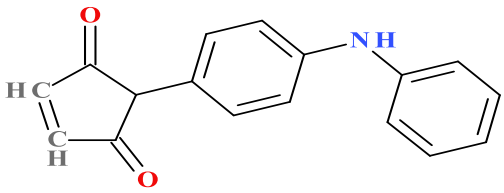
Hindered phenols	HAS & phosphite Esters
 **Irganox 1076**	 **Tinuvin 622**
 **Irganox 1010**	 **Tinuvin 770**
	 **Tinuvin 765**
 **Irganox 1330**	 **Chimassorb 944**
 **Irganox 1081**	 **Irgafos PEPQ**
 **α-tocopherol (Vitamin E)**	 **Irgafos 168**
 **Santox R**	

Table 1. 4: Examples of Reactive Antioxidants

Reactive Antioxidants
 **AOPP**
 **AOTP**
 **AATP**
 **DBPA**
 **BPM**
 **APM**

1.6 Aim of the research work

The overall aim of this research was to investigate non migratory stabilising systems for peroxide crosslinked polyethylene, (PEX) samples prepared in the lab, and produced commercially, as pipes (PEXa) that would give rise to improved long term thermal stability performance before and after solvent and water extractions. This was achieved by grafting of reactive antioxidants on highly crosslinked HDPE backbone where the stabilising efficiency was then assessed in the crosslinked polymer.

1.7 Objectives of the work

To achieve the above aim, this work had the following objectives.

- To synthesis reactive antioxidants (AOs) based on graftable hindered amines (g-HAS), used with and without conventional or reactive (graftable) hindered phenol (g-ph), that would be consequently utilised in melt reactive processing with HDPE.
- To develop laboratory conditions for peroxide crosslinking of HDPE containing the graftable AOs that would simulate the Engel process using an internal mixer (Haake) and/or hydraulic press (Daniels).
- To optimise the chemical composition and the processing conditions that would result in the highest antioxidant (AOPP, AOTP, AATP) grafting efficiency during melt processing in the absence or presence of a reactive hindered phenol, (DBPA), see **Table 1.4** on HDPE backbone.
- To develop stabilising systems for PEX samples and commercially produced PEXa pipes based on (g-HAS and g- Ph), which would result in high stabilisation efficiency with minimum AO losses after solvent extractions.
- To produce PEXa pipes containing synthesised g-HAS or g-Ph combinations using two commercial production processes, Engel and High Speed IR extrusion (the pipe production was done in Uponor, Virsbo, Sweden).
- To develop the most suitable methodology for assessing the retention of the grafted antioxidants (g-HAS or g-Ph) in the polymer after the crosslinking process and after water and solvent extractions
- To develop extraction methodology using pressure solvent extraction system (ASE) to simulate hydrostatic test for investigation of the long term performance of pipes in contact with water under pressure.
- To develop HPLC-MS methods in order to identify compounds, that would migrate into the contact-solvent media, e.g. in water or DCM.

Chapter 2
Experimental and Analytical Techniques

2.1 Materials

2.1.1 Polymer

Two different commercial grades of High density polyethylene were used throughout this work, and were kindly donated by the sponsor company, Uponor Ltd.

i) Unstablised **HDPE powder,** a Basell polyolefin with the trade name Lupolen 5261Z Q456, has a melting point of 135ºC and melt flow index of 2g/10min under 21.6kg load, see **Figure 2.1**.

ii) Stabilised **HDPE powder**, a Borealis with the trade name BORPEX HE1878E, white powder stabilised with 700 ppm of Irganox 1076 and having MFI of 10g/ 10 min under 21.6 Kg load.

Commercial Name	Code Name	Chemical structure	Physical properties	Supplier	FTIR
Lupolen 5261ZQ456	L (Lupolen)		White powder, Unstabilised m.p =135°C MFI 2g/10 min (21.6 load)	Basell PO(Provided by Uponor Sweden)	**Fig 2.1**
BorPex HE 1878E	B (BorPex)		White Powder stablised with 700 ppm Irganox 1076, m.p =133°C MFI 10g/10 min (21.6 load)	Borealis (Provided by Uponor Sweden)	

2.1.2 Initiators

The initiator Azoisobutyronitryle **(AIBN), see Figure 2.2,** which **was** used for homopolymerisation of reactive antioxidants, was supplied by Fisher scientific, and used without further purification**. Trigonox 101 (T101)**,2,5-dimethyl 2,5-bis(t-butylperoxy)hexane,**Trigonox145-E85(T145)**,2,5-Dimethyl-2,5di(tertbutylperoxy)hexyne-3,which was 85% solution in mineral oil, and **Trigonox B (TB),** di-tert-butyl peroxide (**Table 2.1 for structures and Figure 2.3**), were used for free radical grafting of the reactive antioxidants on HDPE and for crosslinking of the polyethylene, all were supplied by Akzo nobel, Netherlands. **Table 2.2** gives the peroxide and AIBN characteristics including their calculated half-lives. The half-life times of the peroxides were calculated from equations **1** and **2** using constants provided in their technical data sheets.

$$t_{1/2} = (\mathbf{In2})/k_d \quad \mathbf{(1)}$$

$$k_d = A \times e^{-E_a/RT} \quad \mathbf{(2)}$$

where:
T = (273.15 +ºC) K
R = 8.3142 j/mol.K
A = 4.2 x10^{15} s^{-1} for Trigonox B
E_a = 153.46 kj/mol for **Trigonox B**

A = 1.68 x10^{16} s^{-1} **Trigonox 101**
E_a = 150.67 kj/mol for Trigonox 101
A = 1.9 x$10^{15}$$s^{-1}$ for **Trigonox 145-E85**
EA = 153.46 kj/mol for Trigonox 145-E85

Table 2. 1: Initiators used in the work

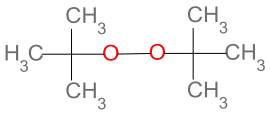
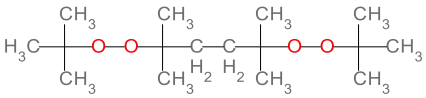
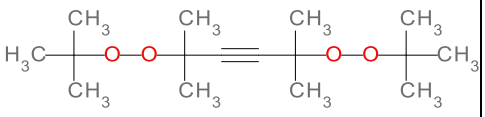
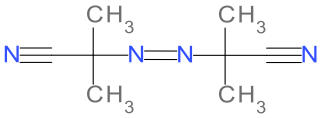
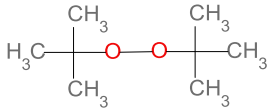
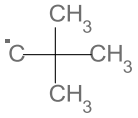
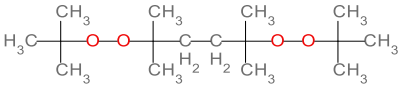
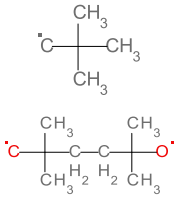
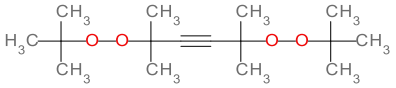
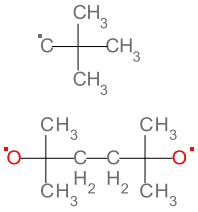
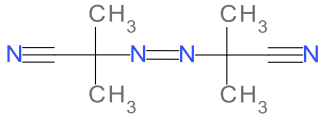
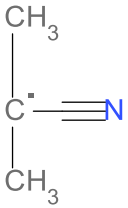
Commercial Name/ Code Name	Chemical structure and Name	Physical properties, Mw	Supplier	FTIR
Trigonox B TB	 Di-tert-butyl peroxide	Colourless liquid Mw=146 Purity 99%	**Akzo Nobel**	**Fig 2.3 (A)**
Trigonox 101 T101	 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane	Colourless liquid Mw=290 Purity 92%	**Akzo Nobel**	**Fig 2.3 (B)**
Trigonox 145-E85 T145	 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexyne-3	Colourless liquid Mw=286 Purity 99%	**Akzo Nobel**	**Fig 2.3 (C)**
AIBN	 Azoisobutyronitryle	White powder Mw=64 M.P: 105ºC Purity 99%	**Akzo Nobel**	**Fig 2.2**

Table 2. 2: Properties and calculated half-life times of peroxide and AIBN

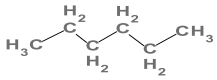
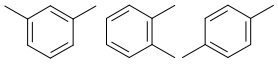
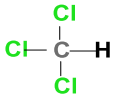
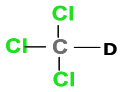
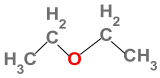
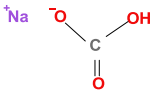
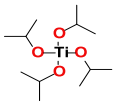
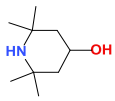
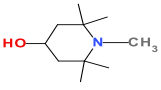
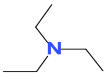
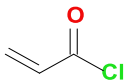
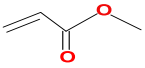
Structure of peroxide	Physical properties, Mw	Radicals formed		Half life time-$t_{1/2}$ at temp. (°C) #											Supplier
		Primary	Secondary	(min)					(sec)						
				120°	140°	160°	170°	180°	190°	200°	220°	230°	240°	250°	
Trigonox B (TB)  Di-tert-butyl peroxide	Colourless liquid Mw=146 99% pure			**675**	**70**	**8.8**	**3.4**	**1.35**	**33.5**	**14.4**	**3**	**1.4**	**0.7**	**0.3**	**Akzo Nobel**
Trigonox 101 (T101)  2,5-dimethyl-2,5-bis(t-butylperoxy)hexane	Colourless liquid Mw=290 92% pure			**314**	**31**	**3.9**	**1.5**	**0.6**	**14.2**	**6**	**1.2**	**0.6**	**0.3**	**0.1**	**Akzo Nobel**
Trigonox 145-E85 (T145)  2,5-Dimethyl-2,5-di(tert-butylperoxy)hexyne-3	Yellowish liquid Pueity 85% Mw=286			**635**	**68**	**9**	**3**	**1.4**	**33.9**	**15.7**	**3.3**	**1.6**	**0.8**	**0.4**	**Akzo Nobel**
Azoisobutyronitryle (AIBN)  Azoisobutyronitryle	White powder Mw=164			**0.5**											**Akzo Nobel**

Half-life times calculated from equation 1 and 2 (see section **2.1.2**) were then converted from seconds to minutes by dividing the result by 60s

2.1.3 Solvents and Reagents

Solvents and reagents used were supplied by Fisher Scientific or Sigma Aldrich and were used without further purification, see **Table 2.3.**

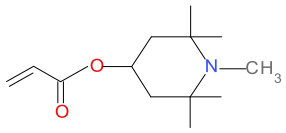
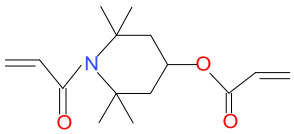
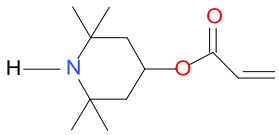
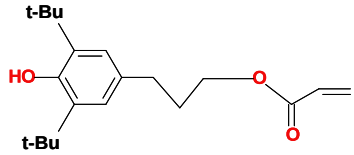
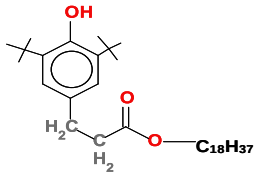
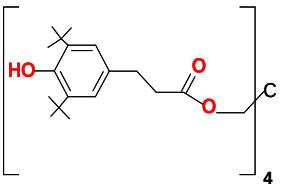
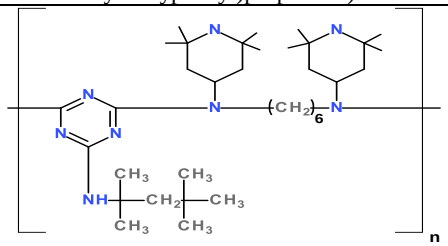
Table 2. 3: Solvents and reagents used in this work

Commercial Name	Chemical structure	Supplier	Physical properties, Mw
Hexane		Fisher scientific	Lab grade solvent B.P. -69ºC Mw: 86 $gmol^{-1}$
Xylene		Fisher scientific	Lab grade solvent B.P. -138-139ºC Mw: 106 $gmol^{-1}$
Di-chloromethane		Fisher scientific	Lab grade solvent B.P. 40ºC Mw: 84 $gmol^{-1}$
Chloroform		Fisher scientific	Colourless liquid B.P. 60-62ºC Mw: 119 $gmol^{-1}$
Chloroform-d		Sigma-Aldrich	Colourless B.P. 60.9ºC 99.8% deuterated Mw:120 $gmol^{-1}$
Toluene		Fisher scientific	HPLC grade solvent B.P. 110ºC Mw: 92 $gmol^{-1}$
Diethyl ether		Fisher scientific	Colourless liquid B.P. 34.6ºC Mw: 74 $gmol^{-1}$
Sodium hydrogen carbonate		Sigma-Aldrich	White powder M.P. 50ºC Mw: 84 $gmol^{-1}$
Titanium isoprpoxide		Fisher scientific	Clear to yellow MW:285 $gmol^{-1}$
2,2,4,4,-pentamethyl-4 piperidinol		Fisher scientific	White powder Mw:157 $gmol^{-1}$
1,2,2,4,4,-pentamethyl-4 piperidinol		Fisher scientific	White powder Mw:171.28 $gmol^{-1}$
Triethyl amine		Fisher scientific	Clear liquid Mw: 101 $gmol^{-1}$
Acryloyl chloride		Fisher scientific	Light yellow liquid Mw: 90 $gmol^{-1}$
Methyl acrylate		Fisher scientific	Clear liquid Mw: 86 $gmol^{-1}$

2.1.4 Antioxidants

Four graftable antioxidants (g-AO) were used for free radical melt grafting on HDPE, three reactive (graftable) hindered amine stabilisers (g-HAS) and one hindered phenol. The g-HAS stabilisers were, 4-acryloylloxy 1,2,2,6,6-pentamethyl piperidine (**AOPP**), 1-acryloyl 4-acryloyloxy 2,2,6,6-pentamethyl piperdine (**AATP**), 4-acryloyloxy 2,2,6,6-tetramethyl piperdine (**AOTP).** The g-AOs were synthesised with some modification of methods given by earlier researchers in the PPP group [93, 94, 122] and are described later in this **chapter**. For their structure and physical characteristics, see **Table 2.4** and **Figure 2.4** for their FTIR spectra. A graftable hindered phenol antioxidant 3-(3,5-tert-butyl-4-hydroxy phenyl)propyl-1-acrylate (**DBPA**), was synthesised and purified by another member of the PPP group [101] and used as received. Two commercial hindered phenol antioxidants Irganox 1076, Irganox 1010 and one hindered amine, Chimasorb 944 were kindly donated by Ciba Speciality chemicals and were used as received, see **Table 2.4 and Figure 2.5.**

Table 2. 4: Graftable and commercial antioxidants used in this work

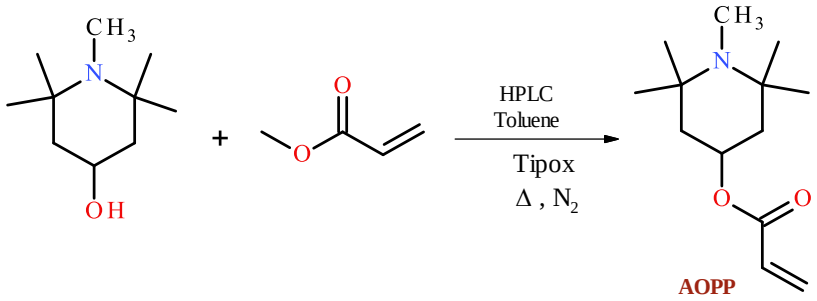
Code Name	Chemical structure and name	Physical properties, Mw $gmol^{-1}$	Supplier	FTIR
AOPP	 4-acryloylloxy 1,2,2,6,6-pentamethyl piperidine	Pale Yellow liquid Mw: 225	Synthesised in PPP	**Fig 2.4 a**
AATP	 1-acryloyl 4-acryloyloxy 2,2,6,6-pentamethyl piperdine	Orange brown Liquid Mw: 264	Synthesised in PPP	**Fig 2.4b**
AOTP	 4-acryloyloxy 2,2,6,6-tetramethyl piperdine	White powder Mw: 211 **M.P: 151°C**	Synthesised in PPP	**Fig 2.4c**
DBPA	 3-(3,5-tert-butyl-4-hydroxy phenyl)propyl-1-acrylate	Thick yellow liquid Mw: 318	Synthesised in PPP	**Fig 2.4d**
Irganox 1076	 octadecyl-3,5-di-tert-butyl-4hydroxyhydrocinnamate	White powder Mw: 531 **M.P: 50-55°C**	Ciba speciality chemicals	**Fig 2.5a**
Irganox 1010	 Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)	White powder Mw: 1178 **M.P:115-118°C**	Ciba speciality chemicals	**Fig 2.5b**
Chimasorb 944	 Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]])	White powder MW:2000-3100 **M.P:100-135°C**	Ciba speciality chemicals	**Fig 2.5c**

2.2 Synthesis of Graftable Hindered Amine Antioxidants, (g-AOs)

These three reactive AO's were synthesised according to previous methods developed in the PPP group [123] with minor modifications as described below.

2.2.1 Synthesis of 4-acryloyloxyl 1,2,2,6,6-pentamethyl piperdine, AOPP

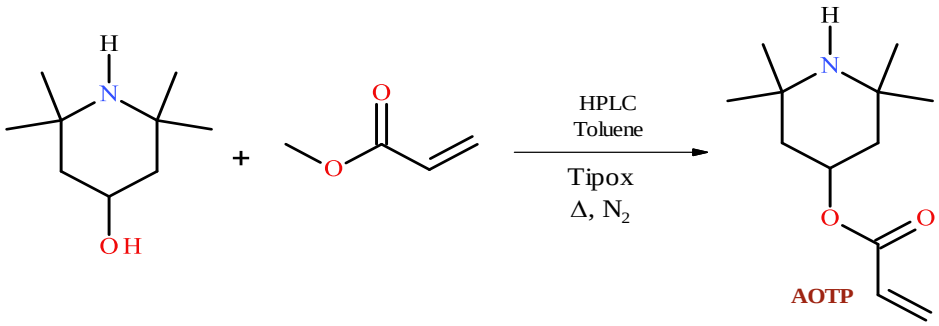
A 0.3 mol of 1,2,2,4,4,-pentamethyl-4piperidinol with 0.27 mol methyl acrylate were dissolved in 250 ml of HPLC grade Toluene. The solution was boiled using an oil bath and 9 ml (0.03mol) of titanium isopropoxide (Tipox) was added, the solution was then refluxed for 48 hours under N_2. After cooling, 100ml of 5% sodium bicarbonate was added, filtered and two layers were separated. The solution in the organic layer was evaporated and the resulting solid was recrystallized from hexane. The unreacted 1,2,2,4,4,-pentamethyl-4 piperidinol remained undissolved in hexane and was removed. The hexane solution was dried over magnesium sulphate and the solvent was evaporated to give yellowish oily liquid characterised as AOPP and the yield was around 80%, see **Reaction Scheme 2.1** and for methodology see **Scheme 2.1.** Full characterisation of AOPP is given in **Chapter 3, see Table 3.8, 3.9 & 3.10,** pg 111-112.



Reaction Scheme 2. 1

2.2.2 Synthesis of 4-acryloyloxy 2,2,6,6-tetramethyl piperdine, (AOTP)

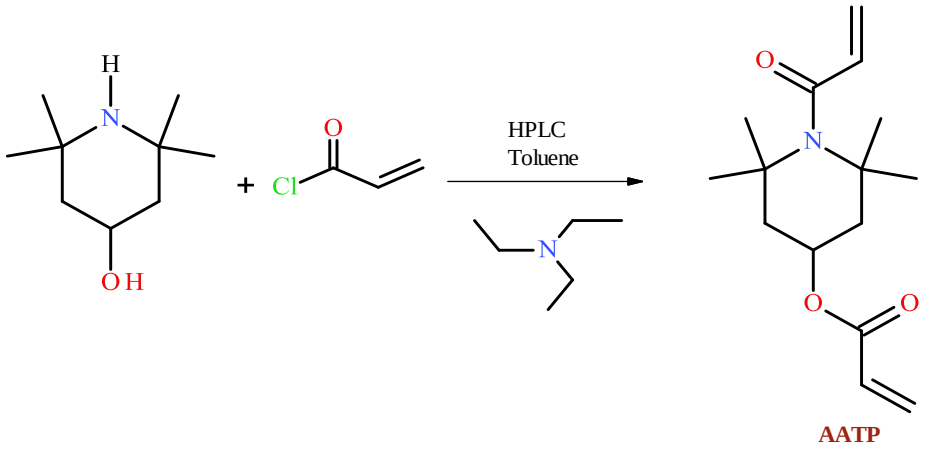
15.7g (0.1mol) of 2,2,4,4-tetramethyl-4-pipereidinol with 8.5 ml (0.093 mol) methyl acrylate were dissolved in 250 ml HPLC grade toluene. The solution was boiled using an oil bath and 3 ml of titanium isopropoxide (Tipox) was added, refluxed for 2 hours then a further 6 ml (0.01mol) of titanium isopropoxide (Tipox) was added. The refluxing was continued for 24hrs under N_2. After cooling at room temperature, 100 ml of 5% sodium bicarbonate was added, filtered and the two layers separated. The solvent in the organic layer was evaporated, and the solid product was recrystallized from hexane with Melting point 151°C and the yield was about 70%. See **Reaction 2.2 and Scheme 2.2** for the methodology. For full characterisation, see **chapter 3, Table 3.8, 3.9 & 3.10,** pg 111-112.



Reaction Scheme 2. 2

2.2.3 Synthesis of 1-acryloyl 4-acryloyloxy 2,2,6,6-tetramethyl piperdine ,(AATP)

15.7 g (0.1 mol) of 2,2,4,4-tetramethyl-4-pipereidinol with 29.2 ml triethyl amine were dissolved in 200 ml HPLC grade Toluene. The solution was cooled down below 10 ºC in an ice bath and then a solution of 18.6 ml of acryloyl chloride in HPLC grade toluene was added drop-wise with constant stirring for 1 hour and stirring was continued for another 12 hours at room temperature. A solid by-product (triethylamine hydrochloride) was formed, which was filtered out. The organic layer was washed with aqueous potassium hydrogen carbonate. The organic solvent evaporated and the liquid product was washed with toluene. An oily orange-brown liquid product was obtained and the yield was 60%, see **Reaction Scheme 2. 3** and for methodology**, see Scheme 2.3 (pg 77).** For full characterisation, see **chapter 3, Table 3.8 , 3.9 & 3.10**, pg 111-112.



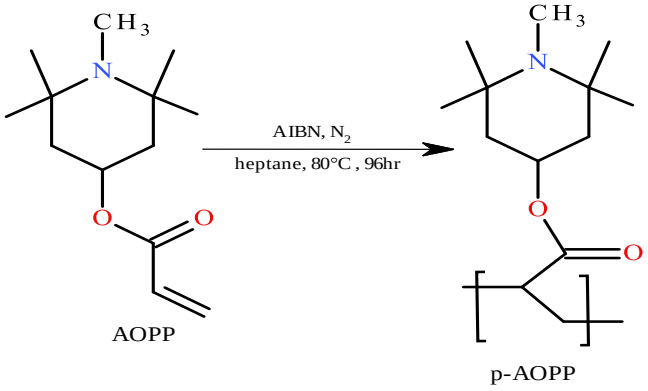
Reaction Scheme 2. 3

2.2.4 Synthesis of Homopolymers of Hindered Amine Antioxidants

Hompolymerisation of AOPP and AOTP was carried out in order to analyse and understand the nature and extent of the main side reaction products that occur alongside the grafting reaction of these antioxidants on PE.

2.2.5 Polymerisation of AOPP (p-AOPP) in Heptane

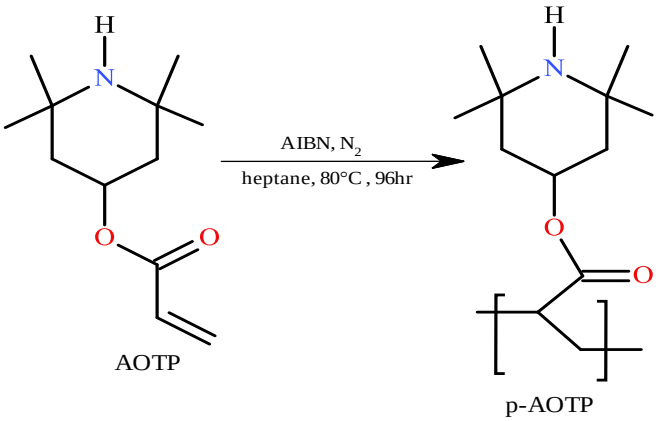
0.5 moles (0.5 g) of AOPP and 0.3 molar ratio of AIBN (0.098 g) were dissolved in 100 ml heptane in a 250cm^3 3-necks round bottom flask. After assembling with thermometer, condenser and purging with nitrogen gas, it was refluxed at 80 ºC for 98 hours. The mixture was then cooled to stop further reaction and the solvent evaporated using rotary evaporator. A clear viscous solution was formed which was dissolved in dichloromethane (DCM) to remove any unreacted AOPP and AIBN, for methodology, see **Scheme 2.4, pg 78.** This step was repeated several times. FTIR and NMR spectra of poly-AOPP were recorded and compared with that of AOPP**.** Full characterisation of p-AOPP is given in **chapter 3, sec 3.2.1**



Reaction Scheme 2. 4

2.2.6 Polymerisation of AOTP (p-AOTP) in Heptane

0.5 mole (0.5 g) of AOTP and 0.3 molar ratio of AIBN (0.098g) were dissolved in 100 ml heptane in a 250cm^3 3 necks round bottom flask. After assembling with thermometer, condenser and purging with nitrogen gas, it was refluxed at 80 ºC for 50 hours. The mixture was then cooled to stop further reaction and the solvent evaporated using rotary evaporator. A clear viscous solution was formed which was dissolved in dichloromethane (DCM) to remove any unreacted AOTP and AIBN, for methodology, see **Scheme 2.5, pg 79**. This step was repeated several times. For full characterisation, see **chapter 3, Table 3.8, 3.9 & 3.10**.



Reaction Scheme 2. 5

2.3 Reactive Processing for Free Radical Melt Grafting of Antioxidants on HDPE

2.3.1 Melt Processing using an Internal Mixer

All polymer processing was carried out using Thermo Haake Rheomix torque rheometer (Rheomix 600), consisting of a pair of rollers positioned in a mixing chamber of 69 cm^3 capacity. The mixing chamber has three plates which are electrically heated and run with a PolyLab motor drive, equipped with a digital torque displaying unit and ram which can be pressed down to offer closed chamber system and exerts pressure on the polymer during mixing. The temperature can be controlled up to 400 ºC and compressed air is used as cooling system. The mixer sensors determined the torque and temperature of the chamber. The data were monitored and recorded via the associated Polylab software.

The net chamber volume (Vn) with the rollers in use was 69 cm^3. However the amount of the polymer needed to fill the chamber depended upon its melt density. The melt density of the polymer was measured using a Ray Ran Melt flow Indexer at 190°C and 21.6 kg. The HDPE was charged into pre-heated cylinder of the Melt flow Indexer and kept for before introducing a load on the piston. The amount of extrudate passing through a standard die (2.095 mm diameter) obtained in a given length of the cylinder was weighed. The melt density of polymer was calculated using **equation 3**. The amount of the polymer needed to fill the chamber was 37g calculated using.

$$Melt\ density\ (Ray\ Ran) = \frac{\text{Mass of extrudate}}{\text{Volume of the cylinder at length of 1cm}} \quad (3)$$

The piston travel distance = 1 cm
Area of barrel (given) = 0.71 cm^2
Volume of the cylinder = 0.71 cm^3
The mass of the barrel (given) = 0.54 g

Melt density of HDPE (ρ) = 0.54/0.71 x 1

= **0.765 g/cm³**

$$\boldsymbol{m = \rho\ V_n\, 0.7} \quad \textbf{(4)}$$

m- sample weight
ρ- melt density of HDPE at temperature 190°C & 21.6kg (0.765g/cm³ as measured in Ray Ran Melt Flow Indexer with a load of 21.6kg)
Vn- net chamber volume with rotors in use (69 cm³)
0.7- filling percentage, 70% full

2.3.2 Reactive Processing for Melt Grafting of Antioxidants and production of 'Normal' Antioxidants Concentration (PE-g-AO) and Masterbatches with High Concentrations of g-AO- (PE-g-AO_{MB})

The melt free radical grafting of the reactive antioxidants (r-AO) high density polyethylene (HDPE) was carried out in Haake Rheomix. The formulations were prepared for processing by initially pre-weighing the required amounts of the polymer, peroxide and antioxidant. The mixture was then soaked in hexane (30 min) for uniform distribution of the additives. The solvent was then removed by evaporation at room temperature. The mixing chamber was initially preheated (electrically, the temperature can be taken up to 300°C with in control of 0.1°C) and flushed with nitrogen for more than 2 minutes to eliminate oxygen from the chamber and minimise polymer oxidation, before loading the polymer, and additive mixture.

The processing temperature and the r-AO concentration were varied but the rotor speed was fixed at 65 rpm. For all processing done in this work, the melt temperature and the processing Torque were continuously monitored using dedicated software "PolyLab Monitor Version 4.16". After completion of the processing, the processed polymer was removed from the mixer and cooled down (in cold water) to avoid thermal oxidation.

Both a low concentration of 0.5%w/w (referred here to as "normal" concentration) and high concentrations of 1% to 6% w/w (referred to here as masterbatch, MB, concentration) of the

different r-AO's were used in this work. PE-AO masterbatches (MB) were also diluted down to the "normal" (0.5%) concentration with fresh HDPE (unstablised) using mild processing conditions of 145ºC for 10 minutes. If the masterbatch was prepared for the purpose of crosslinking, then the dilution was done in the presence of 0.5% of the crosslinking peroxide TB. An example for calculation used for the formulation of 3% AOPP and 0.02 molar ratio of peroxide/AOPP in HDPE for reactive processing (PE-g-AOPP-5) is given below:

Example for calculating grafting composition

$$W_{AOPP} = \frac{3\% \times 37g}{100\%} = 1.11\ \text{g} \quad \textbf{(5)}$$

$$W_{ROOH} = Mw_{ROOH} \times MR \times \frac{w_{AOPP}}{Mw_{AOPP}} = 290g/mol \times 0.02 \times \frac{1.11g}{225g/mol} = 0.029\text{g} \quad \textbf{(6)}$$

$$W_{HDPE} = 37g - 1.11 - 0.029 = 35.9\ \text{g} \quad \textbf{(7)}$$

Where
$w_T = Total\ weight\ of\ ingridents\ used\ in\ the\ processing\ which\ is\ 37g$
$w_{AOPP} = weight\ of\ AOPP\ needed$
$w_{ROOH} = weight\ of\ peroxide$
$w_{HDPE} = weight\ of\ polymer$

$MR = molar\ ratio\ of\ peroxide\ to\ AOPP$
$Mw_{AOPP} = molecular\ weight\ of\ AOPP$
$Mw_{ROOH} = molecular\ weight\ of\ peroxide$
$[ROOH] = molar\ concentartion\ of\ peroxide$

2.3.3 Dilution of g-AO Masterbatches (PE-g-AO_{DMB})

Masterbatches (MB) of PE-g-AO (prepared as described in section 2.3.2) were diluted down with Unstabilised HDPE and processed as follow. MB's of grafted AO with highest grafting level were chosen to be diluted to 0.5% and then granulated. The weight of the MB was calculated (to get a final weight of 0.5g concentration of the grafted AO in 100g of the polymer), the MB was then processed under mild processing conditions of 145ºC for 10 minutes. After processing the polymer was, cooled, dried and compression moulded using Daniels press at 160°C for 2 minutes without pressure followed by 5 minutes with maximum pressure of 22kg/cm^2. Films were analysed for their oxidative induction time (OIT) by DSC and further crosslinking content.

2.3.4 Sample Films, Preparation by Compression Moulding

Compression moulding using Daniels press was carried out to prepare polymer samples for FTIR and DSC analysis as well using it as a method for crosslinking PE in the presence of peroxide. Processed polymer was cut into small pieces of ~ 1g, four pieces were pressed into thin films of ~ 250μ thick, by placing between two stainless steel square plates, covered from inside with Teflon sheets to prevent the polymer sticking on to the plates. The polymer was pressed for 2minutes without applying any pressure, followed by further 5 minutes under pressure of 22 kg/cm^2 at 160°C (for processed samples) or 240°C (for crosslinking). The film samples were then cooled inside the press platens immediately by circulating cold water around the platens until the temperature dropped to 50 ºC after which the polymer films were removed and stored in dark for further analysis.

2.4 Peroxide-Initiated Crosslinking of Stabilised HDPE samples

2.4.1 Commercial process for the crosslinking of PE using the Engel process

To produce chemically crosslinked polyethylene pipes by peroxide, typically the commercial Engel process is used to give an even crosslinked tubing where 70-80% crosslinking can be achieved by this method [29]. This method involves the extrusion of polyethylene in the presence of conventional antioxidants and peroxides, crosslinking takes place in the extruder with a plunger action in the presence of high pressure reciprocating piston that replaces the traditional screw where the melt is pushed through along annular die under high pressure of 200-500 MPa and high temperature to produce crosslinked tubing [29].

2.4.2 Laboratory-based Crosslinking Method of PE using Compression Moulding

High level of crosslinking methodologies of HDPE were developed earlier in the PPP Group by another researcher who worked on a similar project [101] to simulates the commercial (Engel) process for producing PE peroxide chemically crosslinked pipes (PEX_a) and were used without modification as described below.

(i) One-step process of grafting and crosslinking the polymer (g_1-PEX)

For the one-step crosslinking, the polymer, graftable antioxidant and peroxide initiator were mixed using a solvent for good distribution of the additives in the polymer, followed by drying to remove traces of any solvent. The solvents used were hexane for AOPP and DBPA, DCM for AOTP and AATP with the peroxides T145 or T101. Crosslinking was carried out using the peroxide TB, the polymer and antioxidants were premixed in the solvent followed by removal of the solvent. A pre-weighed TB was added to the dried polymer mixture and mixed using a flask shaker for 24 hr in a sealed glass jar.

After premixing, the grafting and crosslinking processes were achieved by compression moulding of the polymer by placing the polymer mixture between Teflon sheets inside two stainless steel sheets at 240ºC for 2 minutes without pressure followed by a further 5 minutes under maximum pressure of 22 kg/cm^2 (20 tons), see **Scheme 4.2, Chapter 4, pg 141.** Crosslinked film samples (120 μm thick) were then analysed for crosslinking level, OIT and AO concentration.

Example for calculating crosslinking composition for the one-Step crosslinking process (and also for Engel process)

Example for calculation for processing 0.5% AOPP and 0.05 % of the peroxide used for HDPE crosslinking.

$$W_{AOPP}=\frac{\%\,AOPP \times W_T}{100\%} \quad \textbf{(8)}$$

$$W_{ROOH}=\frac{\%\,ROOH \times W_T}{100\%} \quad (\textbf{9})$$

$$W_{HDPE} = W_T - W_{ROOH} - W_{AOPP} \quad (\textbf{10})$$

Where
$w_T = Total\ weight\ of\ ingridents\ used\ in\ the\ processing\ which\ is\ 37g$
$w_{AOPP} = weight\ of\ AOPP\ needed$
$w_{ROOH} = weight\ of\ peroxide$
$w_{HDPE} = weight\ of\ polymer$

$$W_{AOPP} = \frac{0.5\% \times 10g}{100\%} = 0.05g \quad (\textbf{11})$$

$$W_{HDPE} = 10g - 0.05 - 0.05 = 9.90\ \text{g}$$

(ii) Two-step grafting and crosslinking (g_2-PEX) including dilution of master batches, (g_{DMB}-PEX_{DMB})

AOPP and AOTP samples grafted on HDPE (PE-g-AO) were crosslinked in the presence of the peroxide TB as an initiator. AO-master batches were diluted down to "normal" concentration (less than 1% total AO content) with Unstabilised HDPE. Pre-calculated weights of MB (mechanically granulated), with or without addition of further commercial AOs were mixed together with unstablised HDPE and 0.5% TB, the mixture was then pre-mixed in sealed glass jars for 24 hr, using a flask shaker. The mixture was homogenised in the torque rheometer (TR) for 10 minutes at 150°C just above the HDPE melting temperature to minimise decomposition of the peroxide, see **Chapter 4, Scheme 4.1 Route A, pg 140**. After homogenisation, crosslinking of the polymer was achieved by compression moulding as described above (see **Section 2.4.2.i**).

If the grafted AO was present at concentration below (<1%) then the polymer mixture was directly crosslinked through, full description of the methodology is given later in **Chapter 4, Scheme 4.1, (pg 140).**

Example of the calculation for crosslinking of HDPE containing PE-g-AOPP with 0.5 wt % TB (peroxide) is shown below. The antioxidant containing MB sample used here to illustrate this example was based on sample **PE-g-AOPP-1** which contains a 3% AOPP master batch (reactively processed in presence of 0.005% MR T101 at 180^{o}C for 5 minutes and had a grafting level of 66%). To obtain 0.5g of grafted AOPP in 100g polymer (0.37g of grafted AOPP in a total polymer weight of 37g of sample processed in a TR), a 6.14g of the above MB was required.

$Total\ weight\ of\ polymer\ used\ for\ procsesing = 37g$
$If\ caluclation\ based\ on\ Total\ weight\ of\ polymer = 100g$
$for\ unpurified\ gAOPP\ MB\ containing\ 3g\ AOPP\ in\ 100g\ HDPE$

$$Weight\ of\ AOPP\ in\ 100g = \frac{\%\ of\ g{-}AOPP\ in\ MB\ X\ 100g\ of\ PE}{weight\ of\ AOPP} \quad \textbf{(12)}$$
$$= \frac{0.5X100}{3g}$$
$$= 16.67g\ needed\ i\ per\ 100g$$

$$weight\ of\ MB\ containing\ 3\%\ AOPP = \frac{weight\ of\ AOPP\ in\ 100g\ PE\ X\ weight\ of\ polymer\ used\ for\ processing}{100} \quad \textbf{(13)}$$

$$\boldsymbol{weight\ of\ MB\ containing\ 3\%\ AOPP} = \frac{16.67X\ 37}{100} = 6.14g\ needed\ in\ 37g\ polymer \quad \textbf{(14)}$$

$$\boldsymbol{weight\ of\ peroxide} = \frac{0.5X37g}{100} = 0.185g\ \ needed\ in\ 37g\ polymer \quad (\mathbf{15})$$

$$\boldsymbol{weight\ of\ PE = total\ weight\ for\ the\ proccessing - weight\ of\ peroxide - weight\ of\ MB}$$

$$\boldsymbol{weight\ of\ PE = 37 - 0.185 - 6.14 = 30.675g\ polymer\ needed\ in\ the\ total\ composition} \quad \textbf{(16)}$$

2.4.3 PEXa pipe production containing g-AOs in the presence or absence of commercial AOs

Two production methods for PEXa pipes containing the synthesised g-AO's alone or in the presence of other commercial AOs, were used and carried out in Uponor Virsbo, Sweden, using their commercial Engel production process and the High speed extrusion IR production process as described below.

2.4.3.1 Engel process for producing crosslinked Pipes (PEX_{Eng})

The production of peroxide crosslinked (PEX_{Eng}) pipes containing graftable antioxidant alone and in presence of additional conventional antioxidants (non-graftable) was carried out at Uponor production plant in Virsbo, Sweden using their commercial Engel process. All PEX_{Eng} pipes produced using conditions set for regular production of PEXa pipes with 16-16.5 mm outer diameter and 2 mm wall thickness. High density polyethylene powder-(Lupolen 5261 ZQ 456, MFI of 2 g/10min) from Basell (with no stabiliser) was used for the

Engel pipe production. Different formulations using specific conditions for the PEX_{Eng} productions are described below.

When using the peroxide T145 or T101, the formulations were prepared by initially pre-weighing in a total batch of 1kg, the appropriate amount of the polymer, the peroxide at 0.4% (except for T145 used at 0.45%) and antioxidants (g-HAS with a graftable hindered phenol "DBPA" or /and with a conventional hindered phenol, mainly Irganox 1076). The polymer mixture was subsequently soaked in hexane (or DCM when AOTP and AATP were used) for uniform distribution of the additives in the polymer, followed by solvent evaporation at room temperature overnight to be ready for the production by the Engel process .When using the peroxide TB, a similar preparation of the formulation was done except in this case the polymer mixture was prepared first without the peroxide and only after the solvent (hexane) has evaporated, then the TB (0.4%) was added to the dried polymer mixture and was left overnight in sealed containers to soak in the polymer formulation.

The AO grafting (if g-AOs were used) and the crosslinking process were then achieved in the Engel production machine using the following set conditions:

Engel Processing Conditions:

Cylinder block: 110°C
Electrical heating (only used for start-up): 150°C
Bushing: 250°C
Manderal/pin: 250°C
Set line speed: 260m/h

In this production, the first pipe extruded was the standard Uponor-Virsbo pipe containing 0.5% Irganox 1076 and 0.4% TB, followed by extrusion of twenty six new formulations. Between each formulation, a standard pipe formulation was extruded to make sure the extruder was cleaned from the last mixture and also to make it easy to separate each new formulation pipe produced. All the observations were recorded during the process, (see **ch4, Table 4.5).** All the pipes were shipped to Aston University.

2.4.3.2 High Speed Extrusion IR Process for Producing Crosslinked Pipes (PEX_{HS})

The production of crosslinked pipes (PEX_{HS}) containing Aston's-PPP graftable antioxidants alone and in the presence of additional conventional (non-graftable) antioxidants, was also carried out at Uponor production plant in Virsbo (Sweden) using a different commercial pipe production method where a High Speed extrusion IR process is used with all the processing conditions set as for regular pipe production giving a pipe size of 20 mm outer diameter and 2

mm wall thickness. The polymer used here was high density polyethylene powder (BORPEX HE1878E, MFI 21.6 g/10min) Borealis, containing a small amount of (700 ppm) Irganox 1076 for storage and transport purposes. Polymer formulations for the pipe extrusion were prepared by pre-weighing the required amount of the antioxidants, HDPE and the peroxide (total of 140 Kg batches). The polymer mixtures were soaked in hexane for 1 hour for uniform distribution of the AOs in the polymer followed by evaporation of the solvent at room temperature overnight, full description of the methodology is given later in the **Ch4**, **Scheme 4.5 (pg-144).**

The extrusion was done in a twin screw extruder at Low temperature of 170^{o}C, followed by crosslinking through heating with a high temperature short wavelength infrared radiation at 250°C (IR lamp 4Kw) with residence time of about 10-15 Seconds.

2.4.3.3 Sample Preparation procedure for Pipe Testing

i. Pipe Production & Separation of Pipes

(a) Engel process

In order to evaluate the homogeneity (in longitudinal direction) of the antioxidants in PEX_{Eng} pipe, the pipes were marked at 4 places and cut in to equal size pieces .Ring shaped slices were cut from each pipe section for analysis, see later, **Ch.4**,**Scheme 4.4, Pg .**

(b) High Speed Extrusion-IR process for PEX_{HS} pipes

In order to evaluate the homogeneity of the antioxidant distribution in these pipes in the longitudinal direction, the extruded PEX_{HS} pipes were separated and marked at 5 places across a10 m pipe lengths and at 7 places for 240 m long pipes (see later **Ch.4, Scheme 4.6, Pg 145**). The pipes were then cut at the marked positions at equal size pieces using a pipe cutter. Ring shaped (1.5cm) long pieces were cut out from each pipe section for analysis (see **Ch.4, Scheme 4.6, Pg 145).**

ii. Microtoming of PEX_{HS} pipes

1.5 cm pipe sections were cut out from each 40 m length (for 240 m long pipes, at 2 m intervals) and placed in a microtome (Leica Ultra cut UCT from Leica Microsystems GmbH) equipped with a microscope and a diamond knife. The pipe sections were microtomed into slices (thin films) of a defined thickness of 100 μm, (see later **Ch.4, scheme 4.6, pg 145) .**

iii. Film Preparation of Pipes

In order to examine the DSC-OIT, FTIR and the extent of crosslinking of the produced pipes, thin films were produced as follows. 1 cm long sample (ring shaped pipe section) was cut out and then divided in to two pieces by cutting vertically in the middle (to form two boats); one of the slices was then pressed into a thin film by placing it between two sheets of aluminium foil films using Specac hot press at 150°C. The platens of the press were closed without pressure followed by further 2 minutes under pressure of 18 kg/cm^2 at 150ºC. The film samples were then cooled inside the press platens by circulating cold water around the platens until the temperature dropped to 50 ºC before removing the films (250 μm) using an appropriate Teflon template

2.5 Purification of HDPE-g-AOs, Determination of Grafting Efficiency, Characterisation and Quantification of the Grafting Reaction

2.5.1 Purification of PE-g-AO Samples

In order to establish correctly the AO grafting degree, AO grafted polymer samples were subjected to a purification process. Polymer films of the PE-g-AO (e.g., PE-g-AOPP) grafted (2x3cm^2; 100-250 μm) were exhaustively Soxhlet extracted in DCM under nitrogen for 48 hours, in order to remove any unbound (free-AO), homopolymerised AO (p-AOPP) and any low molecular mass material (all were soluble in DCM) . The extracted films were dried at room temperature under vacuum oven overnight and analysed by FTIR to determine the grafting level (PE-g-AO). DCM solvents extracted were collected from the round bottom flask and left in a beaker under fume hood for solvent evaporation and were later analysed by NMR for characterisation of the side reaction products (see **Sec 2.6.3**).

The extent of the insoluble gel (crosslinked polymer) was measured. Reactively processed films were cut out in to small pieces of 0.5 g and placed in extraction thimble made of stainless mesh (400 mesh, 8.5cm depth, ϕ= 2.5cm). Three samples of each process were analysed and exhaustively Soxhlet extracted in hot xylene for 25 hrs and the thimbles were dried in vacuum oven at 90°C for gel content determination (see **section 2.6.4**). The level of grafting could in principle also be determined using this method but this was not used in this work as a 48 hour of high temperature extraction with xylene could cause chemical changes to the polymer, so for grafting level determination, a different procedure was used as described in the section below, (**see section 2.5.2 ii)** for details.

2.5.2 Purification of PEX_{HS} sample by sequential extraction using DCM by ASE followed by xylene extraction by reflux

i. DCM-ASE Extraction

Purification of microtomed film samples of the pipes (PEX_{HS}) was carried out in a Dionex Accelerated Solvent Extractor 200 (ASE). Pipe pieces were placed in stainless steel cells and extracted using the ASE equipment. Extraction was achieved at optimised oven temperature of 70°C and pressure of 2000 psi for 5 cycles each cycle being of 30 minutes duration. A solvent mixture of 95% DCM and 5% cyclohexane was used to remove any unreacted and homo-polymerised antioxidant from the samples. Extracted samples were subsequently pressed into 200 μm film thickness using SPECAC press at 150°C under 2 tonnes pressure for 3 minutes for subsequent FTIR analysis, (see **Ch.4** later for further details **Scheme 4.7, Route I and Scheme 4.8, pg 146-147.**

ii. Sequential Xylene Extraction

The microtomed ring shaped sliced PEX_{HS}-pipe samples (about 0.5-1g) that had been DCM extracted (in section 2.5.2.i) were placed in a pre-weighted stainless steel thimbles (of known weight) and Soxhlet extracted for 30 min with 120 ml xylene under oxygen-free nitrogen atmosphere. The crosslinked polymer was separated out as xylene insoluble fraction (XL). Cooling the sample in an ice bath precipitated the xylene soluble fraction (NXL) and the precipitate was separated using suction filtration. The precipitate (containing non-crosslinked polymer, free and grafted antioxidant) was dried and pressed into a discs using KBr accessory under 10 tonnes pressure for 3 min, and then pressed into 200 μm thickness using SPECAC press at 150°C under 2 tonnes pressure for 3 mins (for Subsequent FTIR analysis)**.** The xylene insoluble crosslinked polymer (XL) stayed in the thimble and was dried at 80°C in a vacuum oven for 4 h. The gel fraction left in the thimble was weighed and a slice was cut out using a pipe cutter, pressed into 200 μm thickness using a SPECAC press at 150°C under 2 tonnes pressure for 3 minutes for subsequent FTIR analysis. (See also **Ch.4, Scheme 4.7, Pg 146**)

2.5.3 Water Extraction under Pressure using Accelerated Solvent Extraction (ASE)

As the Uponor commercial PEX_{Eng} and PEX_{HS} pipes are typically used for water applications, HPLC grade water was therefore used under pressure to extract the cross-linked pipes in order to determine the extent of antioxidant retention in a water environment.

10 g Pipe samples (as microtomed films ~150 μm thickness) were placed in a stainless steel cell and water (HPLC grade) extracted using ASE, optimised oven temperature of 110 °C, pressure 2000 psi for 5 cycle with each cycle being of 30 minutes duration under nitrogen. The extracted film samples were subsequently pressed using a SPECAC press at 150° C under

2 tonnes pressure for 3 minutes for subsequent FTIR analysis and the other part of the water extracted samples was further extracted in chloroform, dried and re- dissolved in MEOH/CAN solvent mixture for HPLC-MS analysis, (see also **Ch.4, Scheme 4.8, Pg 147**)

2.6 Characterisation Techniques and Performance Testing of Grafted and Crosslinked (PEXa) and Non-crosslinked HDPE Samples

2.6.1 Determination of AO grafting level in HDPE using FTIR spectroscopy

Fourier Transfer Infrared (FTIR) spectroscopy was used to characterize the grafted antioxidants in HDPE. FTIR measurements were performed on a Perkin Elmer Spectrum One spectrometer over the range of 4000-400 cm^{-1} and spectral collection was taken over 16 scans with resolution of 4 cm^{-1}. The IR spectra of processed samples containing g-AO before and after purification was recorded. The area of the carbonyl absorption of the AO was determined so that the concentration of g-AO can be obtained using an IR calibration curve (**see Sec. 2.6.2**). The grafting degree based on **triplicate samples** was obtained by comparing the mass of the grafted antioxidant after purification with either the mass of the antioxidant initially added (g-AO based on **Target** AO concentration) or with the mass of antioxidant remaining after processing (g-AO based on **Actual AO** concentration remaining in the polymer product).The grafting degree and grafting efficiency were calculated using the definitions, described in equation 17 and 18 shown below.

1. Grafting degree (%) is defined as the weight percentage of grafted antioxidant on to the polymer backbone

$$\boldsymbol{Grafting\ Degree}(\%) = \frac{\boldsymbol{Mass\ of\ grafted\ AOPP\ (after\ purification\ in\ g/100g)}}{\boldsymbol{Mass\ of\ polymer\ sample}}\ \boldsymbol{X\ 100} \qquad \textbf{(17)}$$

For example, if in 10g of purified sample (PE-g-AOPP), there was 0.05g grafted antioxidant, then the grafting degree is,

$$\boldsymbol{Grafting\ Degree}\ (\%) = \frac{\boldsymbol{0.05}}{\boldsymbol{10g}}\ \boldsymbol{X\ 100\% = 0.5\%}$$

2. Grafting efficiency (%) is defined as the percentage ratio of the amount of the reactive antioxidant that becomes grafted onto a polymer to the amount of the same grafted antioxidant initially added to the polymer

$$\boldsymbol{Grafting\ efficency}\ (\%) = \frac{\boldsymbol{Mass\ of\ grafted\ AOPP\ (after\ purification\ in\ g/100g)}}{\boldsymbol{Mass\ of\ AOPP\ initially\ added\ (or\ that\ of\ its\ initial\ concentration\ )}}\ \boldsymbol{X\ 100\%} \qquad \textbf{(18)}$$

For example, if 3g AOPP (in 100g of polymer) was added initially during processing of HDPE, and after purification there was 1g (in 100g) grafted AOPP (PE-g-AOPP after purification, and calculation from IR calibration curve), then the grafting efficiency of AOPP with respect to the target (initial target) concentration is calculated as shown in equation **19A**, or if calculation is based on the actual concentration determined after processing then the calculation was done according to equation **19B**.

$$\boldsymbol{Grafting\ efficency\ (Target, \%) = \frac{1g}{3g}\ x100 = 33\%} \qquad \textbf{(19A)}$$

Where 3g is the actual of AO added to the formulation

$$\boldsymbol{Grafting\ efficency\ (Actual, \%) = \frac{1g}{2.25g}\ x100 = 44\%} \qquad \textbf{(19B)}$$

Where 2.25g is amount of AO calculated (based on FTIR calibration) from remaining AO after processing

2.6.2 FTIR Calibration Curve for Establishing Grafting Levels of AO's

To determine the mass of grafted antioxidants and the antioxidant amount remaining in the polymer after the reactive processing step, a calibration curve based on the carbonyl peak absorption area of the AOs against their exact concentrations was constructed, **see Figures 2.6-2.9 [101, 122]**.

Solutions of antioxidants, for example AOPP, in CCl_4 with exact concentrations (e.g.6g/100cm³, 3g/100cm³, 1.5g/100cm³, 0.375g/100cm³, 0.1875g/100cm³) were prepared in 5 ml volumetric flasks and analysed by FTIR. To meet the Lambert Beer law which states that there is proportional dependence between the absorbance (A) of light through a substance and the concentration of the substance (c) and path length of the material that the light travels through (l) (see equation).

$$A = \varepsilon \times c \times l \qquad \textbf{(20)}$$

Liquid IR cell was used with a spacer of 100 μm thickness placed between two KBr windows. Each solution was analysed three times and a new solution was injected each time. The carbonyl peak absorption area was calculated from each spectrum and a graph was plotted for the absorbance peak against antioxidant concentration. The calibration curves were used to calculate the mass of g-AOPP or actual AOPP concentration (or that of Irganox 1076, AOTP, AATP or of DBPA) remaining after processing or crosslinking, following steps used to calculate g-AOPP after processing, see example of calculation below.

For calculation of PE-g-AOPP after processing

$$\boldsymbol{A_{in\ PE-g-AOPP\ film(1600-1800)} = (peak\ area\ absorbance\ of\ carbonyl\ group > C = O, see\ fig.\ 2.6)}$$

$$\boldsymbol{A_{corrected\ for\ polymer\ film} = \frac{A_{>C=O(1680-1800)film}}{Thickness\ of\ the\ polymer\ film\ (\mu m)}\ x\ 100} \qquad (21)$$

$$Subsequently\ from\ calibration\ curve\ (fig 2.3b), \qquad y = 4.82x + 0.441$$

$$x = \frac{y - 0.441}{4.82}$$

$$where\ y => C = O\ absorbtion\ peak\ for\ (A_{1680-1800})$$

$$x = [AOPP]_{g/100ml}$$

$$\boldsymbol{[AOPP]_{(g/100ml)} = \frac{A_{corrected-0.440}}{4.82}} \qquad (22)$$

$$\boldsymbol{[AOPP]_{(g/100g)} = \frac{AOPP_{(g/100ml)}}{\rho_{PE}}} \qquad (23)$$

Where

$A_{(1680\text{-}1800)}$ *: carbonyl group area absorbance of the analysed sample*
$A_{corrected}$: *carbonyl group peak area absorbance of the sample with value corrected to the thickness of 100μm*
AOPP (g/100g) : *AOPP concentration in the polymer calculated from calibration curve*
AOPP (g/100ml) : *AOPP concentration in the polymer (g/100g)*
ρ *: density of the polymer –HDPE (0.965g/cm^3)*

2.6.3 Determination of Unreacted AOPP and p-AOPP in Processed Polymer Samples Using NMR Spectroscopy.

Analysis of any remaining unbound (free and Polymerised (p-AO)) antioxidant is important so that further optimisation can be conducted in order to improve the efficiency of the grafting process. The extracted unbound material (as described in **section 2.6.1**) were analysed for unreacted AO and p-AO by ^{1}H-NMRspectrsocopy.

The assessment of the ratio of free AOPP (f-AOPP) to p-AOPP from extracted polymer films was obtained by integrations of the ring O-C-H (H4 proton at 5ppm, see **Figure 2.12**) and any one of the acrylic group protons (9, 8 or 9' at 5.5ppm, 5.7 ppm and 6.1ppm). The NMR software was programmed to calibrate all the signals relative to one proton (H4 at 5ppm), used as a reference since this proton is part of the ring structure and does not change in the p-AOPP. To calculate the % free AOPP, the value of the calculated integral of one of the double bond protons, (preferably H9 (at 6.1 ppm) as it appears as sharp and well resolved signal in the polymer extract), is multiplied by 100, see below for example of calculation.

$$[\boldsymbol{f-AOPP}]\%\ \boldsymbol{free = Calibrated\ Integral\ of\ H9\ (\ at\ 6.1\ ppm)\ x\ 100}\quad (\mathbf{24})$$

[f-AOPP] = 0.12 x 100 = 12%

$$[\boldsymbol{p-AOPP}]\% = \mathbf{100}\% - [\boldsymbol{f-AOPP}]\%\quad (\mathbf{25})$$

***[p- AOPP]%* = 100-12 = 88%** (This is total of the f-AOPP and p-AOPP in 100 within the extract)

For example, the calculation of the ratio of **f-AOPP** to **p-AOPP** from **^{1}H NMR** of filtrate 1, **see Figure 2.12**, obtained from sample (PE-g-AOPP-1) of HDPE processed with 3% AOPP, 0.005 MR T101 (180°C for 5 min), which contained g-AOPP, p-AOPP and f-AOPP, was calculated as shown below.

The following calculation is done to calculate Actual % of AO in the PE-g-AOPP-1 sample,

$$\boldsymbol{Grafting\ efficency}\ (based\ on\ Actual\ AO\ amount\ after\ processing, \%) =$$

$$\frac{\mathbf{1.89}\boldsymbol{g}}{\mathbf{2.28}\boldsymbol{g}}\ \boldsymbol{x}\mathbf{100} = \mathbf{83}\%$$

Where 1.89 is the amount of AO (AOPP) remaining in the polymer after DCM extraction and 2.28g is the AO (AOPP) amount remaining after processing (based on carbonyl calibration curve from FTIR).

Total product in DCM Extract = 2.28-1.89 = 0.39g

Therefore,

$[\boldsymbol{f-AOPP}]\% = \mathbf{12} \times \mathbf{0.39} = \mathbf{0.0468}\boldsymbol{g} = \frac{\mathbf{0.0468}\boldsymbol{g}}{\mathbf{2.28}}\ \boldsymbol{x}\mathbf{100}$ **= 2% (**Proportion of f-AOPP in the extract)

$[\boldsymbol{p-AOPP}]\% = \mathbf{88}\ \boldsymbol{x}\mathbf{0.39} = \mathbf{0.3432} = \frac{\mathbf{0.3432}}{\mathbf{2.28}}\ \boldsymbol{x}\ \mathbf{100} = \mathbf{15}\%$ (Proportion of p-AOPP in the extract)

g- AOPP + [f-AOPP] + [p-AOPP] = 83 + 2 + 15 = 100 %

2.6.4 Determination of Insoluble Gel Content in Unstablised and Stabilised HDPE and level of Crosslinking in PEXa samples

Any insoluble gel formed during the melt grafting of AO's on PE and the extent of the polymer crosslinking by peroxide were determined according to ASTM 2765-01 method using xylene extraction. The films were cut into small pieces and weighed ($_{W1}$), placed in weighed stainless mesh thimbles (wt), and Soxhlet extracted in 150 ml xylene for 50 hrs under nitrogen. After extraction, the thimbles were dried in a vacuum oven for 8 hrs at 80ºC until a constant weigh was reached (w2). The gel content or the extent of polymer crosslinking (in PEXa samples) was measured using the following equation.

$$\textbf{\textit{Gel content}}\ \% = \frac{\boldsymbol{W_1}}{\boldsymbol{W_2}}\ \boldsymbol{X}\ \mathbf{100} \quad \textbf{(26)}$$

Where

$\boldsymbol{W_1} - \textit{weight is the residue weight of the extracted polymer}$

$\boldsymbol{W_2} - \textit{weight of the polymer used before extraction}$

Three measurements for every sample were conducted to establish the standard deviation and coefficient of variation from **Eqns 27 and 28**.

$$\textbf{Standard Deviation}:\ S.D\ = \sqrt{\frac{1}{N-1}\sum_{i=1}^{n}(x_i - \overline{x})^2} \ \textbf{(27)}$$

$$\textbf{Coefficient of Variation}: CV\% = \frac{S.D}{\overline{x}} \times 100\% \quad \textbf{(28)}$$

Where

N : Total no of samples
x_i : Numerical result of the ith run
$\overline{x}$: Arithmetic Mean

For example, the gel content results of sample g1-PEX-705 were 73%; 72%; 76% so standard deviation was S.D=2 and CV was 3%.

2.6.5 Determination of Melt Flow Index of processed Unstabilised HDPE

The melt flow index (MFI) is a measure of melt viscosity and is related to the molecular weight of the polymer. It is defined as the molten polymer extruded under a weight of 21.6 kg through a 2.095 mm diameter die in a given time. MFI of High-density polyethylene

samples was measured using a Ray Ran Melt Flow indexer at a constant extrusion temperature of 190 ºC and 21.60 kg load in accordance to the ASTM D1238. A standard die of 1mm diameter was used for all samples. After the samples were granulated, 3 g of each sample was charged in to the barrel within one minute. The sample was preheated for 4 minutes before placing the load to drive the molten polymer through the die. The time interval for the cut off was 1 to 4 min depending on the flow of each sample. Three samples per each measurement were taken and their averages calculated as shown in **Eq. 29.**

$$MFI\left({}^{g}/_{10min}\right) = \frac{m\,x10}{t\,(min)} \qquad (\mathbf{29})$$

Where,
m : the average weight of extrudates (g)
t :time of extrusion (min) = 10 min

2.7 Performance Testing of PEX and Non Crosslinked Samples

2.7.1 Measurement of Crystallinity using Differential Scanning Calorimetery

A Perkin-Elmer Pyris Diamond DSC interfaced with a PC was used to measure the thermal properties of moulded film samples prepared from the PEXa pipes**.** A cut film sample was placed in an aluminium crucible (5mm diameter, 40µl) without lid and weighed on an analytical balance (Perkin Elmer AD6) followed by placing it on the robot panel of the DSC instrument. The procedure used for the DSC measurement was standard procedure according to **ASTM D-3417-99**.

The following measurement programme was used throughout the work. The sample was first heated from 40°C to 190°C at a heating rate of 10°C/min under nitrogen flow, which was kept constant throughout the run at a rate of 40 ml/min. The sample was then held at 190°C for 3 minute. Before cooling down to 40°C at the same cooling rate of 10°C/min. after 5 minutes of maintaining the temperature at 40°C, a second heating cycle was started at heating rate of 10°C/min until terminated at 190°C.

Crystallinity of the polymer was determined from the heat of melting (ΔH) obtained from the second cycle. ΔH was found by integrating the area under the peak (j/g). The percent crystallinity was then determined using **equation 30** below.

$$X_c = \frac{\Delta H_m}{\Delta H_{m^\circ}} \text{ x } 100\% \qquad (\mathbf{30})$$

$X_c - Degree\ of\ crysatallinity$
$\Delta H_m - Enthalpy\ of\ fusion\ measured\ at\ melting\ point$
$\Delta H_{m^\circ} - Enthalpy\ of\ fusion\ of\ a\ completely\ crysatlline\ PE\ at\ equilibrium\ Tm$
$\Delta H_{m^\circ}\ (HDPE) = 293.6\, j/g$ [124]

2.7.2 Measurement of Oxidative Induction Time, (OIT) using Differential Scanning Calorimetery

A Mettler Toledo DSC832e interfaced with a PC was used to measure the thermal properties of the moulded film samples prepared from the PEXa pipes. Empty open aluminium pans, which matched in weight within 0.02mg, were used for both the sample and the reference. The procedure used for the DSC measurement was a standard procedure according to **ASTM D-3895**.

Samples of 4 ± 1 mg were placed in the DSC pans (open pan) and measuring programme was set to heat the sample from 40°C to the test temperature of 190ºC, at a rate of 20°C/min under nitrogen flow (rate of 40ml/min). After 5 minutes at 190°C, the gas was switched from nitrogen to oxygen at a flow rate of 40ml min^{-1}. When all the antioxidant in the sample was consumed, the sample started to oxidize producing a deviation in the Baseline. The oxidation induction time was measured in minutes from the time the temperature reached 190°C and the atmosphere changed from nitrogen to oxygen up to the appearance of oxidation change in the slope. This value was obtained from at least 3 measurements per sample.

2.7.3 Thermal Ageing of PEX Pipes Produced by Engel Process

Accelerated thermal ageing test of processed polymer films was carried out in a single cell Wallace oven at 125°C under air atmosphere. Each sample was contained and suspended in a separate cell to prevent cross contamination of the additives by volatilisation and was subjected to an airflow of 3.0 cubic feet/hour (85 litres/hour). The thermal stability of the film samples was followed by measuring the embrittlement time (EMT) and the increase of the carbonyl group absorption (from FTIR) along with the control sample of processed high-density polyethylene films. All tests were carried out in duplicates to establish the experimental error.

2.7.4 Hydrostatic Test for PEX_{HS}-Pipes

Hydrostatic pressure test for PEX_{HS}-pipes was carried out at Virsbo, Sweden, according to **ISO 1167-1973**. The internal test medium, the pipes were exposed to deionised water and the external medium was air. PEX_{HS}-pipes (lengths of ~1ft) containing graftable antioxidants and a standard commercial pipe (with commercial AOs) were tested either at 110°C or 115°C with 2.5 MPa pressure. A pipe must reach a period of at least one year (~8800 hours) before failure in this test for it to be considered fit for use in commercial applications.

2.7.5 FTIR-ATR Analysis of Pipes

Surface characteristics of PEX_{HS}-pipes that had failed under hydrostatic test, was obtained using Perkin Elmer Spectrum one FTIR equipped with an Attenuated Total Reflectance diamond crystal accessory (ATR). The spectra were obtained in transmittance mode from 32 scans at 4 cm^{-1} resolution between 4000-600 cm^{-1}. No sample preparation was done as the FTIR-ATR was performed directly on the surface of the pipes

2.7.6 Microscope-FTIR (Mic-FTIR) Analysis of PEX_{HS}-Pipes

In order to investigate the antioxidant distribution along the length of the pipes, a Perkin Elmer (Spectrum GX) FTIR-microscope was used to run line marker scans. The polymer pipe samples were microtomed to thickness of 100 µm and were put in between glass slides under weight of 50 g in order to keep the films flat. Microtomed films were assembled between the sample holder, and the samples were then placed on the microscope stage. Line scans and line marker scans were performed on these films, IR spectra in transmission mode were taken (in the range 800-3600 cm^{-1}) with intervals of 100 µm from the inner to the outer walls of the pipes; 32 scans were set for each spectrum.

To obtain the mapping image of the distribution of the antioxidant in the polymer, the ratio of the carbonyl peak of an ester group at 1740 cm^{-1} (belonging to the antioxidants) over a polymer reference peak area at 2019 cm^{-1} was calculated. The calculations were then presented in the form of coloured maps representing different concentrations of the stabilisers across the pipe thickness

2.7.7 High performance liquid chromatography (HPLC) and HPLC-Mass Spectroscopy

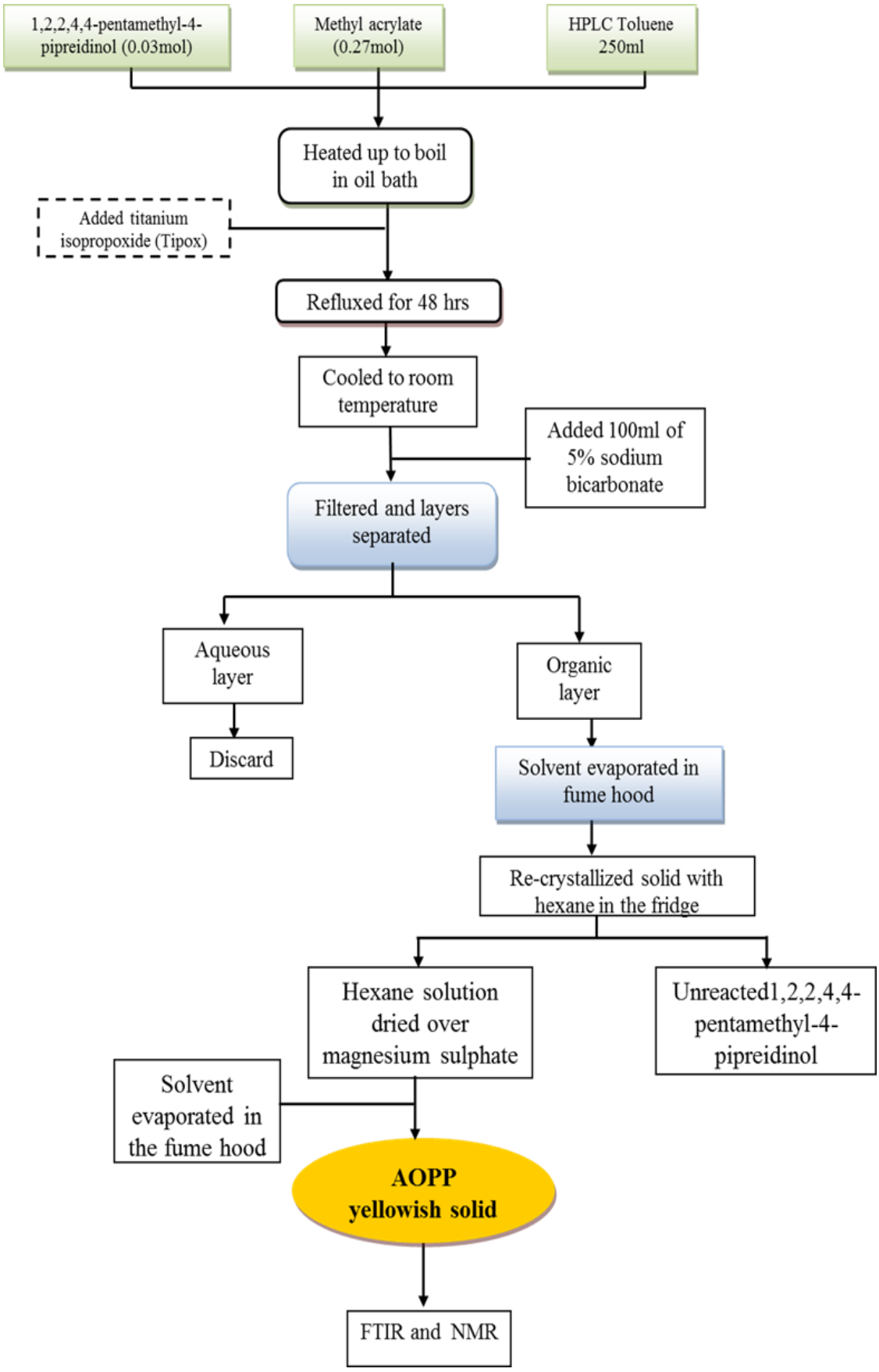
HPLC was performed using thermo scientific UltiMate 3000 Standard LC Systems, equipped with vacuum degasser, quaternary pump, an autosampler and a UV/VIS diode array detector. Mass spectroscopy detection was done by coupling the HPLC with an ion trap spectrometer equipped with an atmospheric pressure chemical ionisation (APCI) source. APCI was utilized in both a negative and a positive ionisation mode, proton transfer occurs on the positive ion

mode to produce [M+H]+ ions and in negative ion mode either electron transfer or proton loss takes place to M^- or $[M-H]^-$ ions. The following optimised mass spectral analysis parameters were used, probe temperature of 600°C for positive ionisation mode and 350°C for negative ionisation mode.

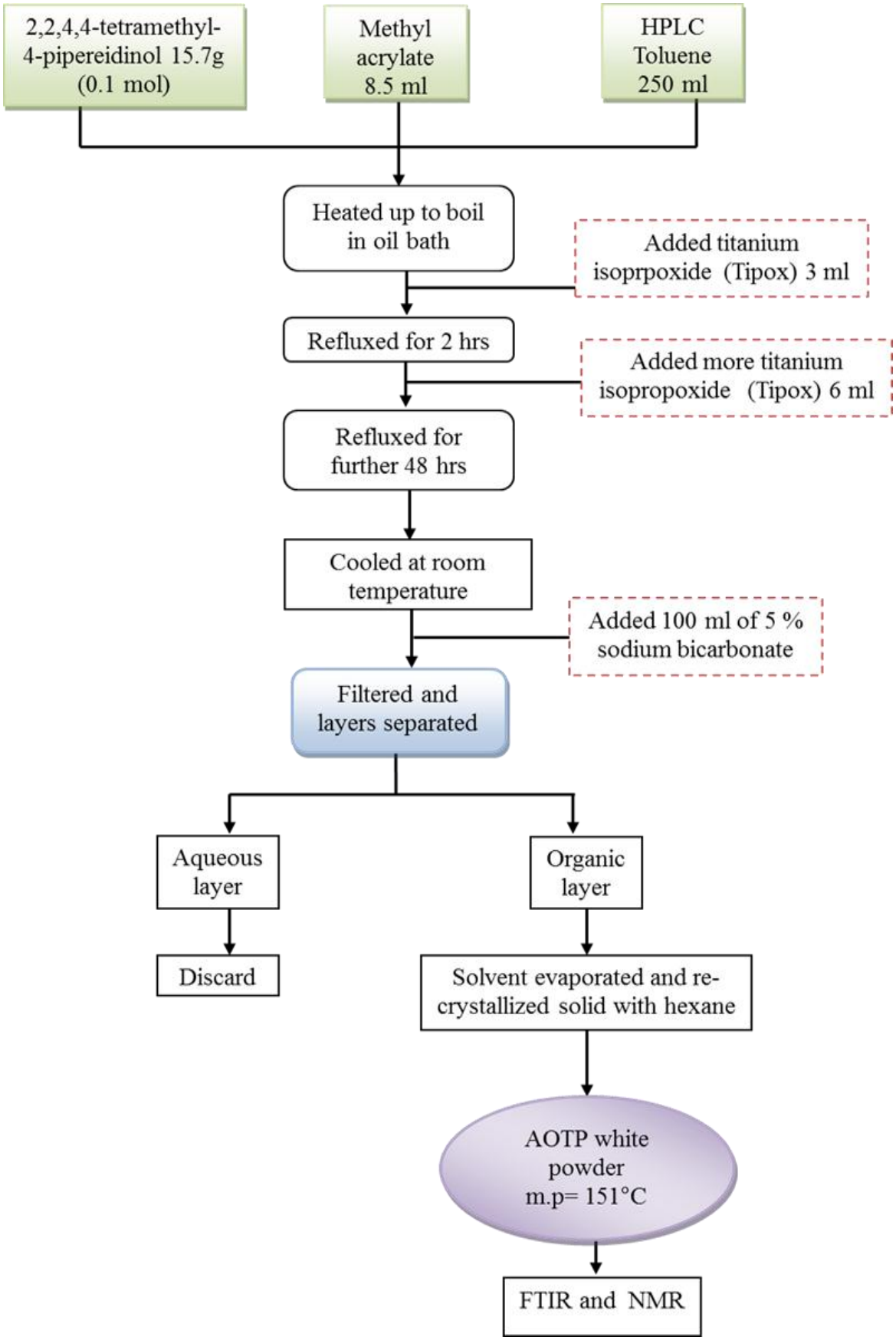
For the chromatographic separation of DCM extracts of pipes, a Zorbax-RX-C18 (4.6 x 250nm, 5microns) Agilent column was used at operating temperature of 20°C, constant flow rate of 1 ml/min and with a 20 µl injection volume. The mobile phase was composed of 90%ACN, 5%THF, and 5% methanol used in isocratic mode for separation. All the solvents used were HPLC grade and were obtained from fisher. The UV wavelengths were set at 205, 225, 280 and 305 nm.

For the chromatographic separation of water extracts of pipes, a Zorbax-RX-C18 (4.6 x 250nm, 5microns) column from Agilent was used at operating temperature of 20°C, constant flow rate of 1 ml/min and with a 20 µl injection volume. The mobile phase was composed of 80% ACN, 20% water used in isocratic mode for separation. All the solvents used were HPLC grade and were obtained from fisher. The UV wavelengths were set at 205, 225, 280 and 305 nm. The following optimised mass spectral analysis parameters were used, a probe temperature of 600°C for positive ionisation mode and 600°C for negative ionisation mode.

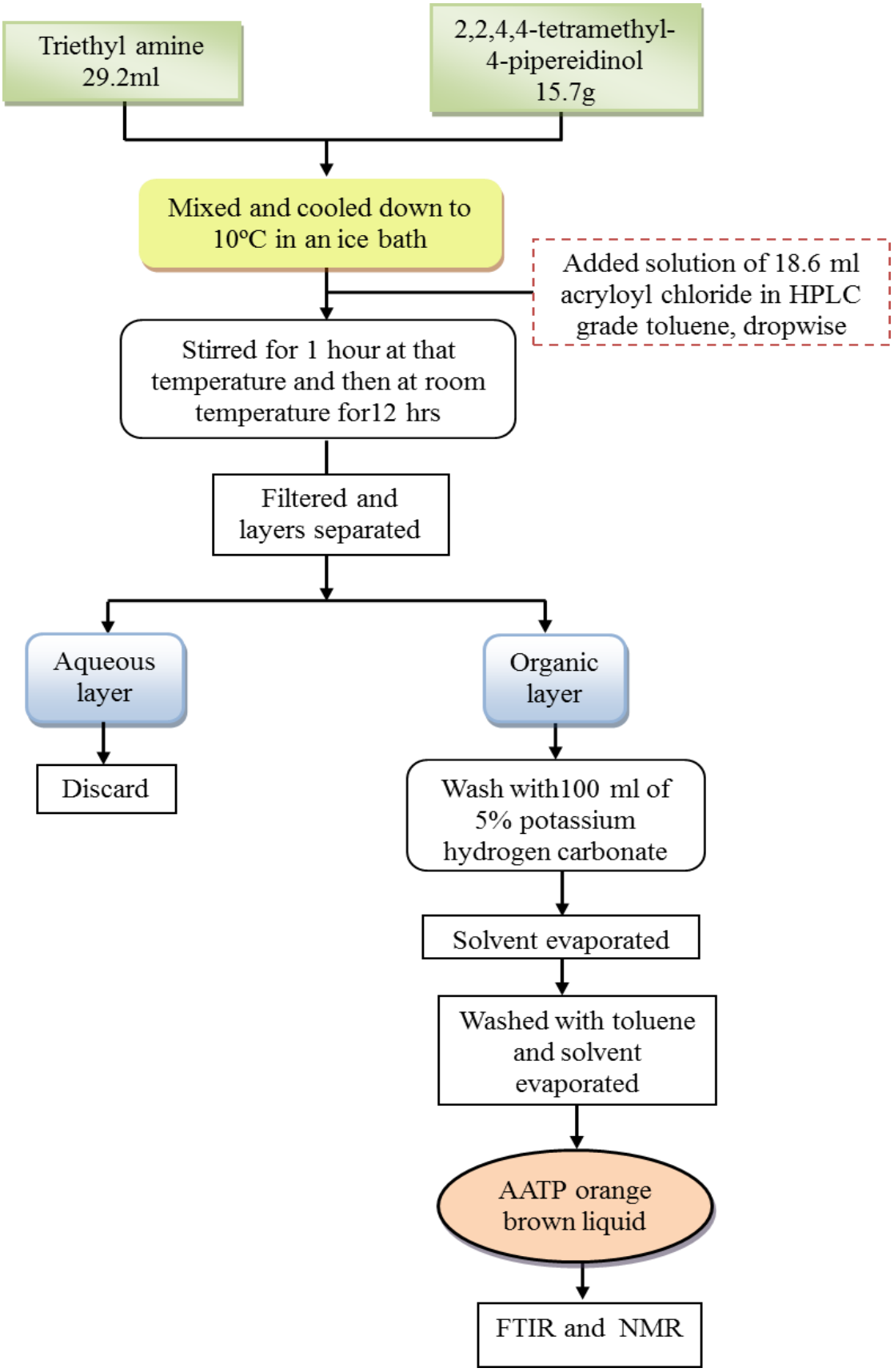
Scheme 2. 1: Synthesis of 4-acryloyloxy 1,2,2,6,6-pentamethyl piperdine (AOPP)



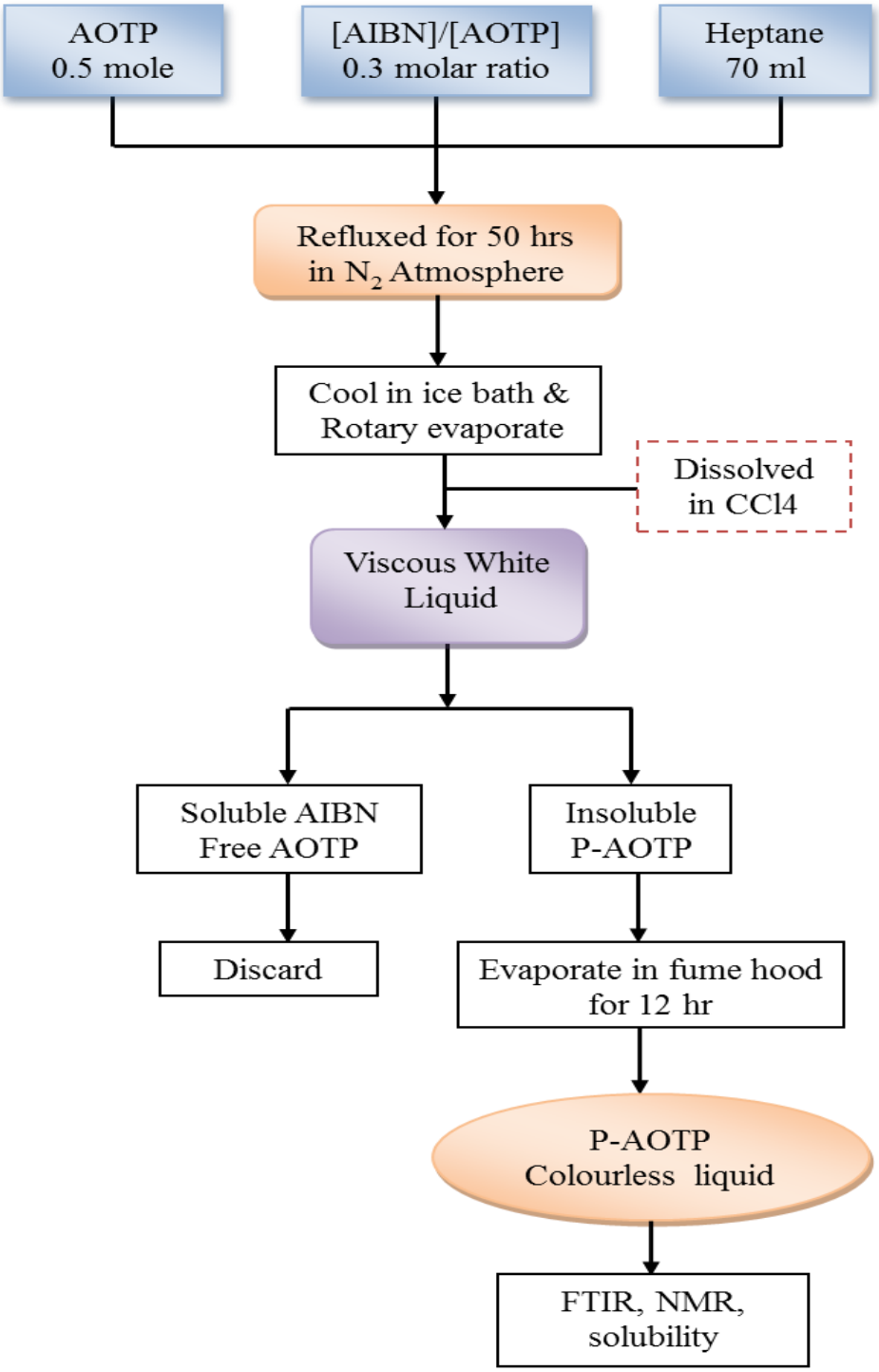
Scheme 2. 2: Synthesis of 4-acryloyloxy 2,2,6,6-tetramethyl piperdine(AOTP)



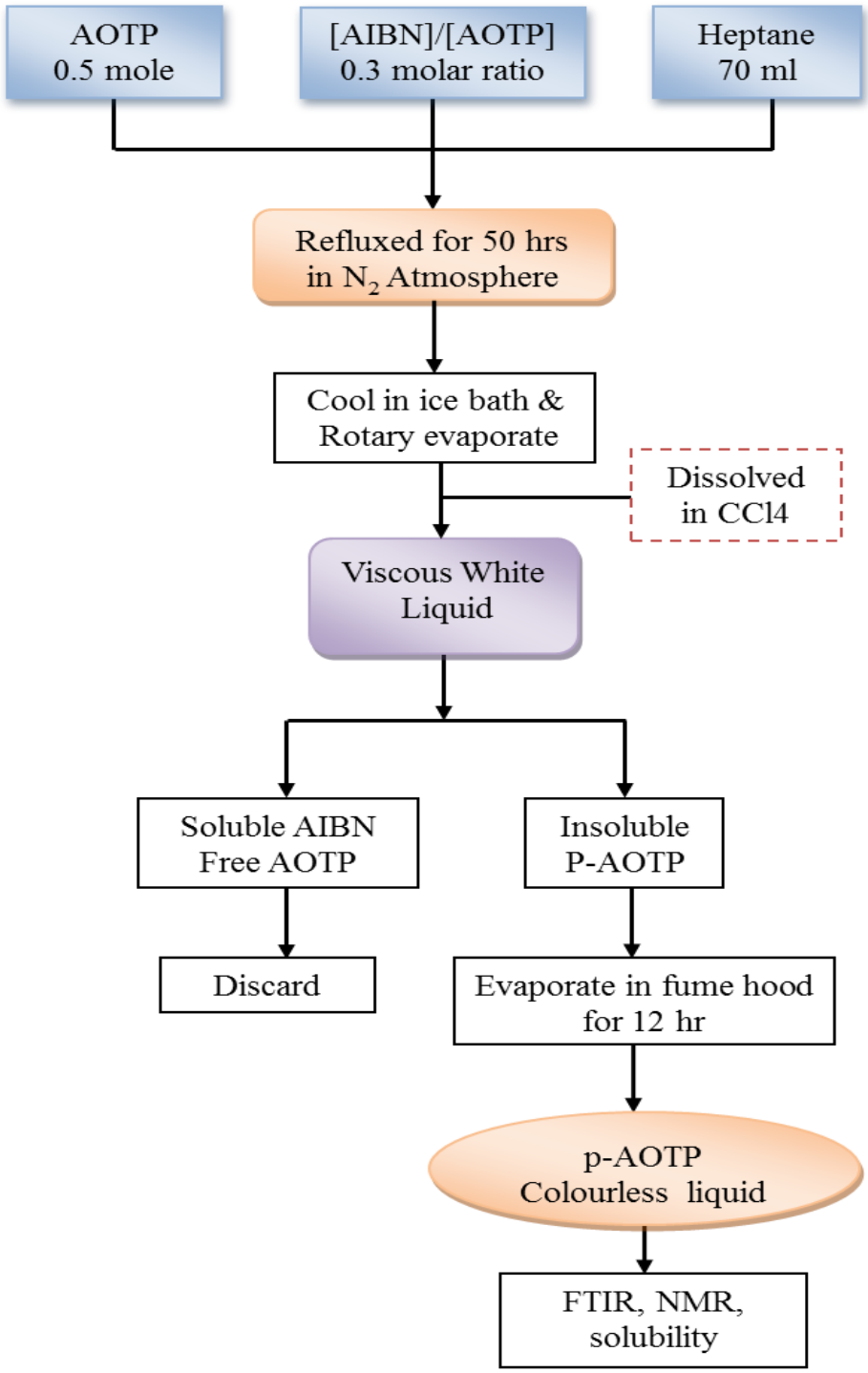
Scheme 2. 3: Synthesis of 1-acryloyl 4-acryloyloxy 2,2,6,6-pentamethyl piperdine (AATP)



Scheme 2. 4: Homo-polymerisation of AOPP (p-AOPP)



Scheme 2. 5: Homopolymerisation of AOTP (p-AOTP)



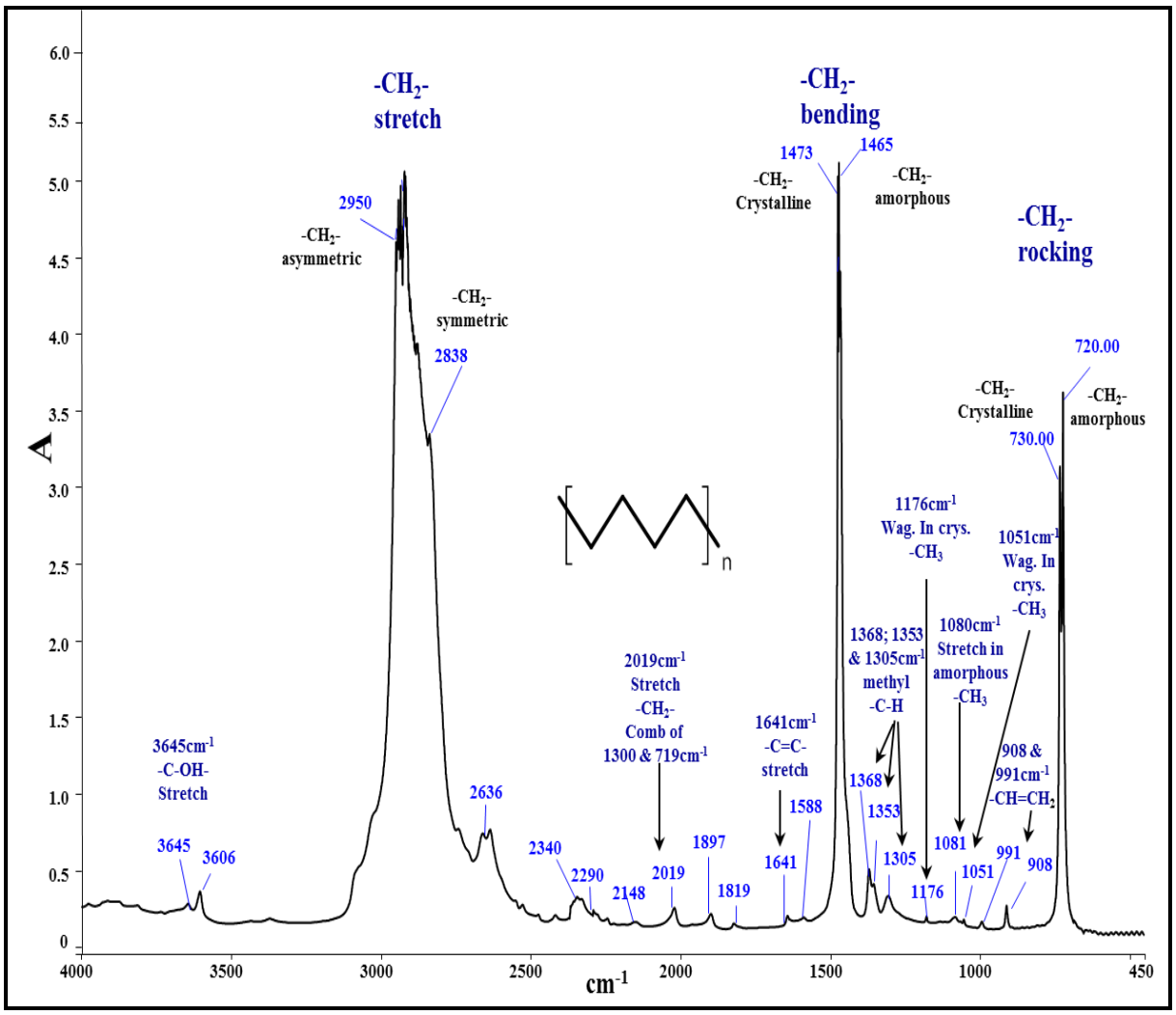


Figure 2. 1: FTIR spectra of HDPE, Lupolen 5261

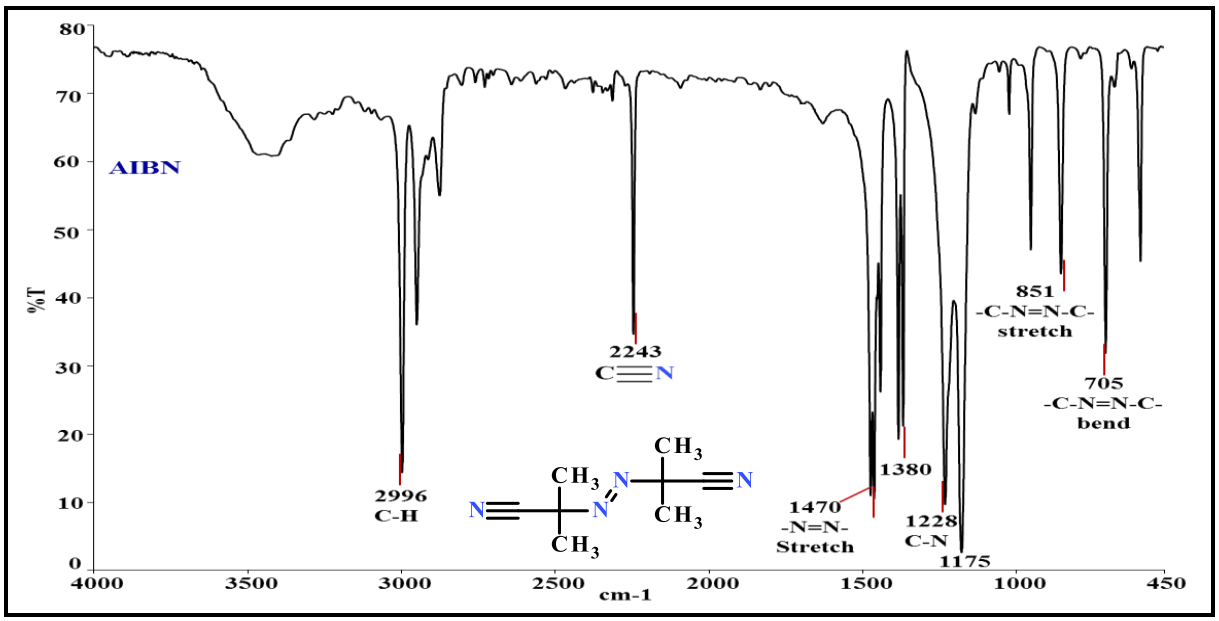


Figure 2. 2 : FTIR spectra of AIBN

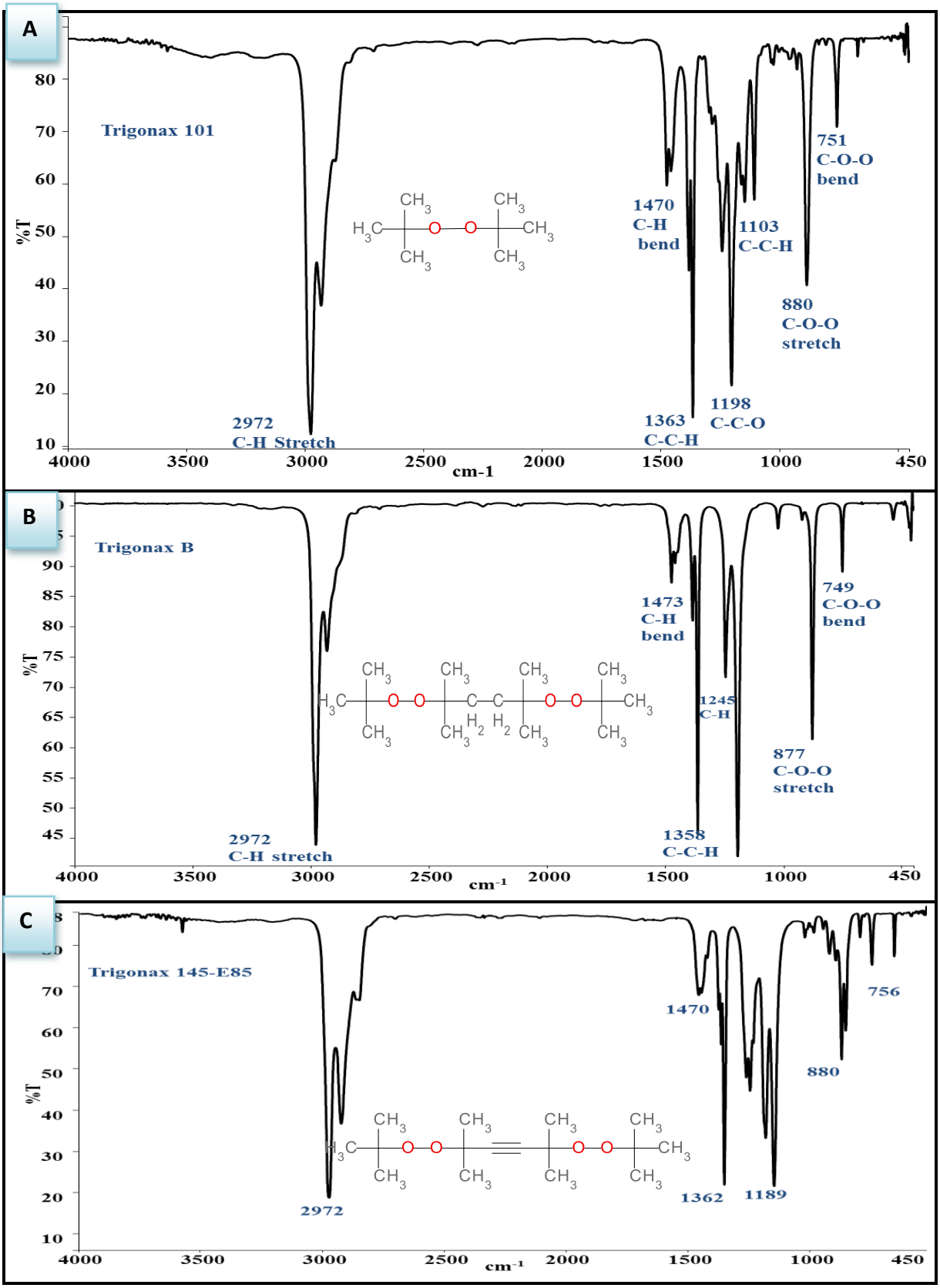


Figure 2. 3: FTIR spectra of (A) Trigonox 101 (B) Trigonox B and (C) Trigonox 145, in KBr.

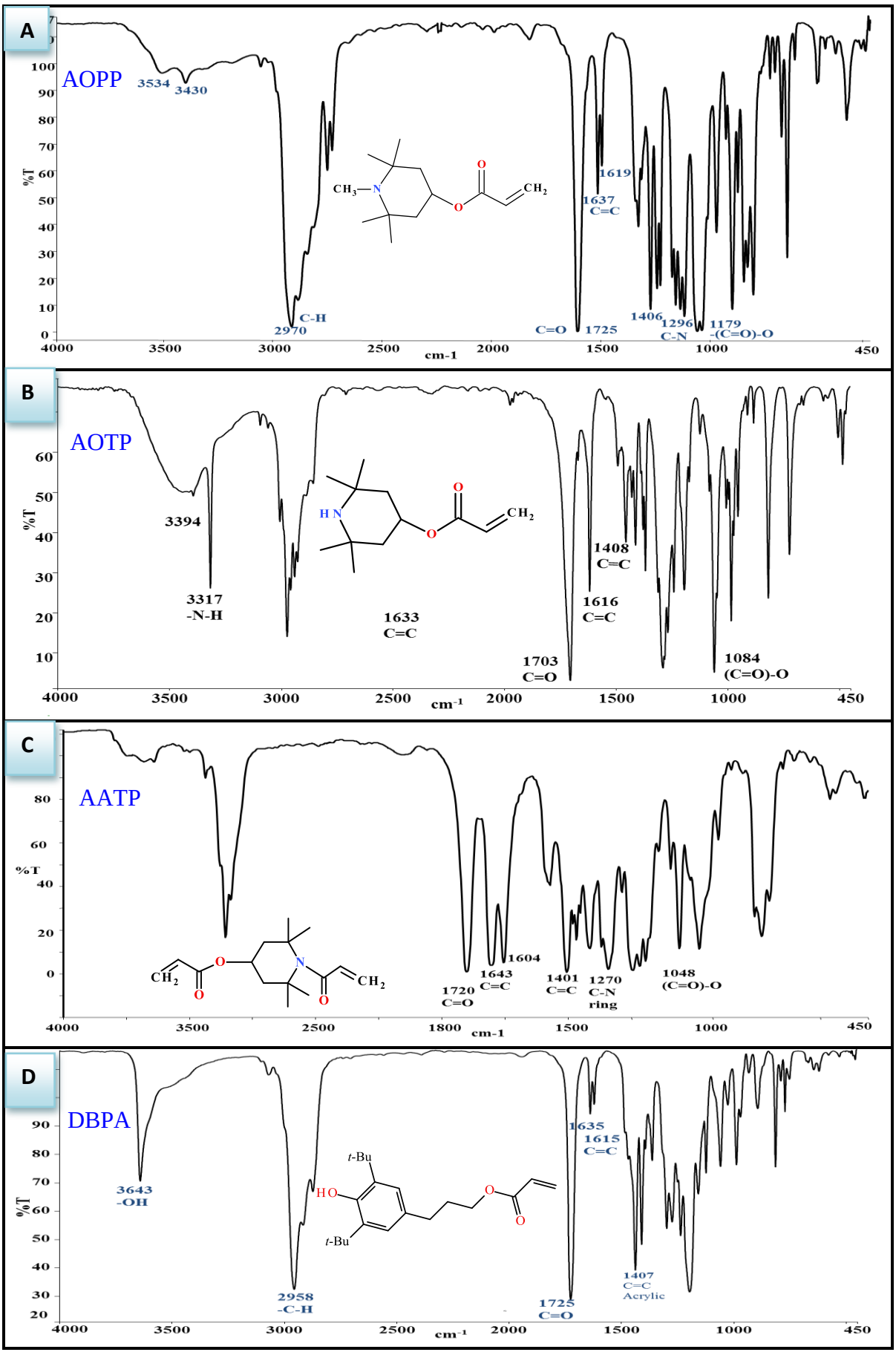


Figure 2. 4: FTIR spectra for (A) AOPP, (B) AATP, (C) AOTP and (D) DBBA.

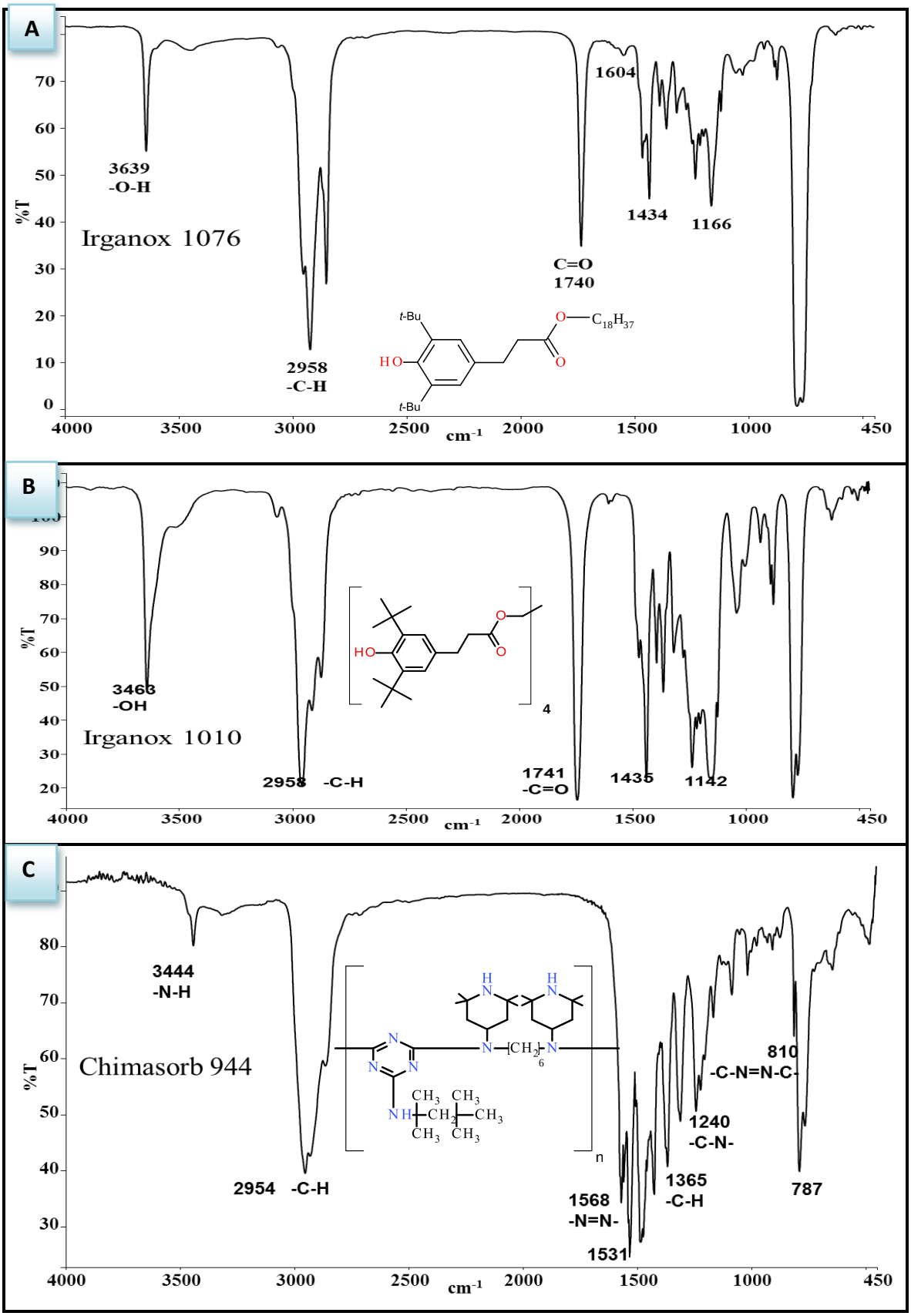


Figure 2. 5: FTIR spectra for (A) Irganox 1076, (B) Irganox 1010, (C) Irganox 1330

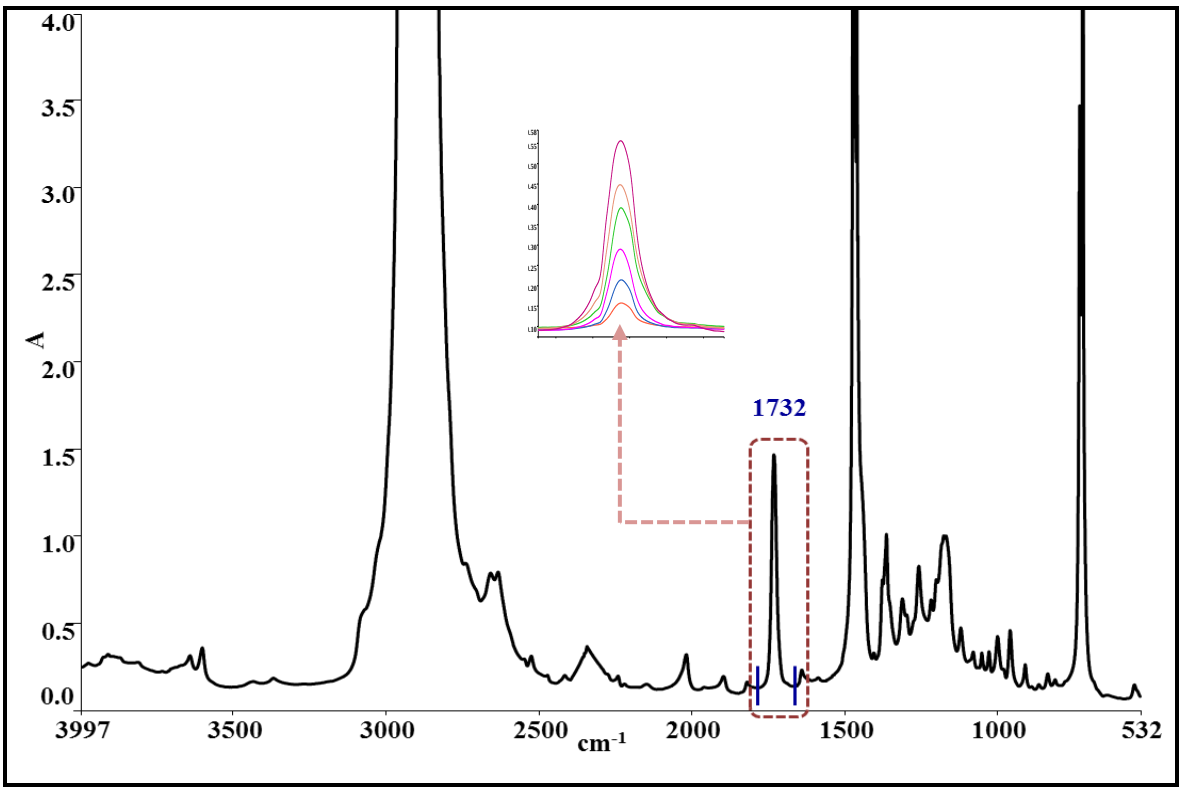


Figure 2.6: peak area of carbonyl absorption in AOPP used for calibration curve

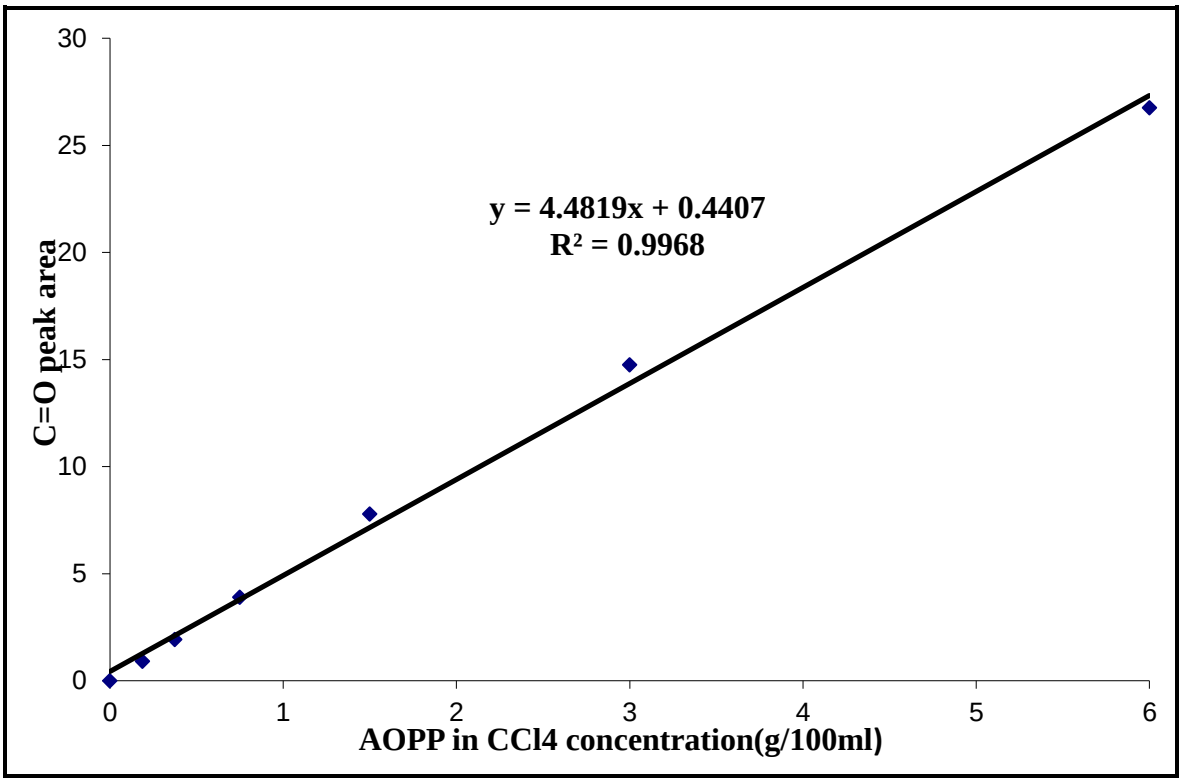


Figure 2. 7: IR calibration curve for AOPP in carbon tetra chloride used for subsequent determination of g-AOPP

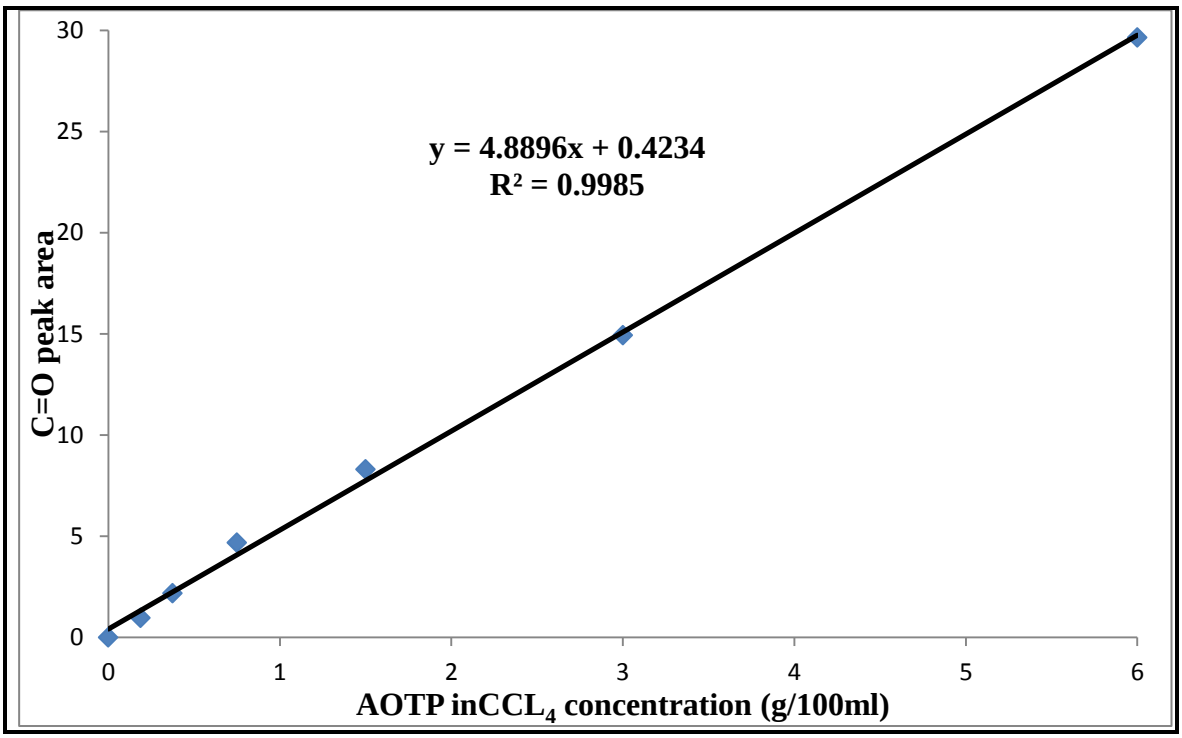


Figure 2. 8: IR calibration curve for AOTP in carbon tetra chloride used for subsequent determination of g-AOTP

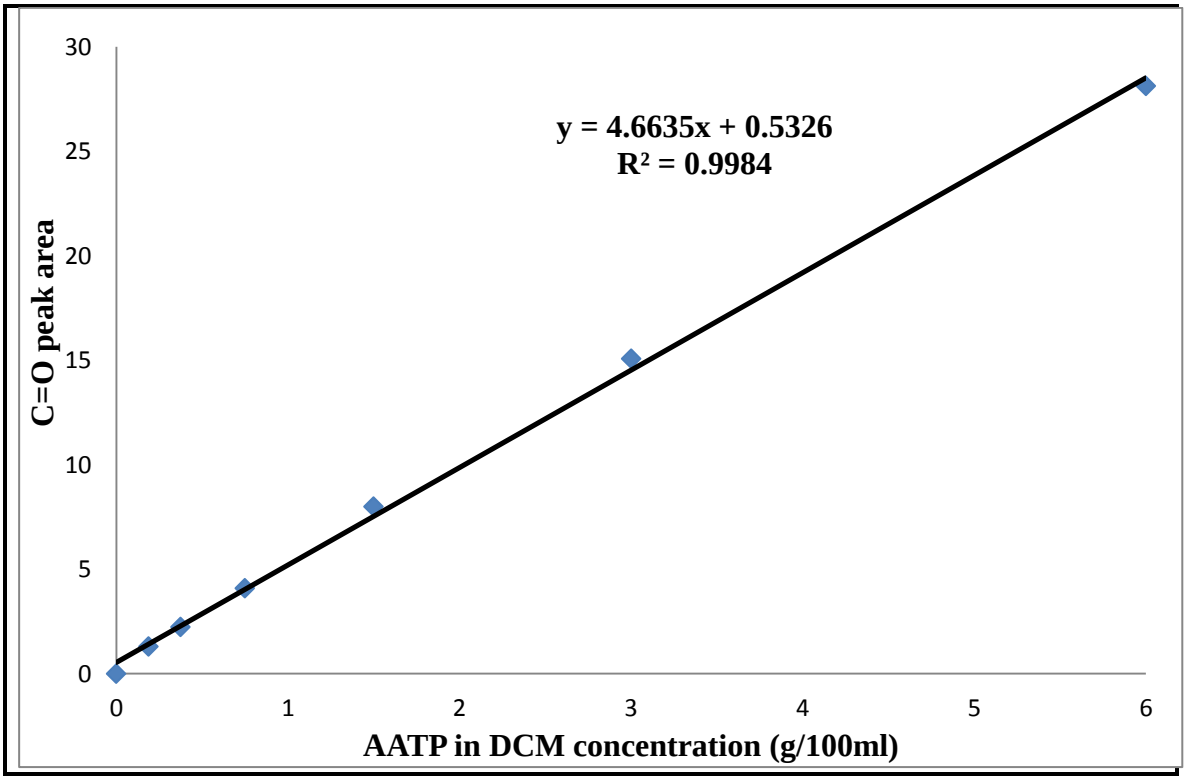


Figure 2. 9: IR calibration curve for AATP in dichloromethane used for subsequent determination of g-AATP

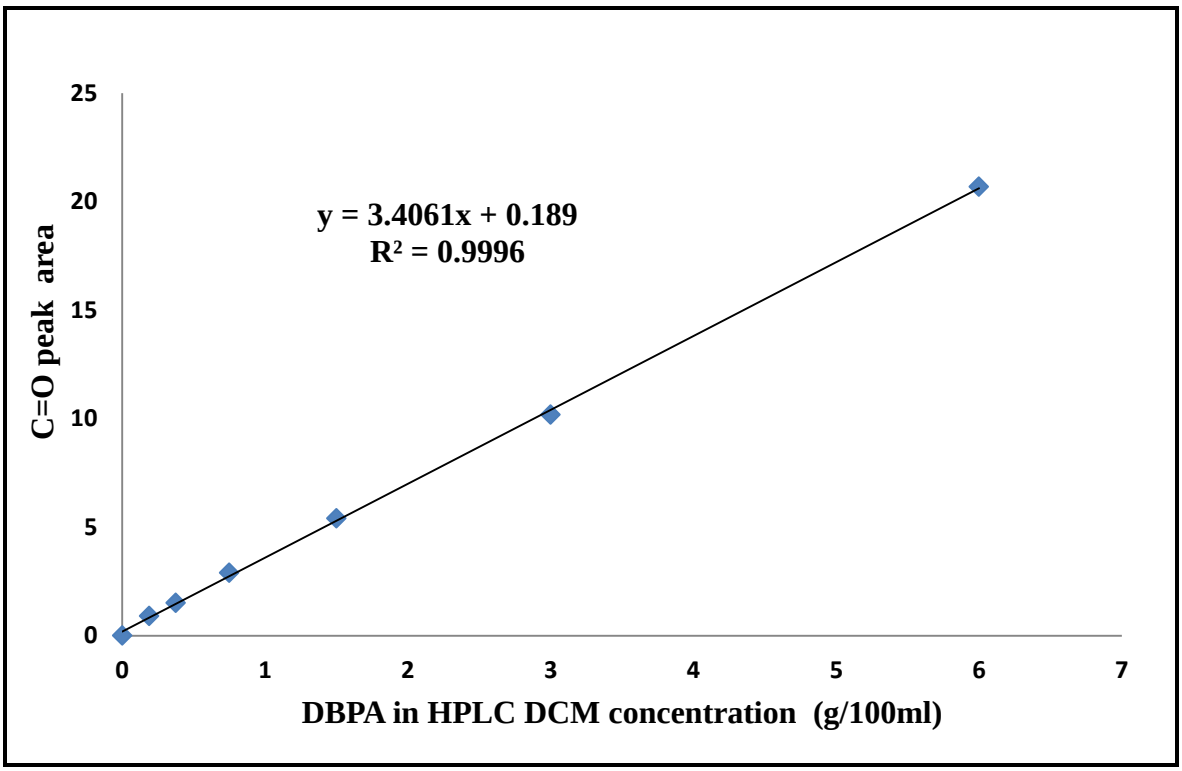


Figure 2. 10: IR calibration curve for DBPA in dichloromethane used for subsequent determination of DBPA remaining after crosslinking.

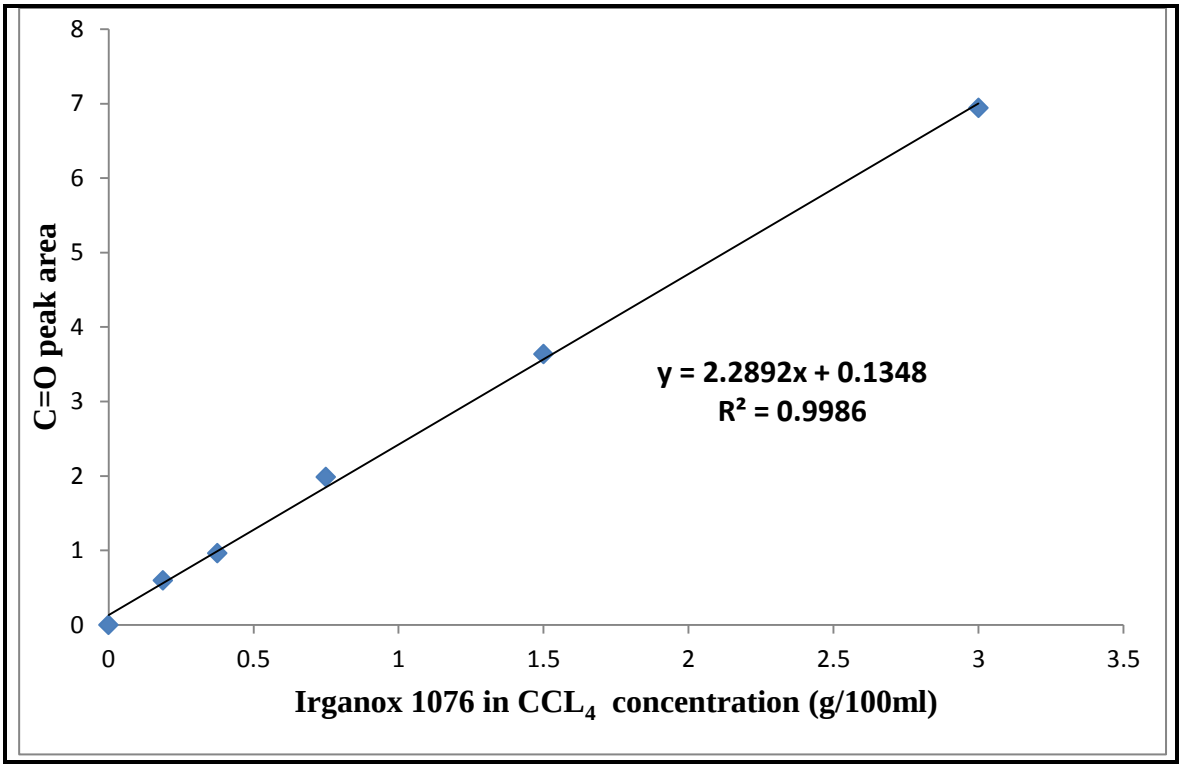


Figure 2. 11: IR calibration curve for Irganox 1076 in carbon tetra chloride used for determination of Irganox 1076 remaining after crosslinking.

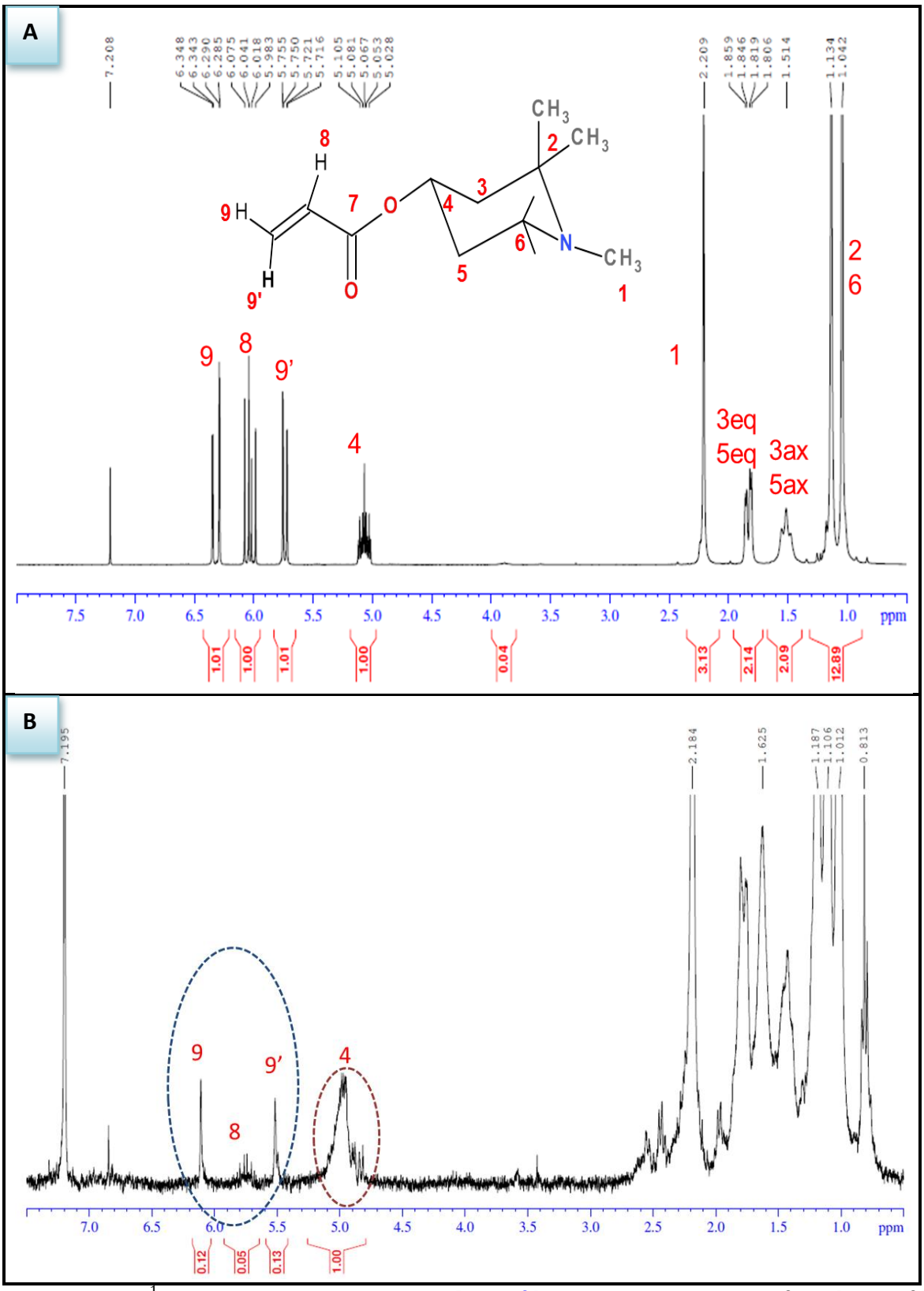


Figure 2. 12: ^{1}HNMR: (A) neat AOPP and (B) filtrate (PE-g-AOPP-1) of polymer films containing free AOPP and p-AOPP in $CDCl_3$ see **Scheme 3.2 in Chapter 3, pg.**

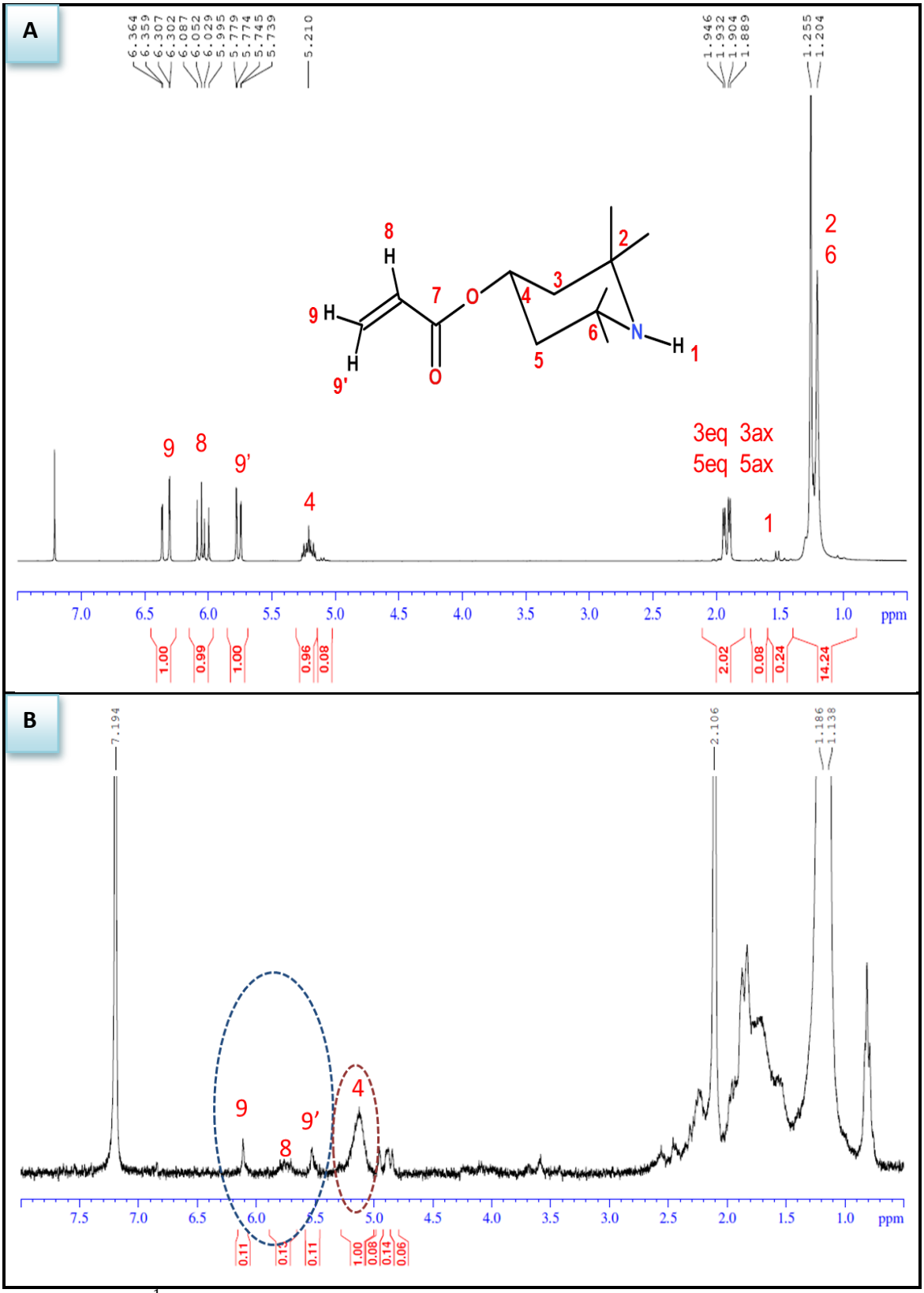


Figure 2. 13: ^{1}HNMR, (A) neat AOTP and (B) filtrate of (PE-g-AOTP-155) of polymer films containing free AOTP and p-AOTP in $CDCl_3$ see **Scheme 3.2**

Chapter 3

Melt Free Radical Grafting of Low Molecular Weight Hindered Amine Stablisers on HDPE

3.1 Objectives and Methodology

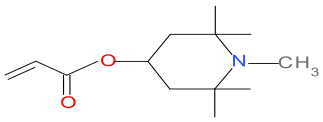
The main objective of the work described in this thesis was to develop a non-migratory effective stabilising system for crosslinked HDPE used for water pipe applications. One of the ways by which substantivity of antioxidants in polymers may be maximized is through their chemical attachment (grafting) on to the polymer backbone in the presence of a free radical initiator (mainly peroxide) during melt processing [64, 87, 89, 92-95, 100, 101, 121, 122, 125-127].

The aim of the work described in this chapter was therefore, to graft synthesised reactive hindered amine antioxidants (g-HAS) onto HDPE (Lupolen 5261 ZQ 456 PE_L, MFI 2g/10min), and to optimise the efficiency of the melt free radical grafting reaction using different g-HAS stablisers: **AOPP** (4-acryloylloxy 1,2,2,6,6-pentamethyl piperidine), **AOTP** (1-acryloyl 4-acryloyloxy 2,2,6,6-pentamethyl piperdine) ,and **AATP** (4-acryloyloxy 2,2,6,6-tetramethyl piperdine), in the presence of the peroxide initiator Trigonox 101 **(T101),** 2,5-dimethyl- 2,5-bis(tert-butylperoxy) hexane, see **Structure Scheme 3.1**.

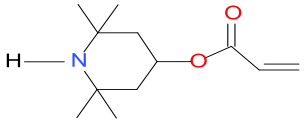
PE-grafted antioxidant (PE-g-AO) concentrates (masterbatches-MB 1-6%) were produced and subsequently diluted down to normal AO concentration (~0.5%) for use in highly crosslinked HDPE samples in a laboratory-based process that was recently developed by another researcher in the PPP group [101] in order to simulate the commercial production process of peroxide crosslinked polyethylene pipes using the Engel process (**see ch.4**).

The melt free radical grafting of (g-HAS) stabilisers (0.5-6 w/w%) onto HDPE in the absence and presence of a peroxide initiator was carried out in a Haake Rheomix 600 at varying processing temperatures between 160-240°C, and with fixed rotor speed of 65 rpm using closed system as described in **Scheme 3.1 and Sec 2.3.2, pg 57.** Film samples prepared by compression moulding were subsequently analysed for the antioxidant grafting level and the gel content (each done in triplicates), see **Scheme 3.2**. The composition and processing conditions used for the reactive processing of g-AO with HDPE are given in **Tables 3.1-3.5**. For full details of sample preparation, purification and analysis see **Sec 2.4.1, 2.5 (Ch.2)**.it is important to point out here that the results of the grafting reaction products of many samples were the average of at **least two repeats**.

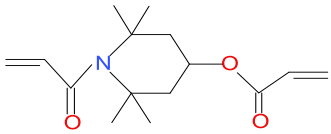
Structure 3. 1: structures of HAS and the peroxide reported in this chapter



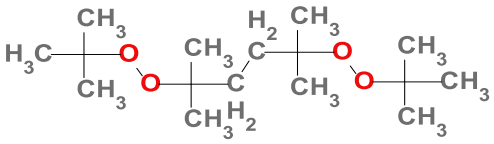
4-acryloylloxy 1,2,2,6,6-pentamethyl piperidine**,** **(AOPP)**



1-acryloyl 4-acryloyloxy 2,2,6,6-pentamethyl piperdine, **(AOTP)**



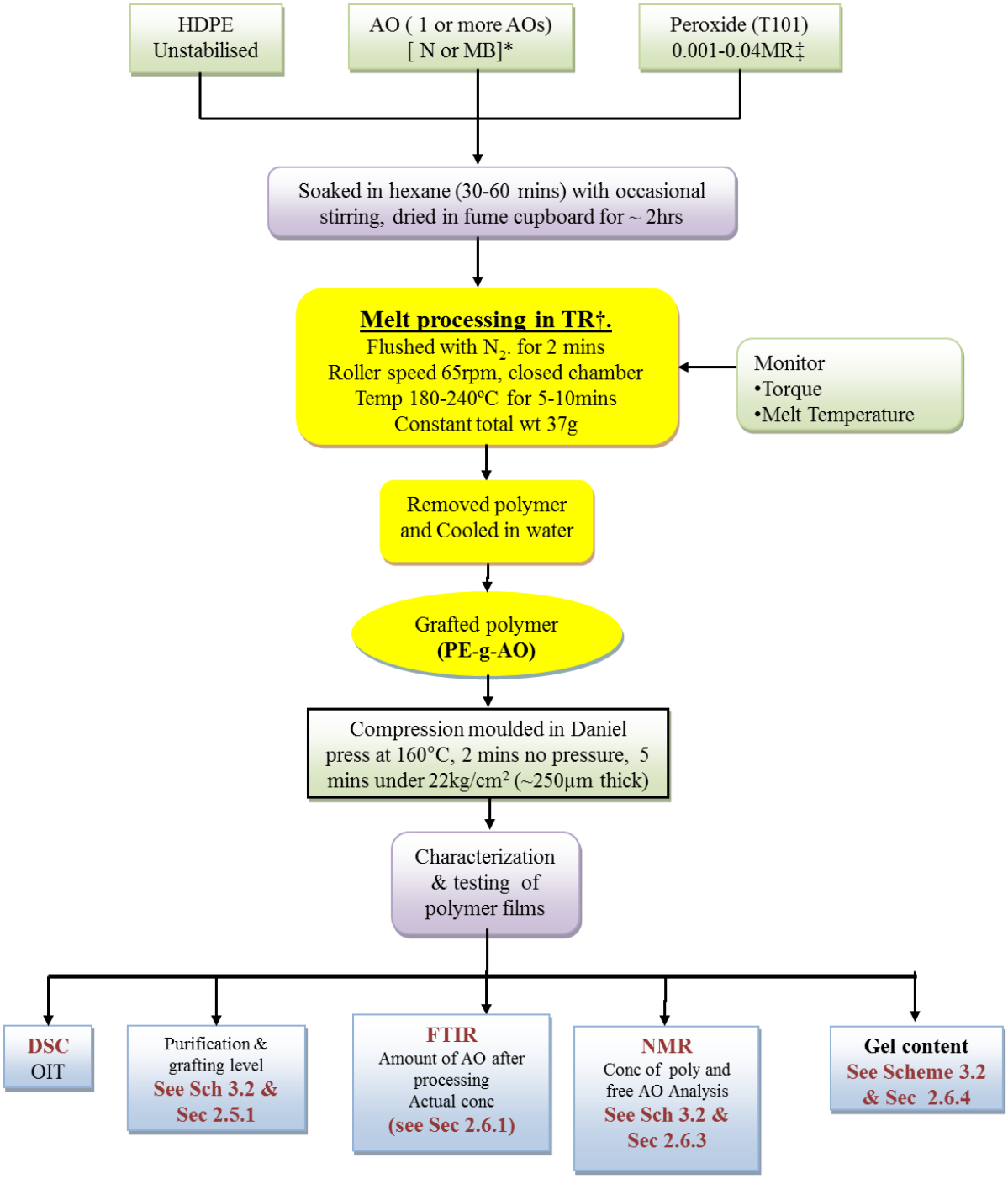
4-acryloyloxy 2,2,6,6-tetramethyl piperdine, **(AATP)**



Trigonox 101, **T101**

The effects of varying the processing temperature and the chemical composition of the system (the HAS and the peroxide concentrations) on the grafting efficiency and the nature and extent of the different side reactions was investigated in order to optimise the grafting efficiency with minimum contributions from the side reactions. The grafted products were purified and the side reaction products were separated using Soxhlet extraction. The antioxidant grafting degree was determined by FTIR spectroscopy, using a calibration curve set up from a plot of the IR antioxidant- carbonyl absorption area index (1720 cm^{-1}), see **Sec 2.6.2**. To ensure that only grafted-HAS was measured, the HAS-g-PE samples were purified by removing the ungrafted-HAS (**free-AO**) and the HAS-homopolymer (**p-AO**) using Soxhlet extraction with dichloromethane as the extraction solvent (see **Scheme 3.2**). The extracts were further analysed by NMR to quantify the amount of p-AO and Free-AO, for details of calculations, see **Sec 2.6.4 Ch.2**.

Scheme 3. 1: Methodology for Melt Grafting of Antioxidants (AO) onto HDPE and product characterisation.



*N = Normal AO concentration (<1%)
*MB = AO Masterbatch (concentration >1%)
‡ MR = Molar ratio of [peroxide]/ [AOs]
† TR = Haake Torque rheometer

Scheme 3. 2: Purification methodology for the quantification of grafting level in PE-g-AO

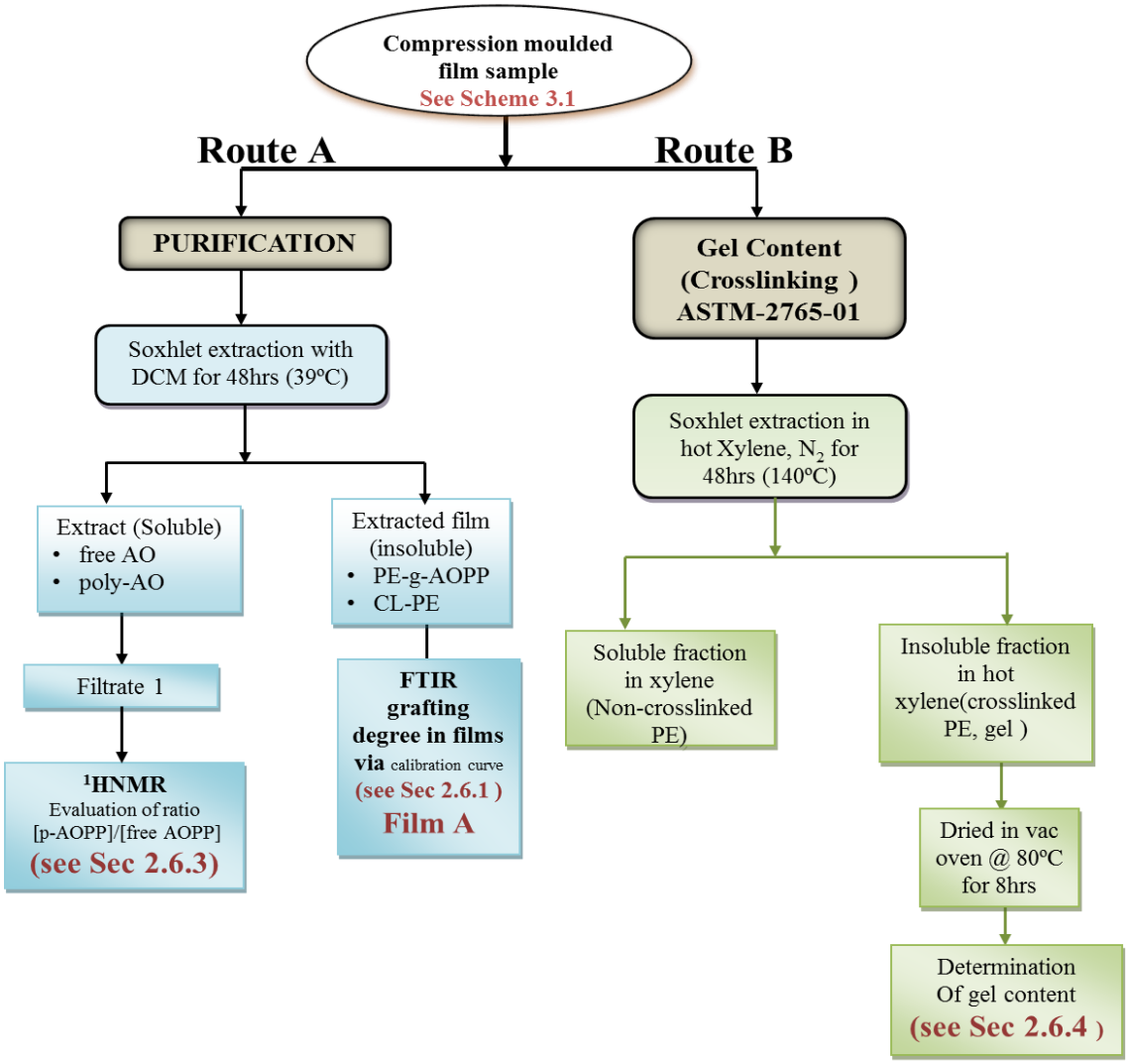


Table 3. 1: Composition and processing conditions used in the melt free radical grafting of AOPP (3-6%) on HDPE in presence of the peroxide Trigonox 101 (T101).

Sample Code	Composition		Processing conditions		[AOPP] grafting Analysis				Gel Content
					Based on FTIR		Based on ^{1}H- NMR		
	MR [T101]/ [AOPP]	Initial AOPP % g/100g	Temp (°C)	Time (min)	[AOPP] After proc. (%) Actual *	g-AOPP Grafting (%) †	Free AOPP % ‡	p-AOPP % ‡	
PE-g-AOPP-3	0	3	180	5	10	0	10	90	0
PE-g-AOPP-6	0.001	3	180	5	70	0	57	43	0
PE-g-AOPP-7	0.002	3	180	5	72	32	13	55	0
PE-g-AOPP-8	0.003	3	180	5	67	49	28	23	6
PE-g-AOPP-1	0.005	3	180	5	76	83	2	15	12
PE-g-AOPP-2	0.008	3	180	5	89	75	2	23	29
PE-g-AOPP-4	0.01	3	180	5	85	91	6	3	29
PE-g-AOPP-5	0.02	3	180	5	84	88	-	-	37
PE-g-AOPP-20	0	6	200	7	38	42	50	8	0
PE-g-AOPP-10	0.001	6	200	7	78	60	5	35	0.27
PE-g-AOPP-11	0.002	6	200	7	86	66	3	30	3
PE-g-AOPP-12	0.003	6	200	7	85	72	12	16	9
PE-g-AOPP-13	0.004	6	200	7	91	75	3	22	13
PE-g-AOPP-9	0.005	6	200	7	99	87	2	11	12
PE-g-AOPP-14	0.008	6	200	7	87	76	1	23	21
PE-g-AOPP-24	0.003	6	180	7	78	76	5	19	4
PE-g-AOPP-25	0.003	6	220	7	78	72	6	22	6
PE-g-AOPP-26	0.003	6	240	5	75	65	5	30	3
PE-g-AOPP-21	0.002	6	180	5	86	69	3	28	5
PE-g-AOPP-22	0.002	6	220	7	80	60	8	33	0.46
PE-g-AOPP-23	0.002	6	240	7	78	67	6	27	0
PE-g-AOPP-9-180	0.005	6	180	6	96	70	2	28	18
PE-g-AOPP-9	0.005	6	200	6	99	87	1	12	15
PE-g-AOPP-9-220	0.005	6	220	6	85	86	2	12	17
PE-g-AOPP-9-240	0.005	6	240	6	86	79	2	19	17
PE-g-AOPP-27	0.005	3	200	5	83	60	6	34	3
PE-g-AOPP-28	0.005	3	220	5	80	64	3	33	1
PE-g-AOPP-29	0.005	3	240	5	70	80	4	16	2

PE Lupolen 5261Z Q456, unstablised, MFI 2 g/10min (21.6 Kg load)

***** This is the actual percent retention of AOPP, remaining concentration after processing (before any purification) actual

† Level of grafting assessed after purification from FTIR analysis (for details see **Ch.2, sec 2.6.1**), calculation as % of the initially added concentration based on actual.

‡ Level of poly-AOPP & Free AOPP in the grafting reaction system assessed by ^{1}HNMR (for details, see **Ch.2, Sec 2.6.3**)

Table 3. 2: Composition and processing conditions for the melt free radical grafting of AOPP (0.5-1%) on HDPE in presence of the peroxide Trigonox 101.

Sample Code	Composition		Processing conditions		[AOPP] grafting Analysis Based on FTIR >C=O		Gel Content (%)
	MR [T101]/ [AOPP]	Initial [AOPP] (%) g/100g	Temp (°C)	Time (min)	[AOPP] After proc. % (Actual)	Grafting (%) Based on actual	
PE-g-AOPP-30	0.001	1	180	5	46	0	0
PE-g-AOPP-31	0.003	1	180	5	55	13	0
PE-g-AOPP-32	0.005	1	180	5	62	45	0
PE-g-AOPP-33	0.01	1	180	5	61	62	0
PE-g-AOPP-34	0.005	1	200	5	70	70	0
PE-g-AOPP-35	0.005	1	220	5	70	60	1
PE-g-AOPP-36	0.005	1	240	5	75	93	2
PE-g-AOPP-37	0.005	0.5	180	7	40	53	0
PE-g-AOPP-38	0.005	0.5	200	7	60	43	0
PE-g-AOPP-39	0.005	0.5	220	7	78	54	0
PE-g-AOPP-40	0.005	0.5	240	7	83	66	3
PE-g-AOPP-41	0	0.5	200	7	35	0	0
PE-g-AOPP-42	0.003	0.5	200	6	42	17	0
PE-g-AOPP-43	0.01	0.5	200	6	43	93	0
PE-g-AOPP-44	0.02	0.5	200	6	42	88	0

Table 3. 3: Effect of temperature on the processing of HDPE without any added AOs

Code	PROCESSING CONDITIONS		Analysis							
	Temp °C	Time min	Final Torque	Final Melt Temp °C	C=O	vinyl 908 cm^{-1}	Vinylidene peak	Trans vinylidene	MFI (g/10min) Density of HDPE: 0.965 g/cm^3	% Gel content
HDPE NOT PROCESSED	-	-	-	-	-				1.96	-
HDPE-180	180	7	15	186	0.15	2.00	0.70	0.00	0.824	0.055
HDPE-200	200	7	19	208	0.64	1.51	0.52	0.03	1.0	0.25
HDPE-220	220	7	20	230	1.73	1.29	0.42	0.11	21	4
HDPE-240	240	7	22	250	2.84	1.06	0.31	0.21	-	24
HDPE-260	260	7	20	267	3.09	0.92	0.27	0.22	-	27
HDPE-280	280	7	18	286	3.12	0.84	0.25	0.22	-	22

Table 3. 4: Composition and processing conditions used in the melt free radical grafting of AOTP on HDPE.

Sample Code	Composition		Processing conditions		[AOTP] grafting Analysis				Gel Content (%)
					Based on FTIR		Based on ^{1}HNMR		
	MR [T101] /[AOTP]	Initial AOTP (%) g/100g	Temp (ºC)	Time (min)	[AOTP] After proc (%) Actual *	g-AOTP Grafting (%) Based on actual	Free AOTP	Poly AOTP	
PE-g-AOTP-154	0	3	180	5	70	70	3	27	0
PE-g-AOTP-151	0.001	3	180	5	85	68	7	25	0.6
PE-g-AOTP-152	0.003	3	180	5	88	80	2	19	11
PE-g-AOTP-153	0.005	3	180	5	80	99	0	1	22
PE-g-AOTP-155	0	6	180	6	34	85	2	13	8
PE-g-AOTP-156	0.003	6	180	5	73	82	2	15	10
PE-g-AOTP-157	0.005	6	180	5	70	83	2	15	12
PE-g-AOTP-176	0.005	6	180	5	92	72	3	25	13
PE-g-AOTP-158	0.01	6	180	5	70	94	0	5	34
PE-g-AOTP-159	0.005	0.5	180	5	63	89	-	-	0
PE-g-AOTP-160	0.005	0.5	200	7	57	82	-	-	5
PE-g-AOTP-161	0.005	0.5	220	7	82	93	-	-	4
PE-g-AOTP-162	0.005	0.5	240	7	100	83	-	-	23
PE-g-AOTP-150	0	0.5	180	7	63	49	-	-	0
PE-g-AOTP-163	0.003	0.5	220	7	63	89	-	-	1
PE-g-AOTP-164	0.01	0.5	220	7	24	92	-	-	26
PE-g-AOTP-165	0.02	0.5	220	7	42	88	-	-	6
PE-g-AOTP-166	0.001	3	220	7	70	84	0	16	0
PE-g-AOTP-167	0.003	3	220	7	70	84	0	16	10
PE-g-AOTP-168	0.005	3	220	5	74	84	0	16	42
PE-g-AOTP-169	0.01	3	220	5	67	87	0	13	26
PE-g-AOTP-170	0.02	3	220	5	80	100	-	-	23
PE-g-AOTP-171	0.005	3	200	5	73	74	2	23	15
PE-g-AOTP-172	0.005	3	220	5	76	68	4	26	26
PE-g-AOTP-173	0.005	3	240	5	79	77	2	20	45
PE-g-AOTP-174	0.005	3	180	5	78	82	0	16	9
PE-g-AOTP-175	0.01	3	180	5	80	80	0	16	16
PE-g-AOTP-177	0.001	1	180	5	71	59	-	-	0.08
PE-g-AOTP-178	0.003	1	180	5	71	56	-	-	0.14
PE-g-AOTP-179	0.005	1	180	5	73	74	-	-	0.72
PE-g-AOTP-190	0.01	1	180	5	73	82	-	-	2
PE-g-AOTP-191	0.005	1	200	5	75	87	-	-	2
PE-g-AOTP-192	0.005	1	220	5	83	87	-	-	4
PE-g-AOTP-193	0.005	1	240	5	86	79	-	-	8

* This is the percent retention of AOTP, remaining concentration after processing (before any purification) actual

† Level of grafting assessed after purification from FTIR analysis (for details see Ch.2, sec 2.6.1), calculation as % of the initially added concentration based on actual.

‡ Level of poly-AOTP & Free AOTP in the grafting reaction system assessed by ^{1}HNMR (for details, see Ch.2, Sec 2.6.3)

Table 3. 5: Composition and Processing conditions for optimising free radical melt Grafting of AATP.

Code	Composition		Processing conditions		Analysis		
					[AATP] grafting Based on FTIR >C=O		
	T101 MR	[AATP] % g/100g initial	Temp (ºC)	Time (min)	% [AATP] remaining after processing [Actual]	Grafting efficiency % based on Actual	Gel Content (%)
PE-g-AATP-55	0.005	6	180	7	-	-	-
PE-g-AATP-54	0.005	6	180	5	-	-	-
PE-g-AATP-52	0.005	6	160	5	72	97	70
PE-g-AATP-53	0.005	6	170	5	70	100	69
PE-g-AATP-51	0	1	180	5	55	16	0.3
PE-g-AATP-56	0.001	3	170	5	28	100	56
PE-g-AATP-57	0.002	3	170	5	27	78	30
PE-g-AATP-58	0.003	3	170	5	37	157	58
PE-g-AATP-59	0.005	0.5	180	5	41	32	9
PE-g-AATP-60	0.005	0.5	200	5	42	90	18
PE-g-AATP-61	0.005	0.5	220	5	47	87	28
PE-g-AATP-62	0.005	0.5	180	7	43	65	27
PE-g-AATP-63	0.003	0.5	180	5	41	20	7
PE-g-AATP-64	0.01	0.5	180	5	37	35	20
PE-g-AATP-65	0.02	0.5	180	5	42	76	-
PE-g-AATP-66	0	3	180	5	65	49	-
PE-g-AATP-67	0.001	3	180	5	69	65	66
PE-g-AATP-68	0.002	3	180	5	64	91	50
PE-g-AATP-69	0.003	3	180	5	71	85	43
PE-g-AATP-70	0.005	3	180	5	75	88	50
PE-g-AATP-71	0.005	3	200	5	-	-	-
PE-g-AATP-72	0.005	3	220	5	-	-	-
PE-g-AATP-73	0.005	3	180	5	75	84	-

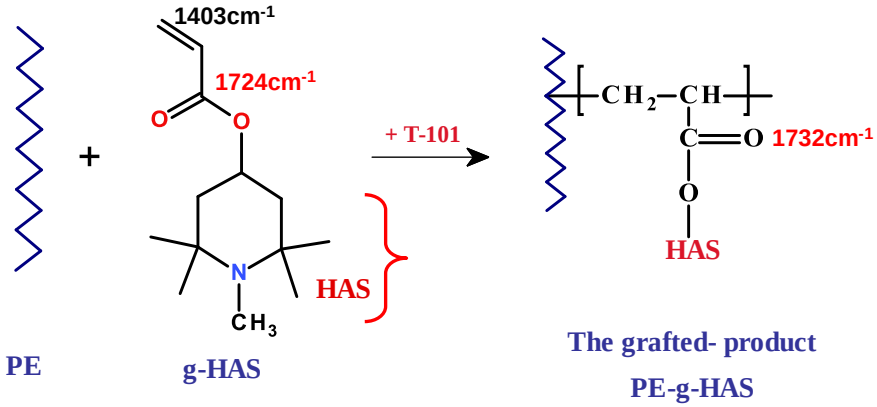
3.2 Results

3.2.1 Characterisation of PE-g-AOPP and polymerised HAS antioxidants

The melt free radical grafting system is expected to contain not only the PE-g-AOPP but also a number of undesirable reaction products including unreacted AOPP (free), homopolymerised AOPP (p-AOPP) and crosslinked PE; hence the polymer was subjected to purification by solvent extraction in order to report an accurate level of grafting yield in the system. In order to identify a suitable solvent for the purification of the polymer, the solubility of a synthesised p-AOPP was examined and both AOPP and p-AOPP were found to be completely soluble in dichloromethane (DCM). DCM was therefore used for extraction, whereas xylene was used to remove the crosslinked PE.

i) Characterisation of PE-g-AOPP

The FTIR spectra of AOPP (neat) and that of a purified PE-g-AOPP film, **Figure 3.1** shows clearly that the absorbance of the unsaturated carbonyl group of the neat AOPP at1724 cm^{-1} shifts to longer wavenumber at 1732 cm^{-1} in the PE-g-AOPP due to the formation of saturated carbonyl in the grafted polymer. The double bond absorption of the acrylic group of AOPP at 1406 cm^{-1} also disappears from the PE-g-AOPP spectrum confirming the grafting of AOPP through the double bond, see **Reaction Scheme 3.1**.



Reaction Scheme 3. 1: grafting reaction of AOPP on to PE in presence of T101.

ii) Characterisation of p-AOPP

Figure 3.2 shows a comparison of the FTIR spectra of a synthesised homopolymer of AOPP (p-AOPP) (see **Chapter 2, Sec 2.2.5** for synthesis) and a neat AOPP. The spectrum of p-AOPP is quite similar to that of PE-g-AOPP showing the ester carbonyl absorption at 1724 cm^{-1} (unsaturated ester group) to have shifted to 1729 cm^{-1} due to formation of saturated ester groups and the double bond of the acrylic group at 1639 cm^{-1}, 1618 cm^{-1} and C-H stretching absorption (ν $CH=CH_2$) at 1406 cm^{-1} to have disappeared.

^{1}H NMR and ^{13}C NMR analyses were also used to characterise the synthesised p-AOPP. **Figure 3.3** shows clearly the disappearance of the acrylic proton signal of AOPP H8 and H9 at 6.3, 6.0 and 5.1 in the spectrum of p-AOPP, with new saturated proton signals appearing at δ_H = 2.2 ppm (see also **Table 3.9**). It is also clear that all NMR signals in p-AOPP spectrum have lost their sharpness in comparison to that of the neat AOPP which is also an indication of the occurrence of the polymerisation reaction.

The ^{13}C NMR spectrum of polymerised AOPP shows that both carbons of the acrylic group (C8 and C9 at 130 and 129 ppm in **Table 3.10** and **Figure 3.4 A**) had disappeared and new signals (see **Figure 3.4 B**) were formed as a result of formation of new saturated carbons (C8 and C9 in p-AOPP) at δc =41 and δc = 33.

iii) Characterisation of p-AOTP

The synthesised homopolymer of AOTP (p-AOTP) was soluble in chloroform, dichloromethane, acetone, toluene and xylene but insoluble in hexane, heptane, ethanol and methanol (**see Table 3.7**). Characterisation of AOTP was based on its FTIR and NMR. The FTIR spectrum of p-AOTP is compared with that of AOTP (see **Figure 3.5**) The ester carbonyl stretching absorption (ν C=O) of AOTP at 1702 cm^{-1} (unsaturated ester group) has shifted to 1730 cm^{-1} in p-AOTP due to the formation of saturated ester groups. The stretching of the acrylic double bond at 1669 cm^{-1}, 1616 cm^{-1} and the C-H stretching absorption (ν $CH=CH_2$) at 1411 cm^{-1} have disappeared.

Further confirmation of the structure of p-AOTP is revealed from its NMR spectra, **Figure 3.6 and Table 3.9** show clearly that the ^{1}H NMR signals of the acrylic protons (H8 and H9 at 6.3, 6.0 and 5.7) at in AOTP have disappeared in p-AOTP and new saturated proton signals appeared at $\boldsymbol{\delta_H}$ = 2.208 ppm. All signals in p-AOTP spectrum have lost sharpness compared to those in AOTP which is typical of a polymer spectrum. The ^{13}C NMR spectrum of

polymerised AOTP shows that both carbons of the acrylic group (C8 and C9 in **Table 3.10** and **Figure 3.7A**) had disappeared and new signals (see **Figure 3.7 B**) were formed as a result of saturated carbons at δc =40 and at δc = 29 ppm.

It is worth pointing out that the other reactive HAS, AATP was also polymerised and characterised but was not used subsequently in the work. The FTIR and NMR of the parent AATP is given **in Figure 3.8.**

3.2.1.1 Effect of processing temperature on the melt behaviour of HDPE

Before performing reactive processing of PE in the presence of reactive HAS (g-HAS) in the presence of an initiator, the effect of the processing temperature (**180-280°C**) on the melt behaviour of the PE (in absence of HAS and peroxide) was first investigated. **Figure 3.9** shows the melt characteristics and chemical changes of HDPE at the different processing temperatures examined. The final torque showed an increase with increasing temperature from 180-240°C but started to decrease at higher temperatures and this was paralleled by a continuous increase in the melt temperature, see **Figure 3.9 H**.

The gel content of the processed polymer increased also with increasing processing temperature reaching a maximum of 27% at 260°C followed by a decrease down to 20% at 280°C, see **Figure 3.9F**, which confirms the occurrence of polymer degradation (chain scission) at these high temperatures. FTIR analysis shows that the degradation products started to form already at the temperature of 180°C with significant development of carbonyl degradation products dominated by ketones and aldehydes forming at processing temperature of 200°C (see **Figure 3.9A**), these degradation products increased with increase in temperature. Furthermore, the increase in temperature showed also peaks at 908cm^{-1} characteristic for vinyl group, which decreased, and a peak at 965cm^{-1} assigned to trans-vinylene group which formed and had increased with increasing temperature (see **Figure 3.9 B & D**). Similarly the Melt flow index (MFI) values increased dramatically at higher temperature see **Figure 3.9 E,** suggesting polymer degradation by crosslinking reactions.

3.2.1.2 Effect of the peroxide initiator and the initial AOPP concentration on the grafting reaction

The peroxide concentration is one of the most important chemical variables that can affect the grafting efficiency during melt processing. The efficiency of the grafting reaction is also dependent on the rate of diffusion of the antioxidant in the polymer. This could be increased

by increasing the AOPP concentration. Therefore the effect of peroxide concentration at two initial concentrations of AOPP (3 % & 6%) on the grafting efficiency was examined.

Figure 3.10 shows changes in the time torque curves of PE-g-AOPP samples reactively processed with 3% and 6% AOPP with varying T101 concentrations. The final torque increased more significantly when 6% AOPP was used and the level of the torque increased further at higher peroxide concentrations. **Figure 3.11** shows the effect of the peroxide concentration on the grafting of AOPP and the extent of different side reactions during polymer processing at 180°C in the presence of 3% and 6% AOPP. The use of higher AOPP concentration under these conditions gave higher levels of grafting at lower peroxide concentrations along with lower amount of free AOPP remaining in the systems; see **Figure 3.11C & D** and **Table 3.1**. Furthermore, at both initial AOPP concentrations, the level of grafting increased with increasing the peroxide concentration at both processing temperatures of 180 and 200°C (**Figure 3.12 A**) but the level of grafting was found to then decrease with a further increase in the peroxide concentration. This is due to the formation of side reaction products (p-AOPP and polymer crosslinking), see **Figure 3.12 C &D**.

3.2.1.3 Effect of processing temperature on grafting reactions of AOPP

In order to investigate the extent of grafting of AOPP on PE, a set of experiments were done at fixed composition of T101 concentration of 0.005 MR and antioxidant concentration of either 3% or 6% at various temperatures (180-240°C). Increasing the processing temperature increased the AOPP distribution and diffusion in the polymer but higher temperatures were also expected to affect the decomposition rate of the peroxide. Hence the processing temperature has a direct effect on the balance of the competing reactions (AOPP homo-polymerisation, PE crosslinking and chain scission) and the target grafting reaction of antioxidant.

Figures 3.13 and 3.14 show the effect of processing temperature on the antioxidant grafting reactions at a fixed peroxide concentration of 0.005 with either 3 % or 6% AOPP. It is clear that under these conditions and at 3% AOPP, the optimum grafting level was obtained at 240°C, where the rate of the reaction was fastest as was determined by the time for the polymer to reach max torque in the melt, (see **Figure 3.13 B**). At this temperature, the extent of homopolymerisation has also decreased substantially, **Figure 3.13D** paralleled by a minimum amount of free AOPP and gel content. In the presence of 6% AOPP under the same conditions (see **Figure 3.14**), on the other hand, the optimum grafting level was reached at a

lower temperature of 200°C (compared to 3% AOPP) which is paralleled by a significant drop in the amount of p-AOPP formation, **Figure 3.14 C& D**.

3.3 Free Radical Melt grafting of other antioxidants

3.3.1 Free radical grafting of AOTP on PE

The aim of this work was to form a grafted HAS antioxidant on PE with optimum grafting, hence a second synthesised low molecular weight reactive HAS antioxidant, AOTP was investigated.

When AOTP (3%, 1% and 0.5%) was processed at various temperatures, the level of grafting was found to increase initially with increase in temperature when using 1% AOTP, whereas at 3% and 0.5%, the level of the HAS grafting decreased initially under the same conditions (see **Figure 3.15**). The grafting trend of AOTP followed a similar pattern to that of AOPP with an initial increase in the peroxide (T101) concentration resulting in an increase in grafting that was paralleled by a decrease in the extent of the side reactions, see **Figure 3.16 .**

3.3.2 Free radical grafting of AATP on to PE

AATP was also synthesized, characterized and used in the melt free radical grafting reactions on PE. Limited numbers of experiments were conducted in this case, as the initial grafting results were not satisfactory.

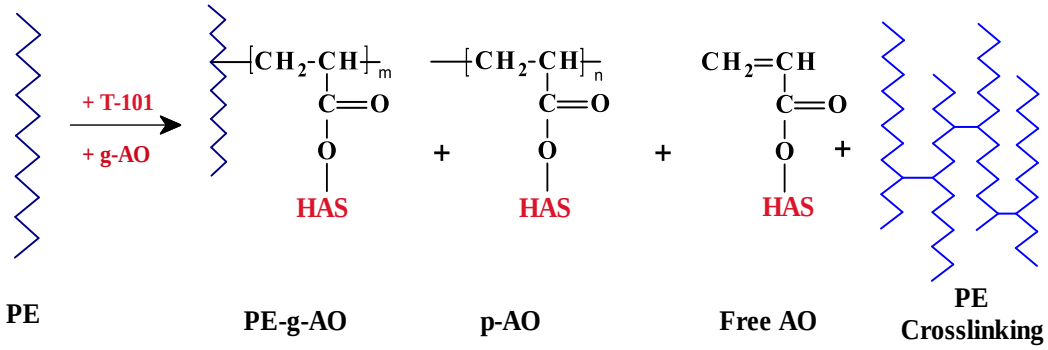
6% AATP was processed at various temperature from 160-180°C. It was found that increasing the processing temperature caused the polymer to crumble, even at the low processing temperature of 160°C, the gel formation was very high (70%), thus further 6% AATP experiments were abundant (see **Figure 3.17 C & Table 3.5**). Increasing the processing temperature in the presence of 3 or 6% AATP resulted in the formation of highly crumbled polymer, for e.g. at 3% AATP, a processing temperature of 180°C resulted in 63% grafting with 50% gel formation (see **Figure 3.17 B & Table 3.5**). At much lower AATP concentration of 0.5%, an increase in the processing temperature resulted in high level of grafting with a lower extent of gel formation.

3.4 Discussion

3.4.1 Reactive Melt Processing of Functional AOs on Polyolefins and the Grafting of AOPP on HDPE

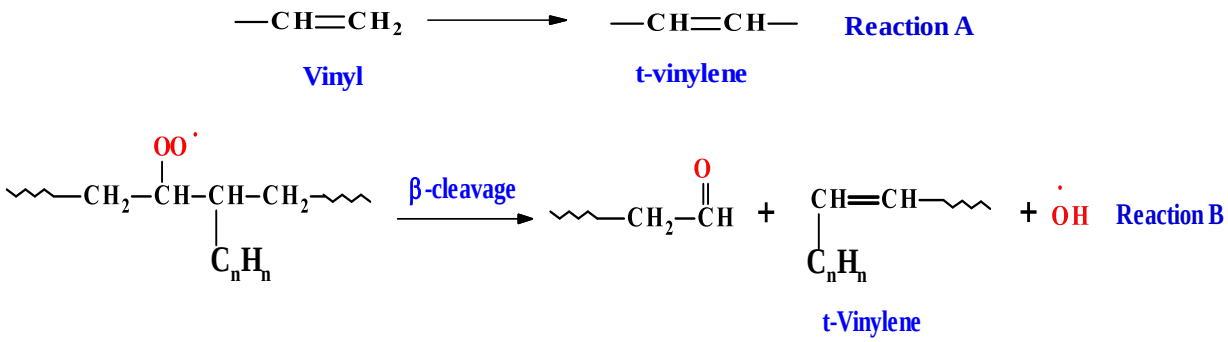
Over the last 30 years, much work has been devoted by the polymer processing and performance group (PPP) at Aston University to chemically attach reactive antioxidants and monomers on to a wide range of polymers using polymer melt processing procedures , a process referred to as "reactive processing" [64, 87, 89, 92-95, 100, 101, 121, 122, 125-127]. Polymer bound masterbatches were prepared and diluted down in the polymer to a low (normal) antioxidant concentration including the grafting of hindered amine stabilisers (HAS) and hindered phenol antioxidants on polyolefin [87, 92-95, 101, 126, 127]. An optimum grafting system would be dependent on the correct choice of the chemical system and the processing variables that would reduce the interference of side reactions without altering the polymer characteristics [93-95]. Typically a higher initiator concentration has been used in order to increase the grafting yield is to be increased [87, 101, 122], but the problem with such an approach is that this would also results in higher extent of all the competing side reactions such as homo-polymerisation of the reactive antioxidant and degradation of the polymer via crosslinking or chain scission reactions [90-92, 96, 101].

Free radical grafting of AOPP on HDPE during melt processing was carried out in this work giving rise to the formation of HAS-grafted polymer (PE-g-HAS), but the grafting reaction under all conditions used was shown to be accompanied by the formation of side reaction products, mainly AOPP homopolymer (p-AOPP) formation and crosslinked HDPE (see **Reaction Scheme 3.2**). The relative contribution of all the competing reactions depends on the choice of the chemical composition and the processing conditions of the grafting system.

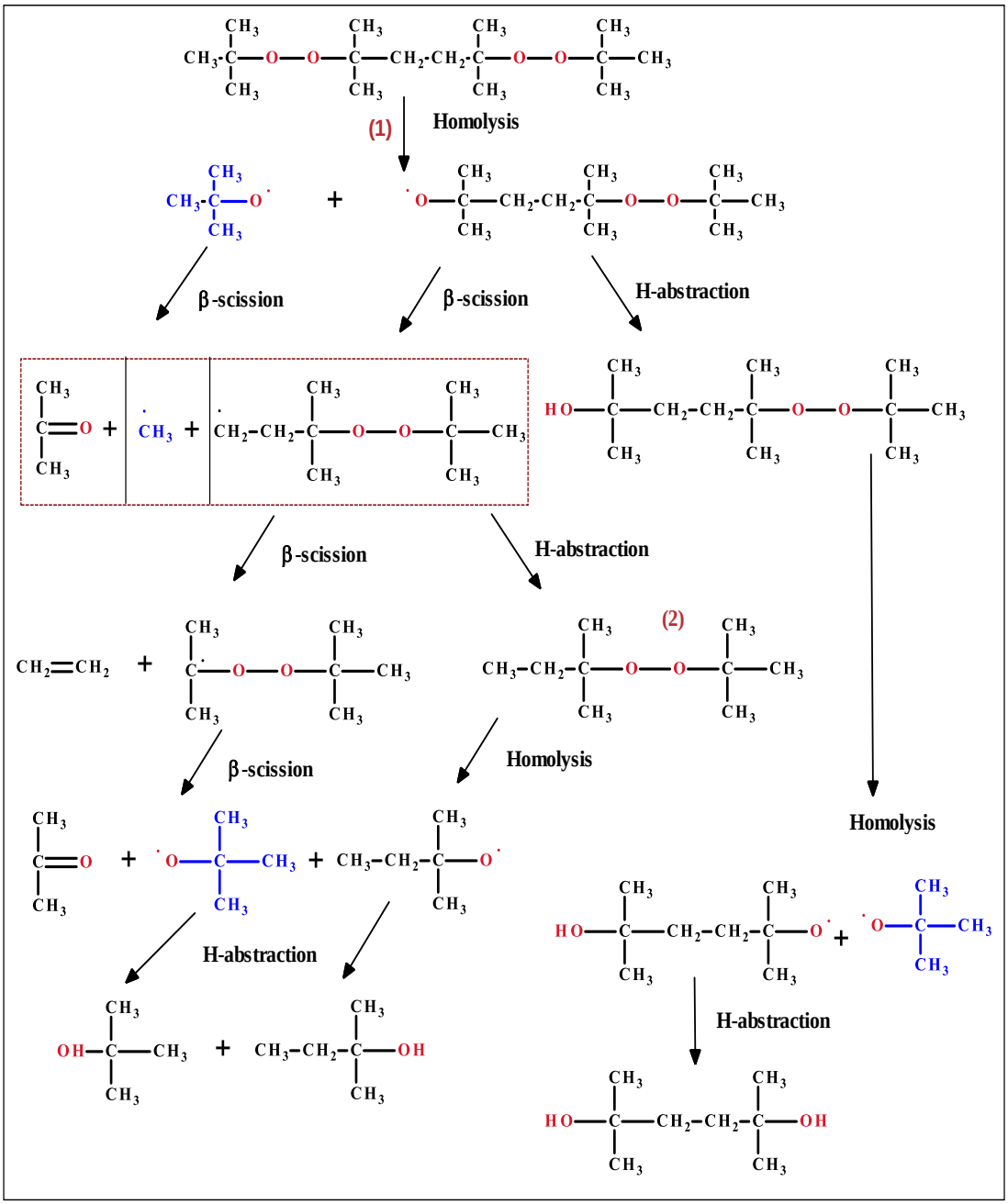


Reaction Scheme 3. 2

It is well known that polyethylene typically undergoes crosslinking during melt processing, the extent of which increases with increasing temperature [49-51, 54, 55, 128-131] and this was evident here during processing of HDPE (with no peroxide) from the observed increase in gel content and torque values (**Figure 3.9 F and H**), at temperatures 180°C to 240°C. However with a further increase in temperature, the extent of chain scission reaction started to dominate as is clearly evident from the observed significant decrease in both gel and final torque. This is paralleled by a sharp increase in the melt temperature, as well as, a significant increase in MFI, and a decrease in the concentration of the vinyl groups, see **Figure 3.9 F, D & H,** confirming literature finding for the processing behaviour of polyethylene [50, 51, 130, 132].The reduction in vinyl concentration maybe partially attributed to an isomerisation reaction of the vinyl to *trans*-vinylene groups, which is supported by the observed increase in the *trans*-vinylene concentration (see **Reaction A and** see **Figure 3.9 D**. The build-up of *trans*-vinylene at higher temperatures may be further associated with chain scission processes involving β-cleavage of secondary alkyl radicals, or secondary α,β-alkylperoxyl radicals adjacent to a branch point, in the polymer with the latter reaction also generating aldehydes, see **Figure 3.9A** [132].



The use of peroxide initiators would increase the rate of polymer degradation due to the peroxide-generated free radicals, See **Scheme 3.3** [133]. The rate of polymer degradation would be further increased if the processing temperature was to be increased and this would be further exacerbated when a small concentration of peroxide was added to the system as the half-life of peroxides decreases at higher temperatures, see half-life time of the peroxide T101 in **Table 3.6**.



Reaction Scheme 3. 3. The mechanism for free radical generation for **Trigonox 101**

Table 3. 6. Half life time ($t_{1/2}$) of peroxide T101, calculated using above equation.

Temperature (°C)	Trigonox 101 # Half-life $t_{1/2}$ (min)
100	4014
150	11
170	1.46
180	0.58
190	0.24
200	0.10
220	0.02
240	0.005

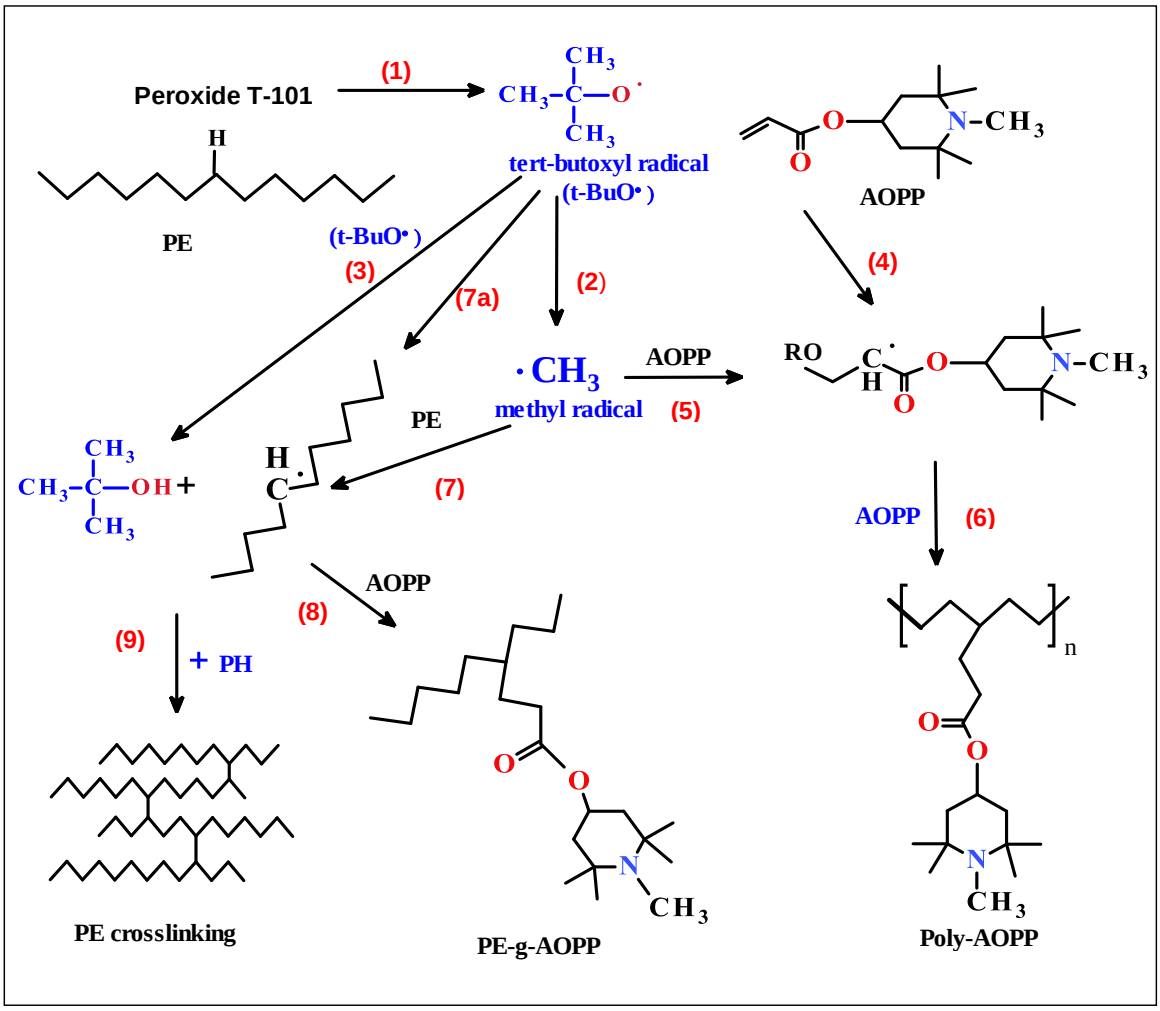
see equation 1 & 2 in chapter 2 for calculation of half-lifetime

In contrast, the use of g-HAS stabilisers (e.g. AOTP and AOPP) at high temperatures in the presence of peroxide (e.g. T101 at 0.005MR at 240°C) resulted in a clear inhibition of the oxidation and the crosslinking of the polymer, as can be seen from the significant reduction in the gel content compared to that of the unstablised PE, see **Figure 3.18.** It is interesting to find that the overall behaviour of the grafting of AOPP when used at 3% and 6% w/w concentration is consistently different when the samples were reactively processed with either a different initiator concentration or when using different processing temperatures at a fixed peroxide concentration. **Figure 3.19**, shows that when a higher concentration of AOPP (at 6%) is used with either increasing peroxide concentration at a fixed temperature (e.g. **at 180°C, Figure 3.19 B**), or at varying temperatures but with a fixed peroxide molar ratio (e.g. **0.005 MR, Figure 3.19** D), the grafting level was shown to initially increase followed by a decrease at higher peroxide concentrations or at higher temperatures. This is shown to be paralleled with mirror-image behaviour in the formation of p-AOPP, in that the latter concentration decreased initially and then increased at higher initiator concentration and at higher processing temperatures. In contrast, when 3% AOPP was used, the grafting level increased continuously with increasing peroxide concentration or increasing the processing temperature, and this was paralleled by a continuous decrease in the p-AOPP formation under both conditions, **Figure 3.19 A and C**.

The behaviour of AOPP when present at the higher concentration of 6% may be expected, as increasing either of the two parameters (the peroxide concentration or the temperature), would give rise to an increase in the extent of homopolymerisation of the AO paralleled by a consistent decrease in the grafting level of the AO [92, 101]. In the case of the use of 3% AOPP, the consistency in the overall unexpected behaviour of the grafting trend (where it continues to rise with increasing temperature or peroxide concentration) suggests that the

point at which the balance of the grafting versus homopolymerisation reactions changes over may not have been reached under the conditions used. If a further increase in either the peroxide or the temperature was examined, it would perhaps have resulted in a flip-over in the balance of the reactions giving rise to an overall similar behaviour trend to that observed for the 6%. This, however, needs to be experimentally checked before confirmation.

The mechanisms of free radical generations from the peroxide T101 [134, 135], and that of the free radical melt grafting of AOPP on to high density polyethylene in the presence of the peroxide T101 are shown in **reactions schemes 3.3 and 3.4 respectively**. Thermal decomposition of T101 (alkyl peroxide initiator) involves initial O-O bond homolysis to generate the corresponding alkoxyl radicals (tert-butoxyl radical), see **Reaction Scheme 3.3** , which are highly reactive towards hydrogen abstraction, hence giving rise to formation of PE macro radicals on reaction with PE (**see Reaction Scheme 3.4, Rn 7a**). The initial radicals would subsequently breakdown independently to give variety of alkoxyl and alkyl radicals see **Reaction Scheme 3.3**. Further decomposition of the alkoxyl radical through β scission forms methyl radicals and it has been shown [133, 135, 136] that based purely on a consideration of bond dissociation energies, methyl radicals should be equally proficient at hydrogen abstraction from the polymer, however, they were also shown to prefer abstraction of hydrogen from double bonds. Therefore, these radicals would not only initiate the grafting reaction of AOPP, but also would lead to the crosslinking of the polymer and homopolymerisation of AOPP (**Rn 5 and 6 in the reaction Scheme 3.4**). The grafting reaction takes place through the formed PE macro radicals (see **Reaction Scheme 3.4, Rn 7, 7a and 8**). The p-AOPP is produced through reaction of AOPP radical with more AOPP molecules, **Reaction Scheme 3.4, Rn 6**. However the extent of the production of each of these reactions is dependent on the type of the peroxide its concentration and the processing temperature used in the grafting process. By increasing the processing temperature, the half-life of the peroxide decreases, which increases the decomposition of the initial tert-butoxyl radical through β scission reaction, thus increasing the subsequent concentration of the methyl radicals, which in turn would react with more AOPP molecules resulting in higher level of grafting reaction via more hydrogen-abstraction from the polymer, **see Reaction scheme 3.4, Rn 2, 7 and 8**.



Reaction Scheme 3. 4: The melt free radical grafting reaction mechanism of AOPP on PE

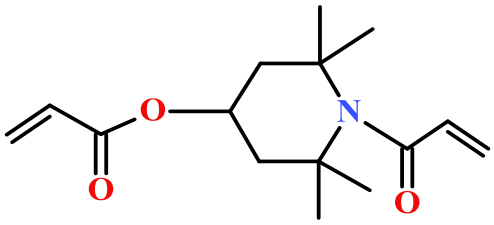
3.4.2 Grafting reaction of AOTP on PE

AOTP, 4-acryloylloxy 1, 2, 2, 6, 6-pentamethyl piperdine, another reactive HAS stabiliser, was synthesised and successfully grafted on PE in the presence of alkyl peroxide initiator, T101. **Figure 3.20** shows that the overall AOTP-grafting system behaviour when 3% and 6% AOTP was used is similar to that of AOPP discussed in the previous section. Addition of a small molar ratio of the peroxide (0.001 MR) at processing temperature of 180°C, gave rise to an initial slight decrease in the grafting level paralleled by an increase in the p-AOTP (for 6% initial concentration) or the amount of free AOTP remaining in the system (for 3% initial concentration). However increasing the molar ratio ([T101]/[AO]) of the peroxide from 0.002 up to 0.01MR has resulted in an increase in the level of grafting up to values of >90% at 0.005MR for 3% AOTP and at 0.01MR for 6% AOTP (**see Figure 3.20**). This increase in grafting level was also paralleled by a decrease in both the p-AOTP and the free AOTP remaining in the grafting system. This very high level of grafting of AOTP on PE contrasts results from previous work on polypropylene (PP) from the Aston, PPP group where grafting

of AOTP on PP was shown to be achieved to its maximum at less than 50% [122]. This may be due to a much higher extent of PP degradation by chain scission in the presence of excess peroxide, compared to PE which undergoes predominantly crosslinking reactions.

3.4.3 Grafting reaction of AATP on PE

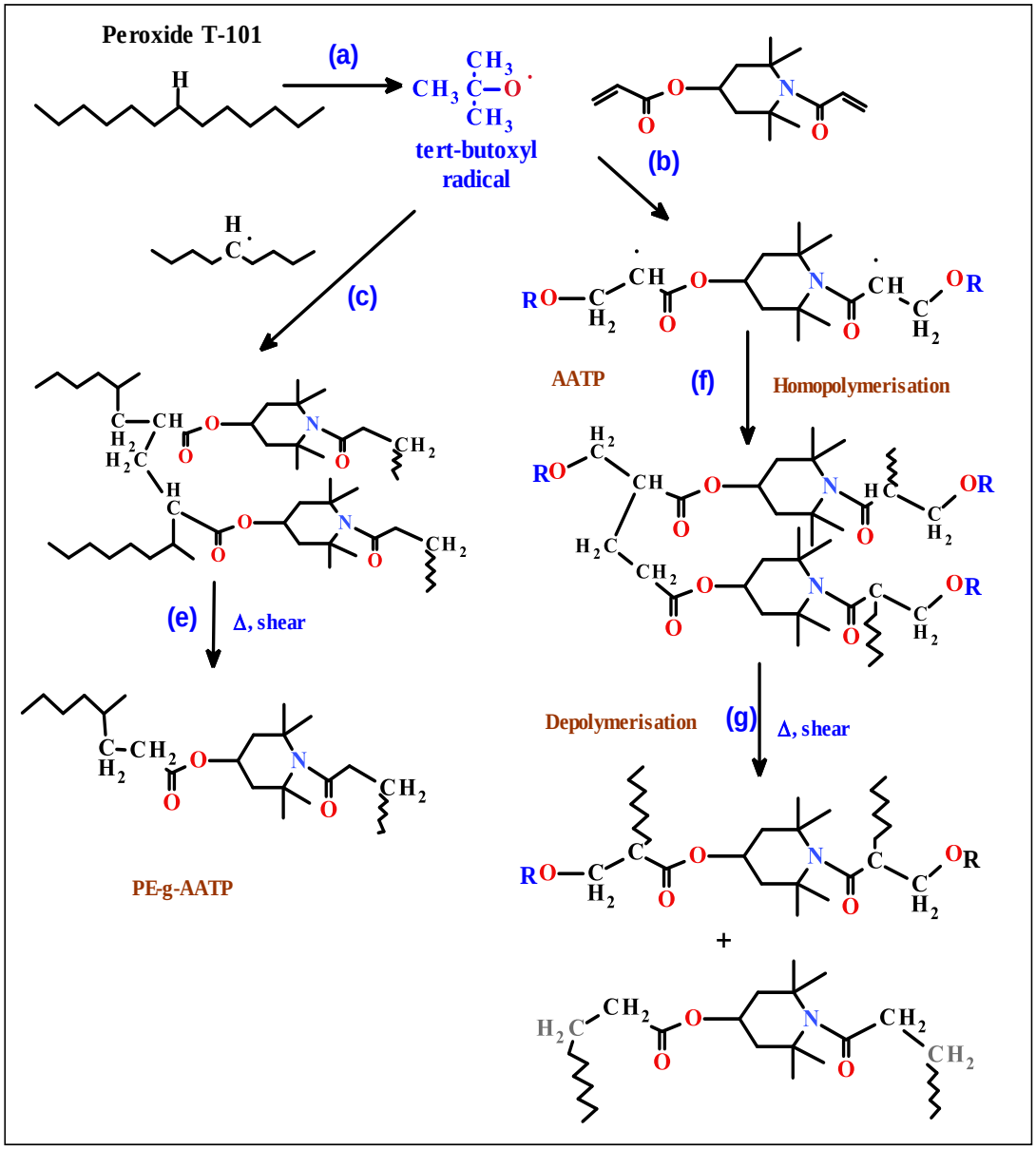
AATP,1-acryloyl 4-acryloyloxy 2,2,6,6-pentamethyl piperdine, a bifunctional HAS, is much more reactive than the monofuntional reactive HAS antioxidants AOPP and AOTP due to the presence of two polymerisable reactive functions, see structure below. It was shown previously that AATP reacts in polyolefin grafting system by initially crosslinking with the polymer (in PP), but on further processing structural rearrangements takes place and leads to 100% AATP grafting on to the polymer [93].



AATP

When AATP is reactively processed at higher temperatures, several competitive chemical reactions take place. Linear homopolymerisation may take place leaving the second pendant acrylic group unreacted. Further linear homopolymerisation may be followed by inter or intra crosslinking reaction by the pendant groups (see **(f) in Reaction scheme 3.5**), in addition to the grafting of the antioxidant on to the polymer backbone, see **(e) in Reaction scheme 3.5 [93, 122]**.

The high processing temperature used in this work with PE would give rise to much higher extent of homopolymerisation of this reactive HAS [93] , which would end up phase separating from the polymer, thus giving rise to the observed crumbled polymer,(see **Figure 3.17A**) . **Figure 3.17** showed that at low processing temperature of 160° or 170°C, resulted in a very high extent of gel, almost 100%, and a further increase in the temperature resulted in a completely useless crumbled polymer. For this reason, grafting experiments with AATP were abandoned and AATP was not used in subsequent experiments involving peroxide crosslinked pipes produced as described later in Ch.4.



Reaction Scheme 3. 5: The melt free radical grafting mechanism of AATP [122]

Table 3. 7: Solubility for AO and p-AO's in organic solvents

Solvent (boiling point)	AOPP		p-AOPP		AOTP		p-AOTP	
	Room temp	Boiling temp	Room temp	Boiling point temp	Room temp	Boiling point temp	Room temp	Boiling point temp
DCM (40)	Yes	Yes	Yes		Yes		Yes	
Chloroform (61.2)	Yes	Yes		Yes	Yes		Yes	
THF (66)	Yes	Yes	Yes	Yes	Yes		Yes	
Hexane(69)			Yes	Yes				
Acetonitrile (82)	Yes		No		Yes		Yes	
Diethylether (34.6)	Yes				Yes			
Heptane (98)			No		Yes		Yes	Yes
Toluene (110)	Yes	Yes	Yes		Yes			
Methanol	Yes		Yes		Yes			

Table 3. 8: FTIR spectral characterisation of reactive antioxidant and their homopolymers.

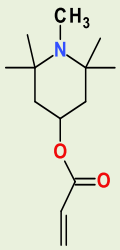
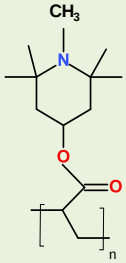
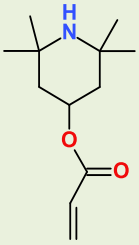
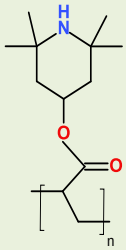
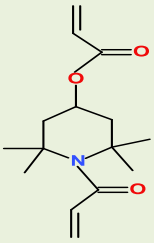
Assignment	cm^{-1}				
	AOPP	p-AOPP	AOTP	p-AOTP	AATP
	Fig 3.2	Fig 3.2	Fig 3.5	Fig 3.5	Fig 3.8A
					
C=O	1725	1728	1703	1730	1725
C=C aliphatic	1635	-	1633	-	1635
C=C aromatic	1618	-	1616	-	1618
C=C acrylic	1404	-	1408	-	1404
C-N ring	1253	1253	1274	1274	1253
(C=O)-O	1179		1184	1184	1179
N-H	-	-	3327	3327	-

Table 3. 9 : ^{1}H- NMR δ_H for reactive antioxidants and their homopolymers

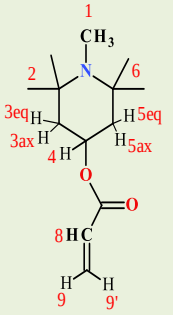
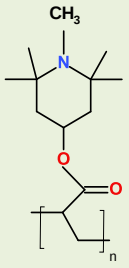
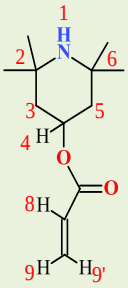
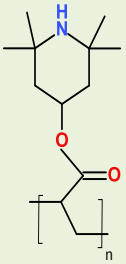
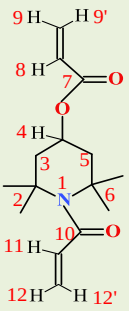
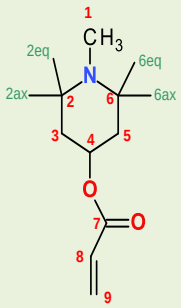
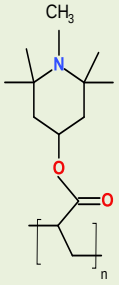
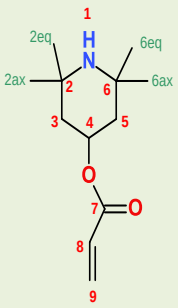
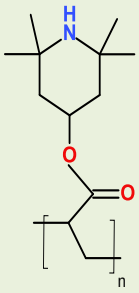
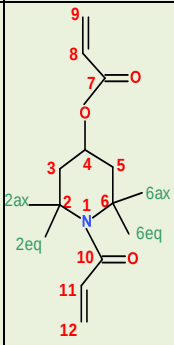
Assignment		δ_H / ppm				
		AOPP	**p-AOPP**	**AOTP**	**p-AOTP**	**AATP**
		Fig 3.3A	**Fig 3.3B**	**Fig 3.6A**	**Fig 3.6B**	**Fig 3.8B**
						
C-H cyclic eq	**H3, H5**	1.9	1.8	1.9	1.9	2.2
C-H cyclic ax	**H3, H5**	1.5	1.5	1.8	1.8	1.9
O-C-H-Ring	**H4**	5.1	4.9	5.2	5.1	5.2
-CH_3 ring	**H2&H6**	1.1, 1.0	1.1, 1.1	1.3, 1.2	1.3, 1.3	1.5, 1.4
-CH=CH_2	**H9,H8,H9'**	6.3,6.0, 5.1	2.2,1.2	6.3,6.0, 5.7		(H12) 6.5, (H9) 6.4, (H11) 6.1, (H8)5.8, (H9') 5.5, (H12')5.2
N-H	**H1**				H1 1.6	
N-CH_3	**H1**	H1 2.2	2.2			

Table 3. 10 : ^{13}C-NMR for reactive antioxidants and their homopolymers

Assignment		δc / ppm				
		AOPP	**p-AOPP**	**AOTP**	**p-AOTP**	**AATP**
		Fig 3.4A	**Fig 3.4B**	**Fig 3.7A**	**Fig 3.7B**	**Fig 3.8C**
						
C=O	**C7**	165	174	165	174	165 &169
C ring C-H	**C3 & C5**	46	49	44	43	43
O-C-H cyclic	**C4**	68	68	69	68	66
C ring -CH_3	**C2 & C6**	55	55	50	52	56
CH_3	**C2 & C6eq** **C2 & C6ax**	28 33	31,33	29 &34	34, 28	26 &30
AcrylateC=C	**C9 & C8**	130 & 129	41, 33	130 &129	40 , 29	128,131, 124
N-CH_3	**C1**	20	22			

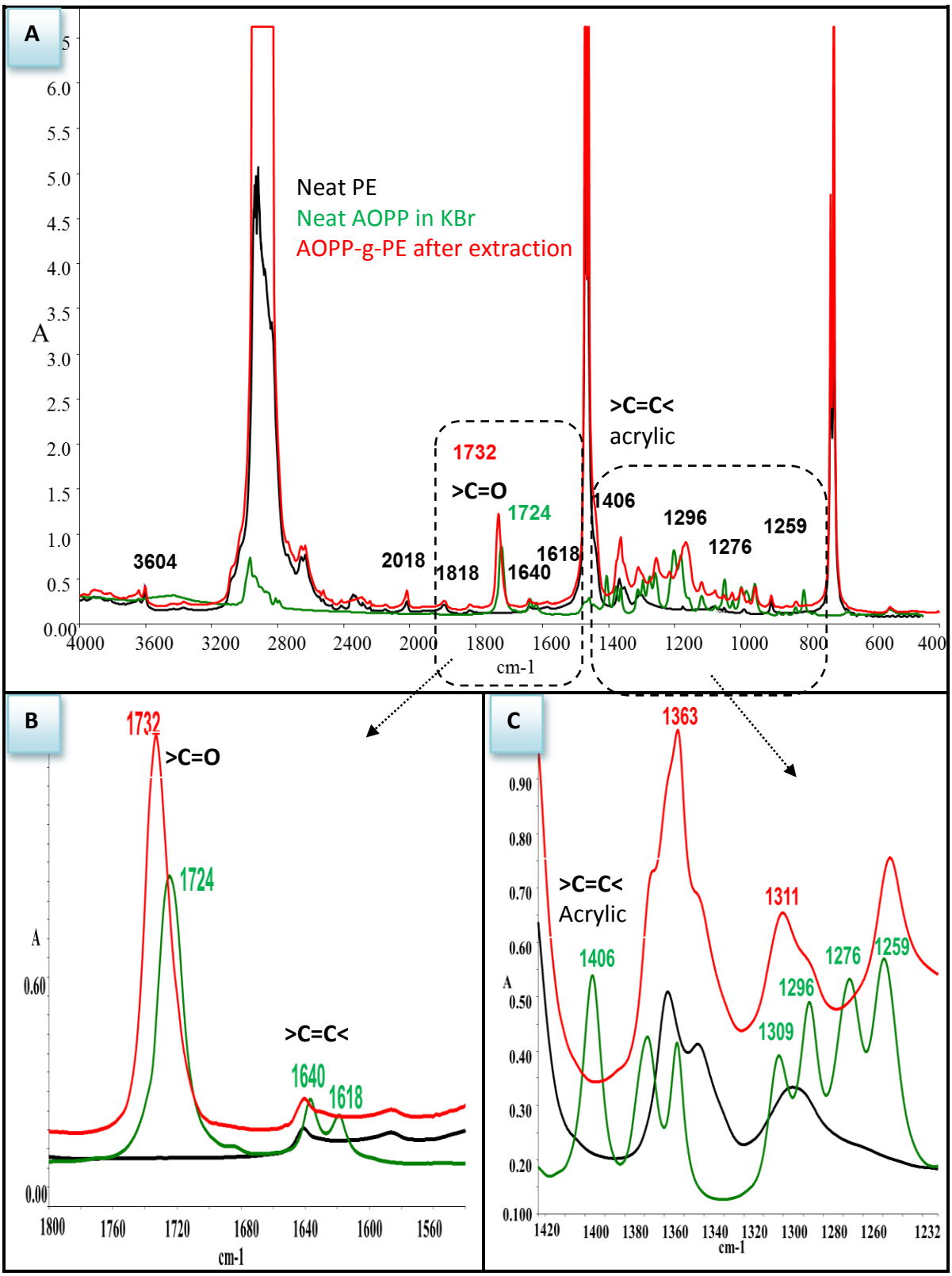


Figure 3. 1: FTIR absorbance spectra of HDPE (black), AOPP neat in KBr disc (Green) and purified film of PE processed with AOPP and peroxide (Red) full FTIR spectra (A) , FTIR spectra region 1800-1600 cm^{-1} (B) and 1500-1200 cm^{-1} (C)

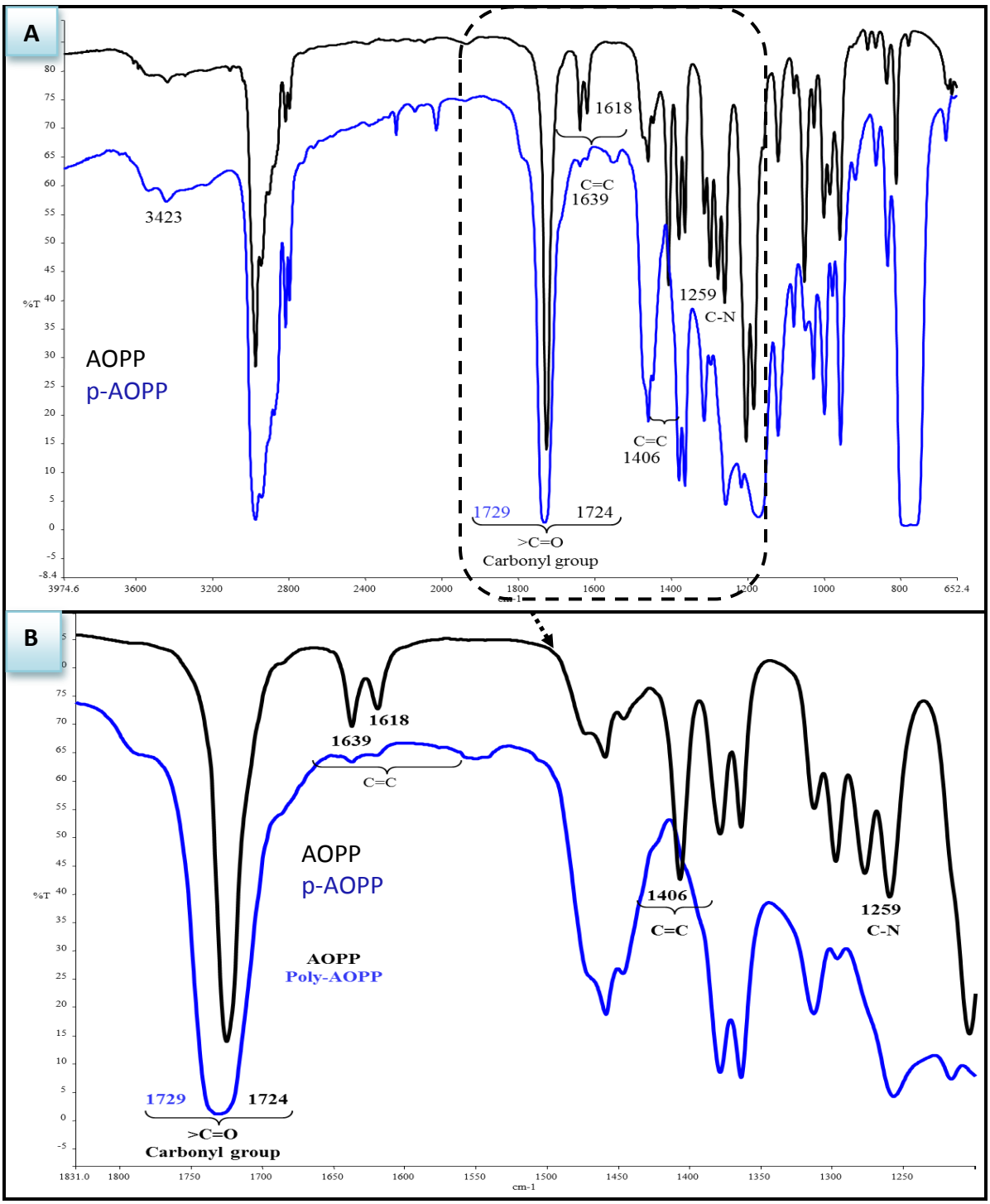


Figure 3. 2: FTIR spectra of synthesised p-AOPP (blue) in KBr disc and Neat AOPP (black) in KBr disc

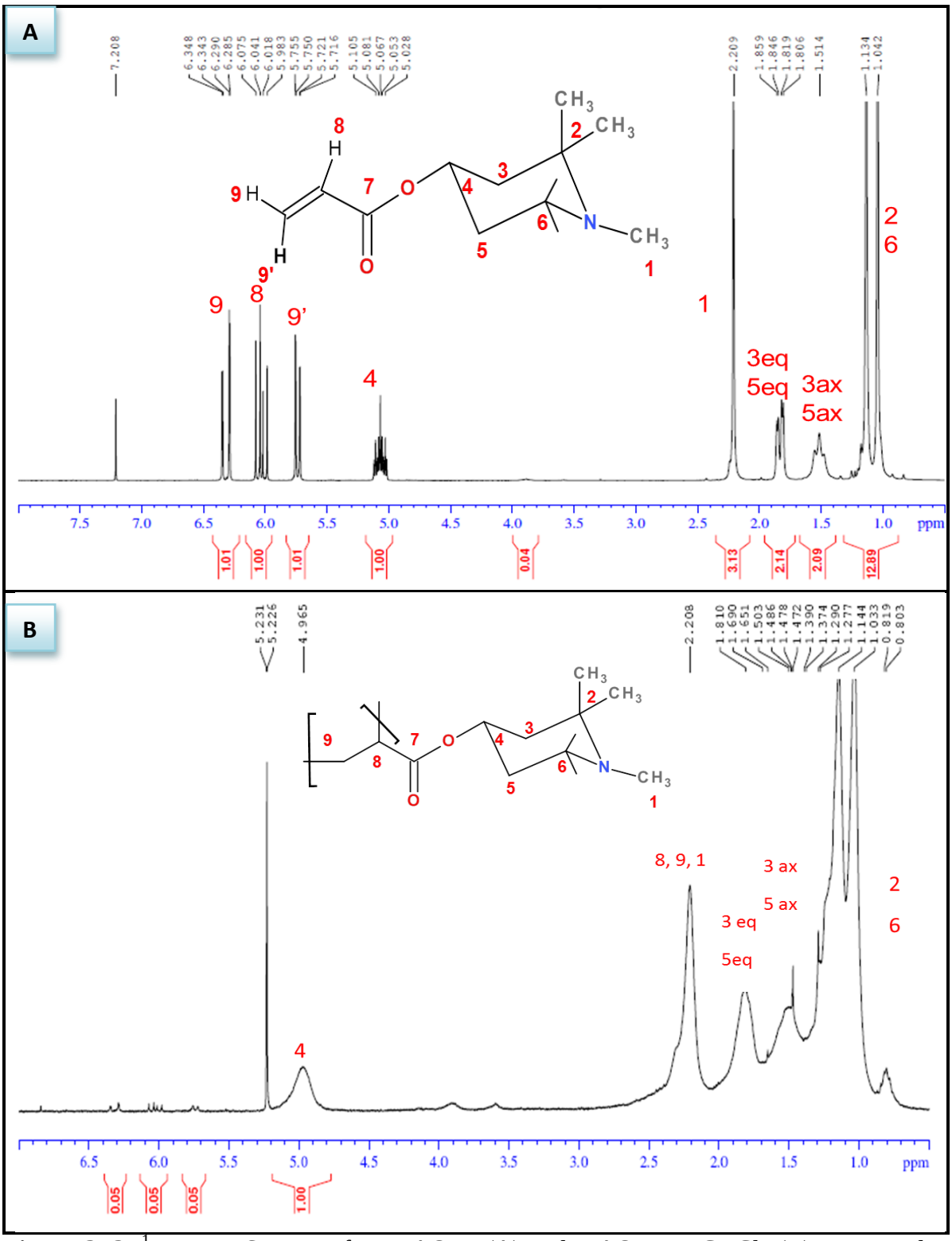


Figure 3. 3: ^{1}H NMR Spectra of neat AOPP (A) and p-AOPP in $CDCl_3$ (B), measured at room temperature.

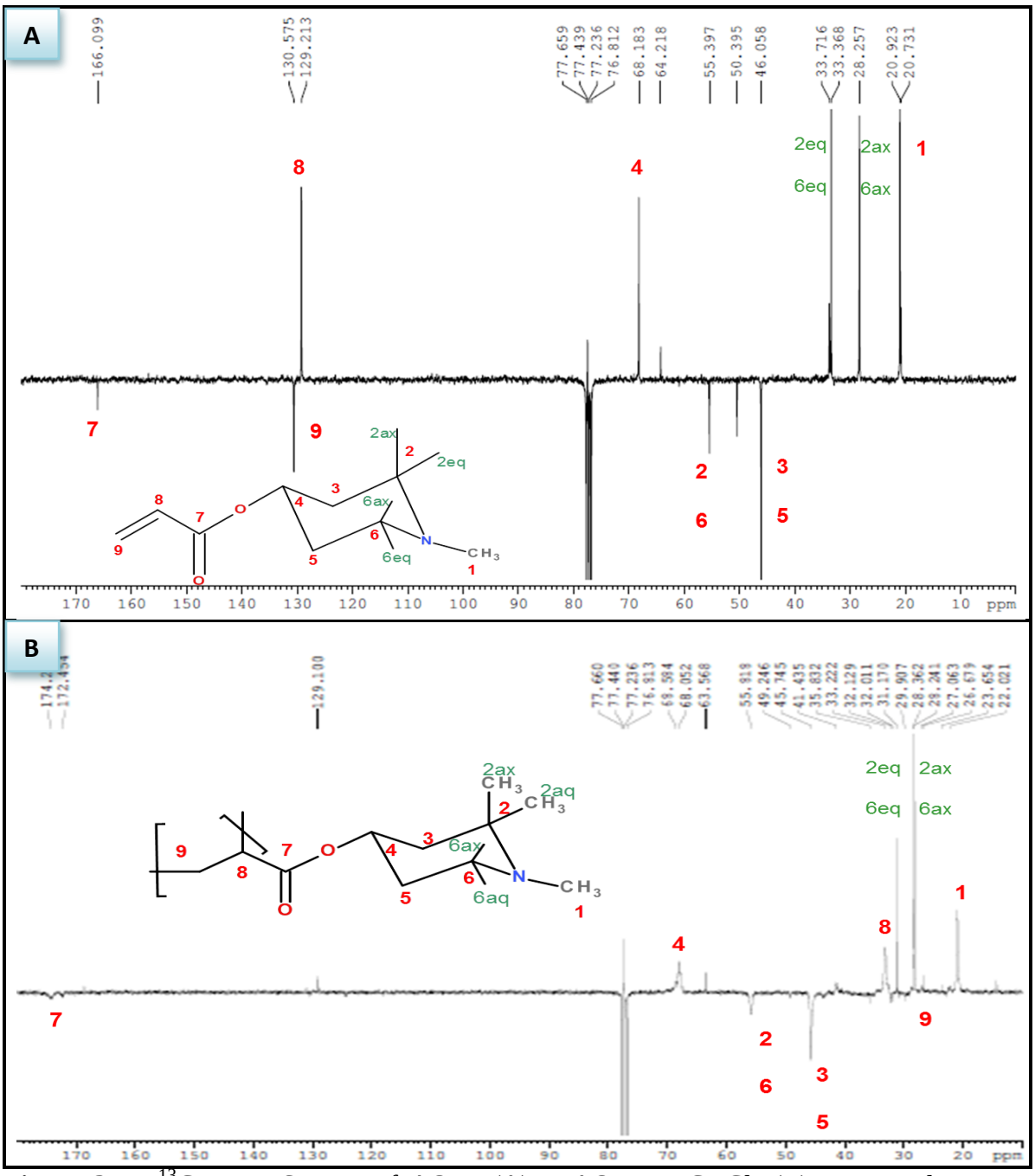


Figure 3. 4: ^{13}C NMR Spectra of AOPP (A), p-AOPP in $CDCl_3$ (B), measured at room temperature.

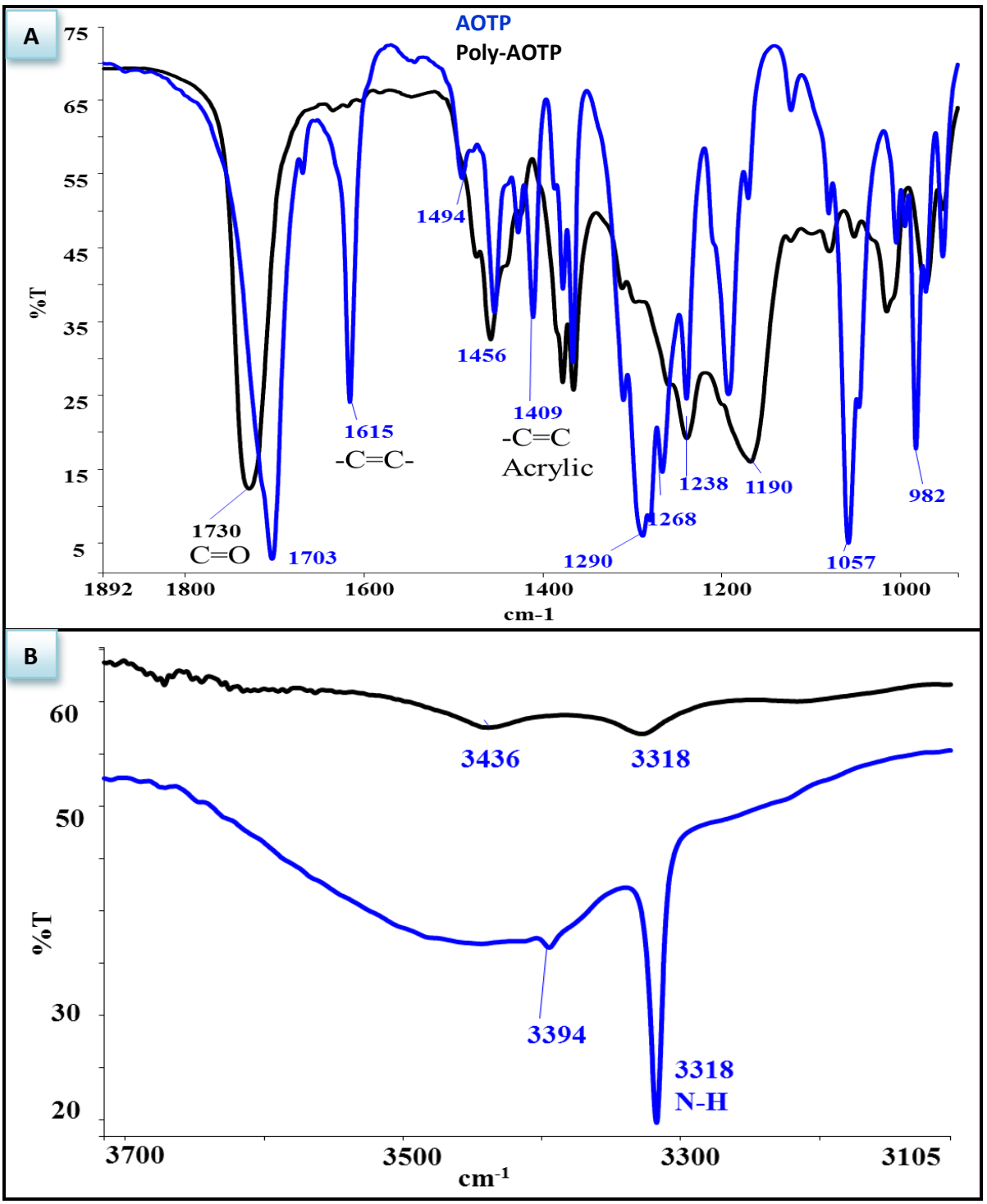


Figure 3. 5 : FTIR spectra of synthesised p-AOTP (black) in KBr disc and Neat AOTP (blue) in KBr disc.

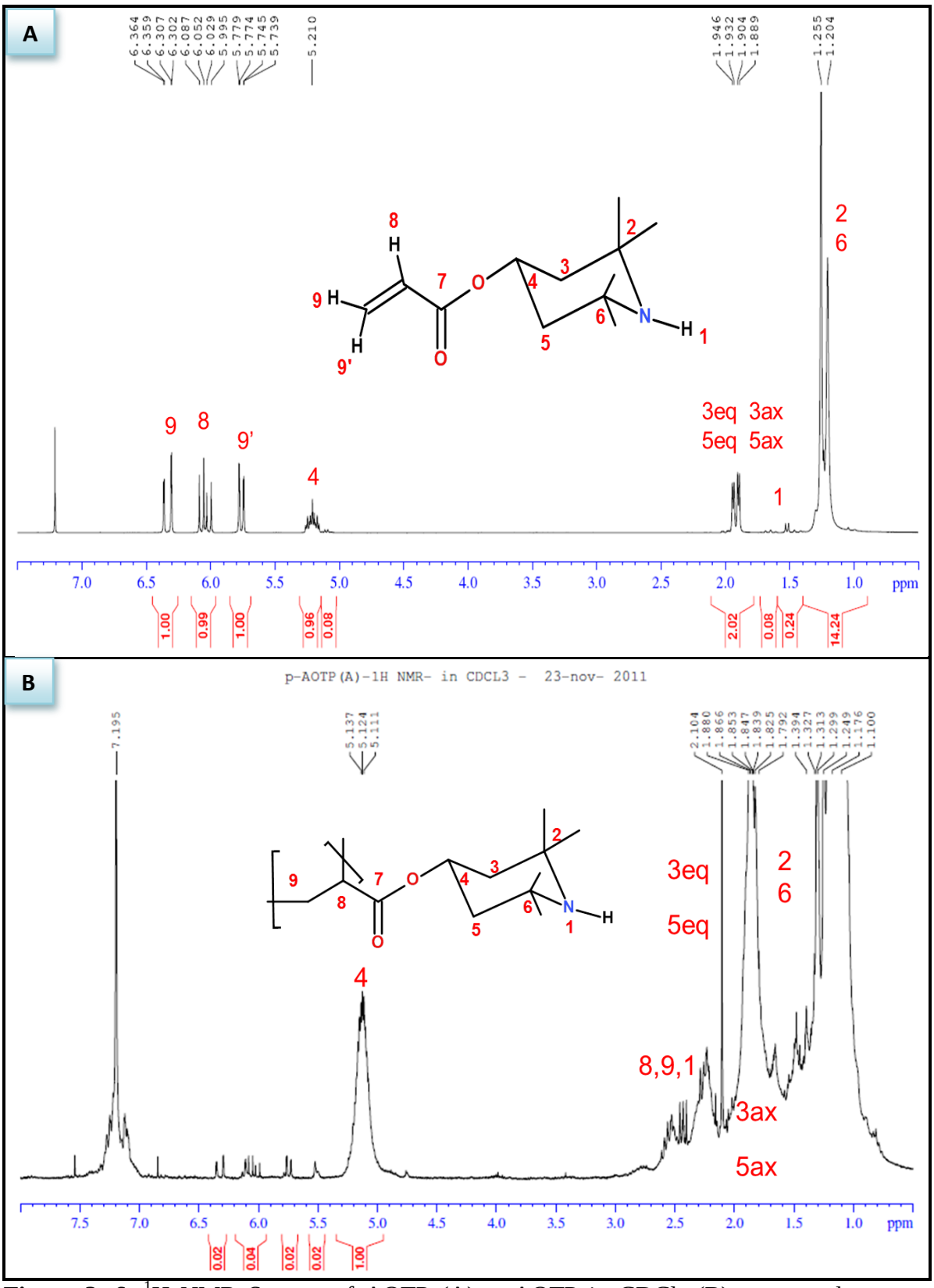


Figure 3. 6: ^{1}H NMR Spectra of AOTP (A), p-AOTP in $CDCl_3$ (B), measured at room temperature.

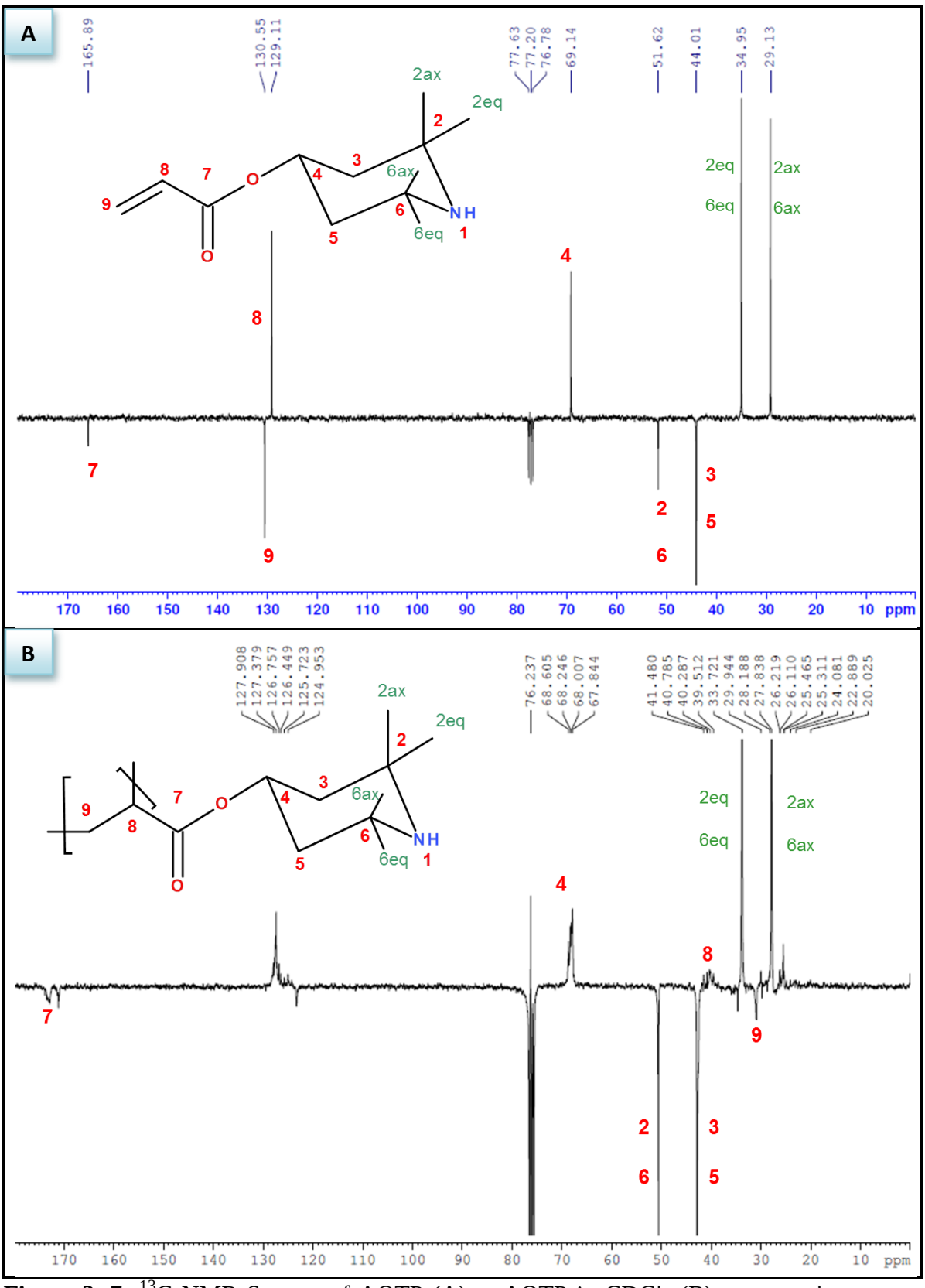


Figure 3. 7: ^{13}C NMR Spectra of AOTP (A), p-AOTP in $CDCl_3$ (B), measured at room temperature.

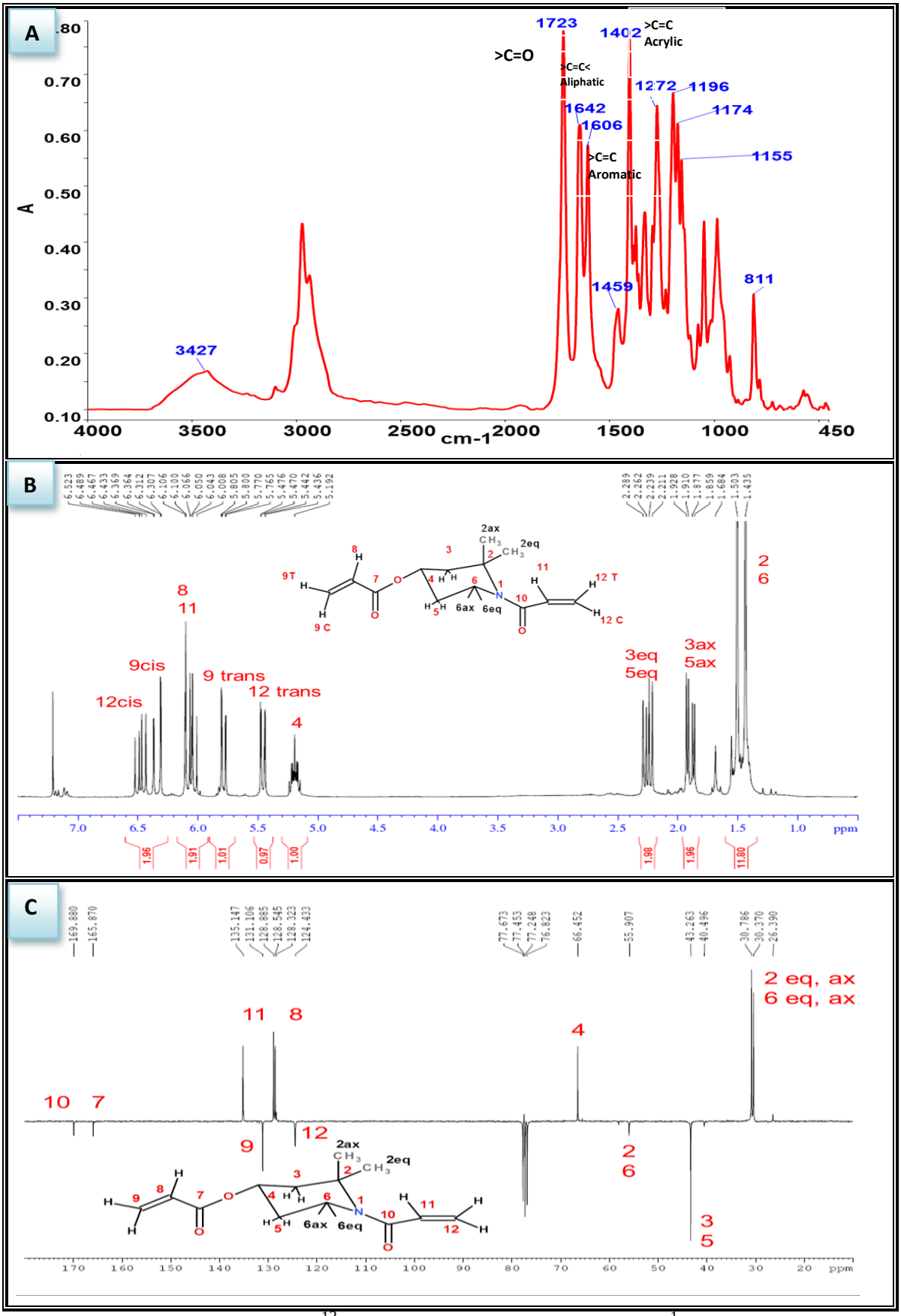


Figure 3. 8: FTIR in KBr (A), ^{13}C NMR of AATP in $CDCl_3$ (B), ^{1}H NMR of AATP in $CDCl_3$ (C), all measurements were done at room temperature.

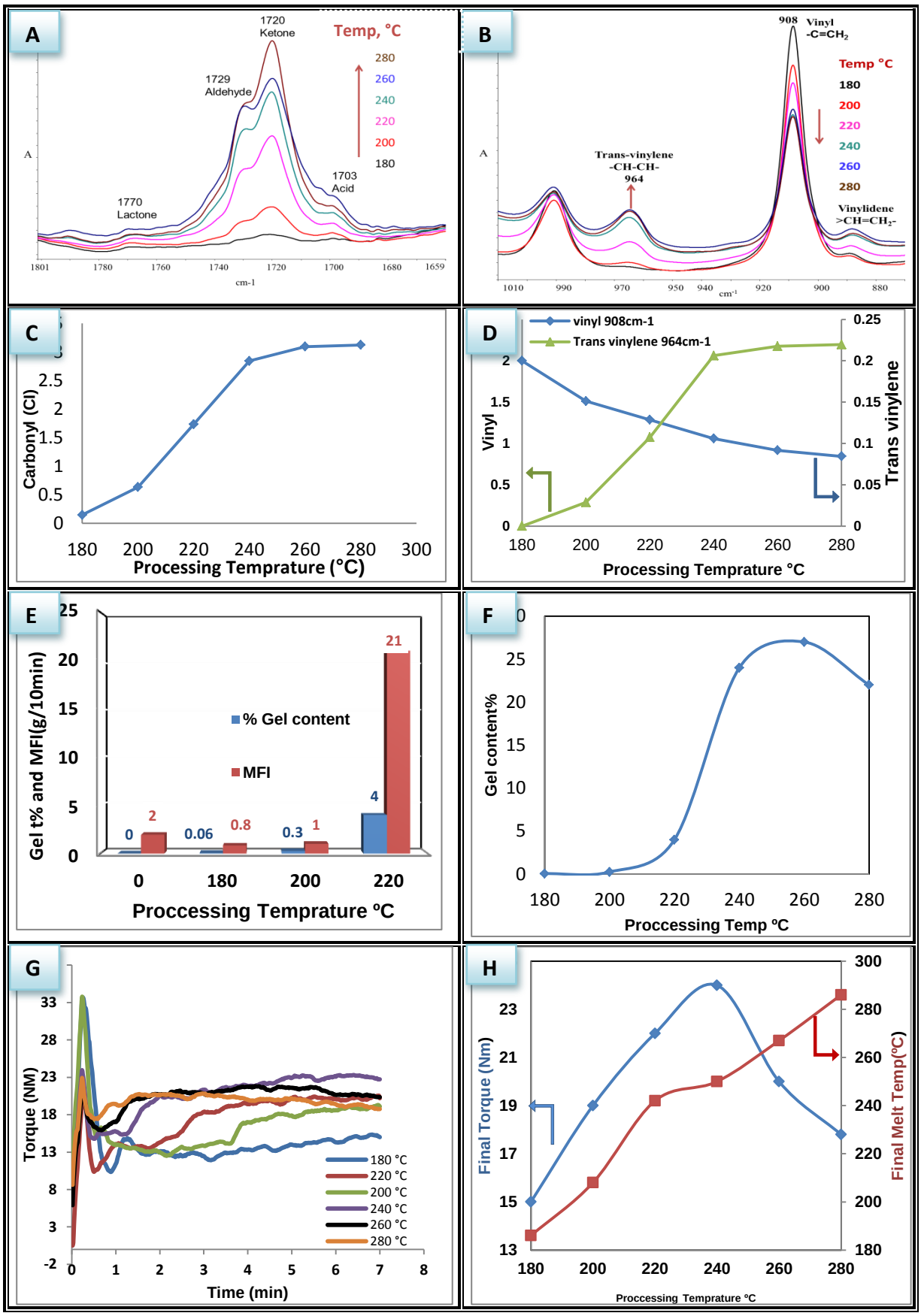


Figure 3. 9: Effect of processing temperature on chemical changes observed in IR spectra of PE processed in absence of AO's and peroxide (A-D), the gel and MFI (E&F) and the torque behaviour (G &H), processed for 7 mins, 65rpm

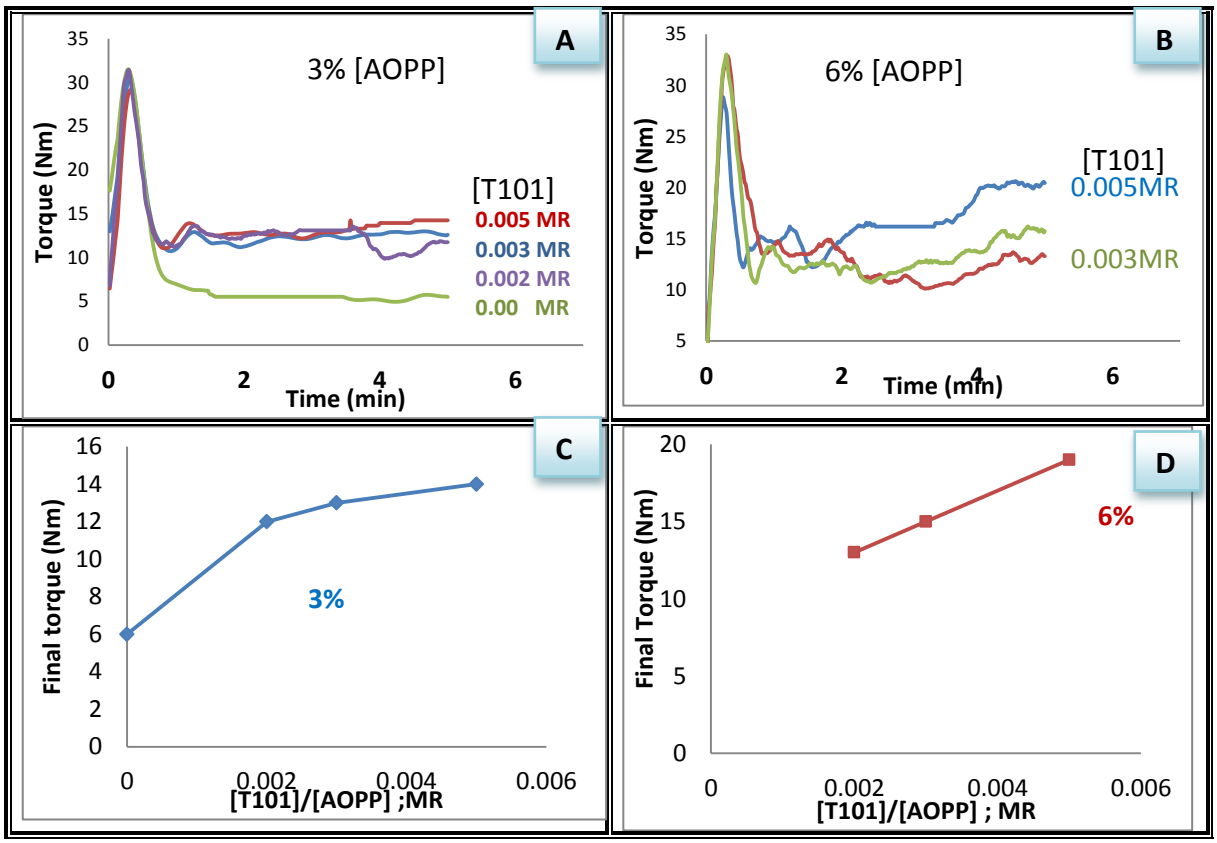


Figure 3. 10: Effect of [T101] concentration on torque behaviour of HDPE (**180°C; 5min; 3% or 6% [AOPP]**).

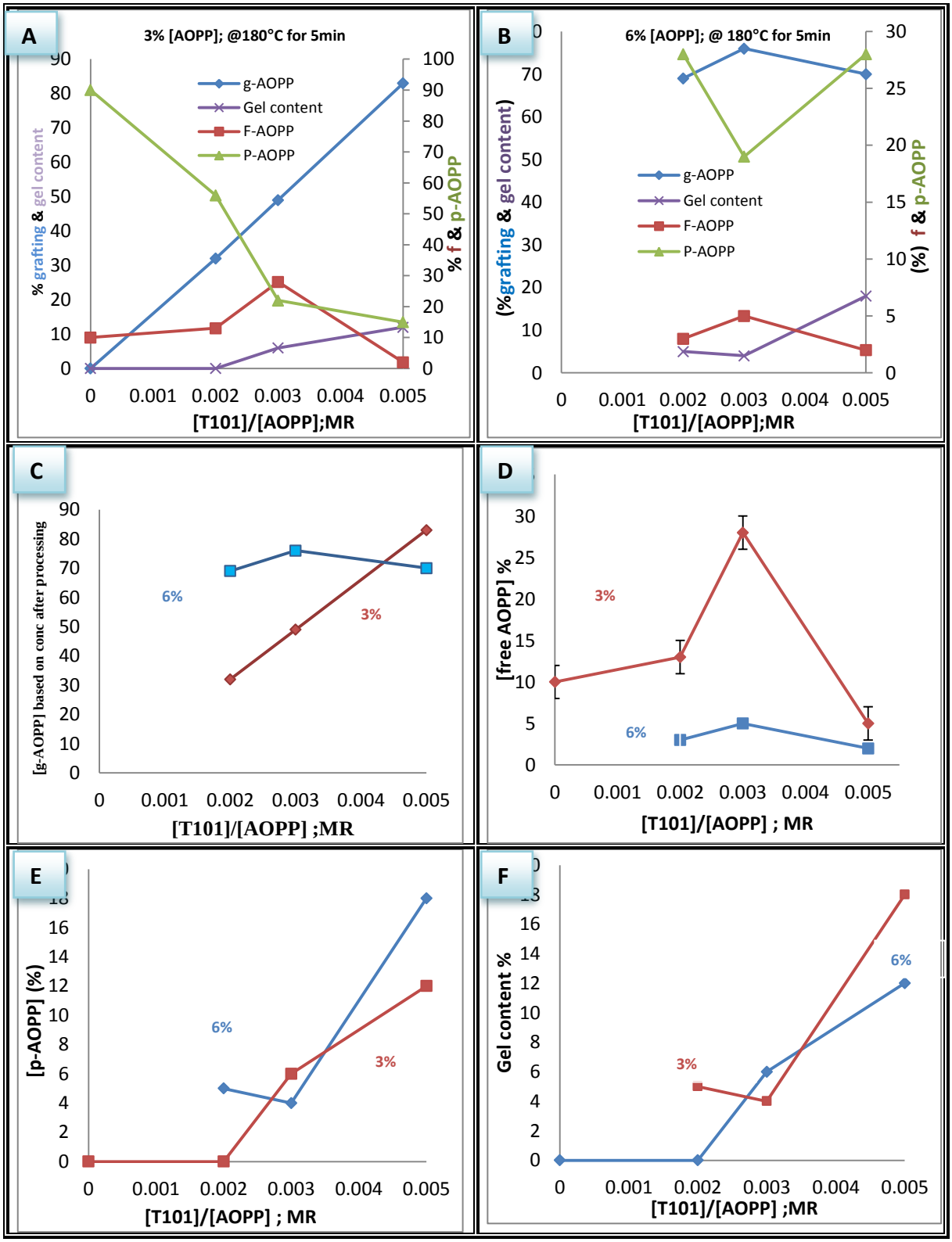


Figure 3. 11: Effect of [T101] concentration on **[g-AOPP] (from FTIR), [P-AOPP], [f-AOPP]** (from ^{1}H-NMR) & gel content, C-F is comparison of the processed polymer with **3% & 6% AOPP (180°C; 5min)**, see also **Table 3.1**.

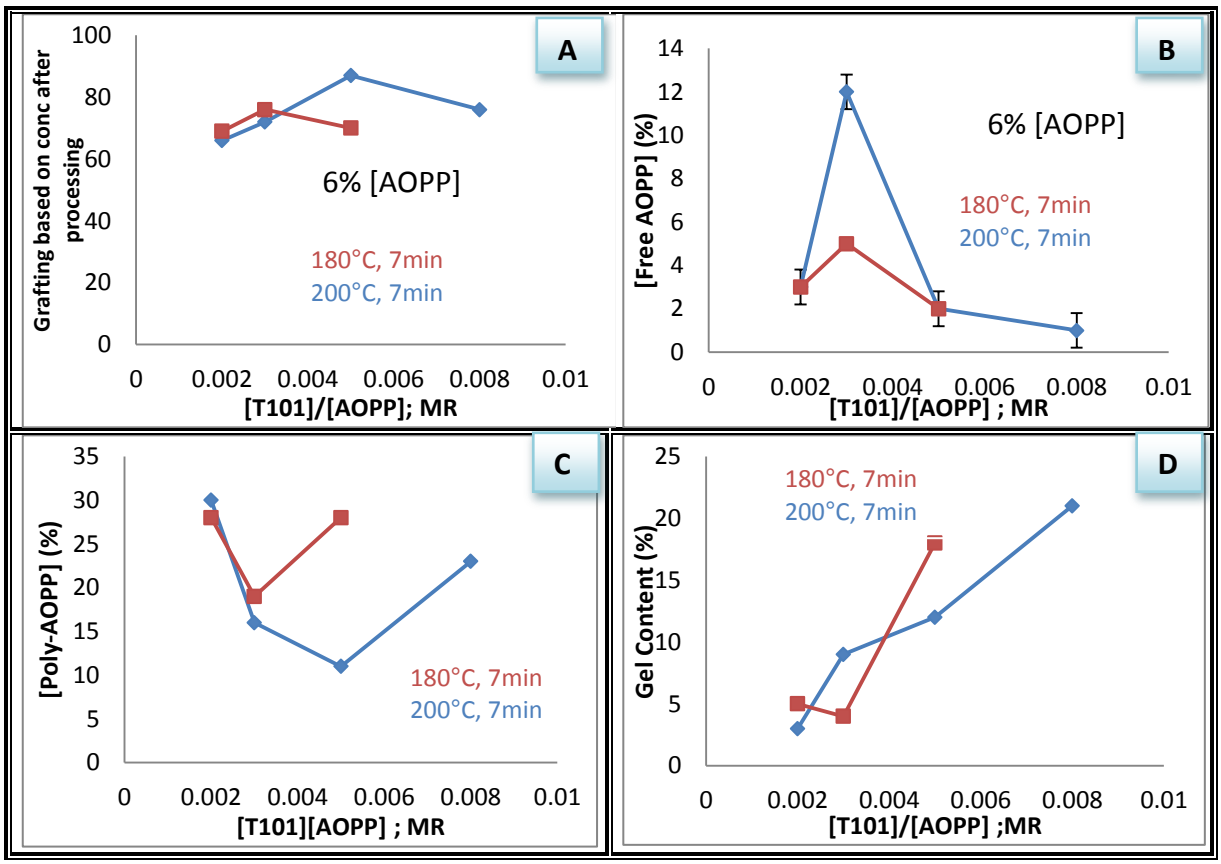


Figure 3. 12 : Effect of [T101] concentration on **[g-AOPP], [p-AOPP], [f-AOPP] and gel content**, in presence of **6% AOPP** in PE processed at **180°C and 200°C**.

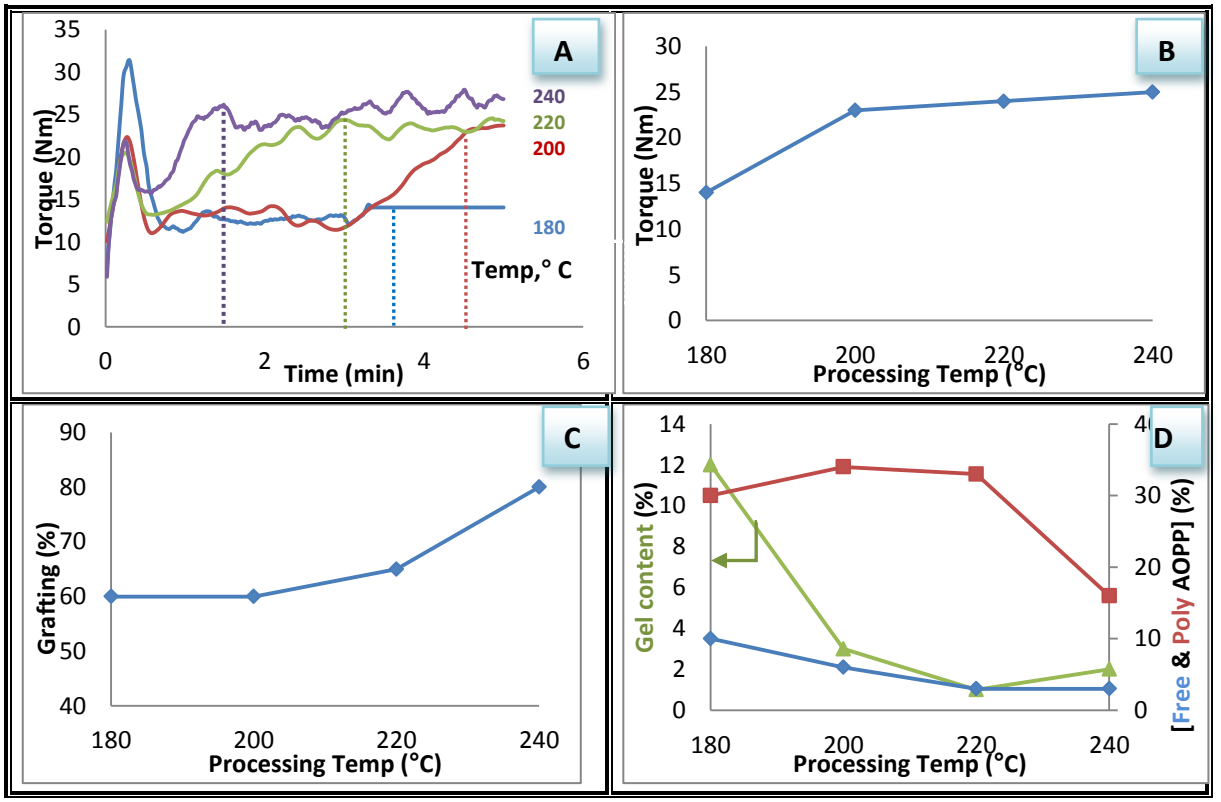


Figure 3. 13: Effect of **processing temperature** on grafting efficiency of 3**% [AOPP]** in PE in presence of constant **0.005 MR [T101]/[AOPP]**

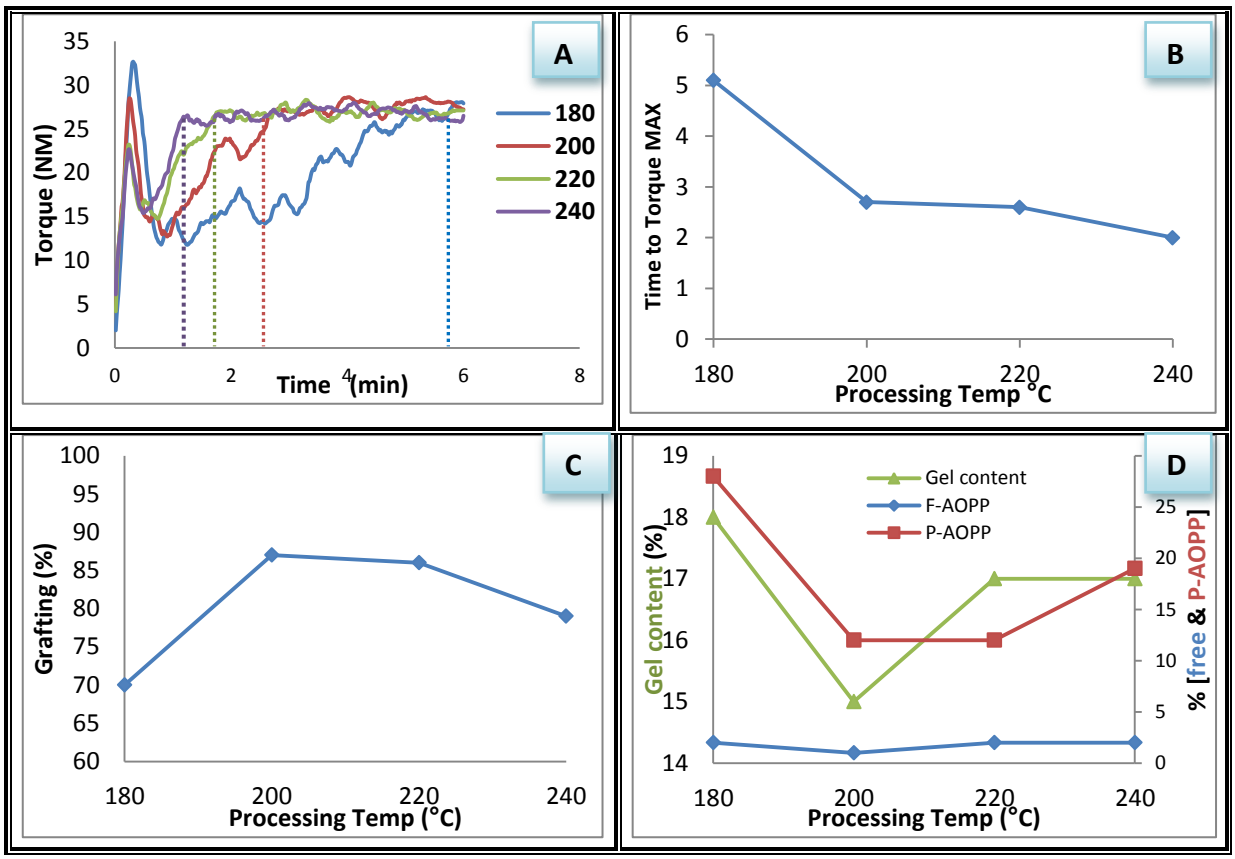


Figure 3. 14: Effect of processing temperature on grafting efficiency of **6% AOPP** in PE in presence of constant **0.005 MR[T101]/[AOPP]**

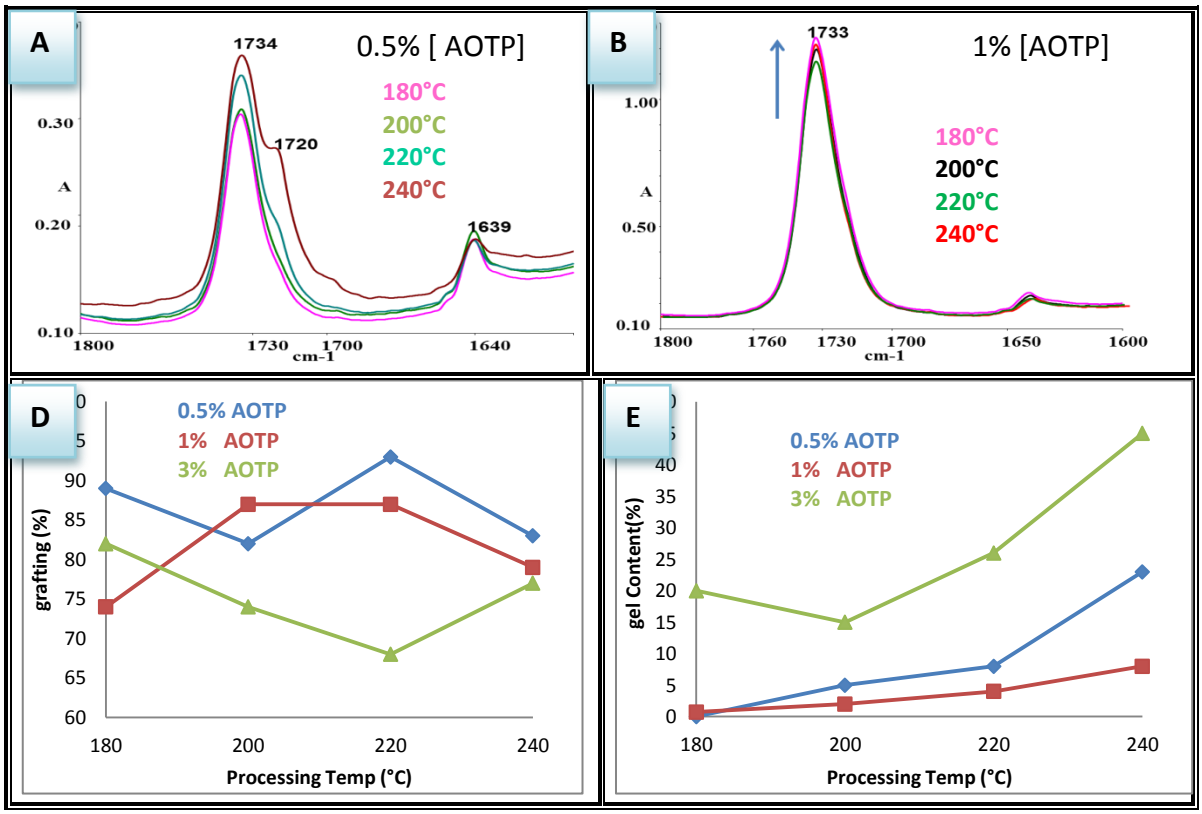


Figure 3. 15 : Effect of processing Temperature on grafting of **AOTP** on HDPE **(5min; 0.5%, 1% & 3% [AOTP]**at **0.005MR [T101]/[AOTP]).**

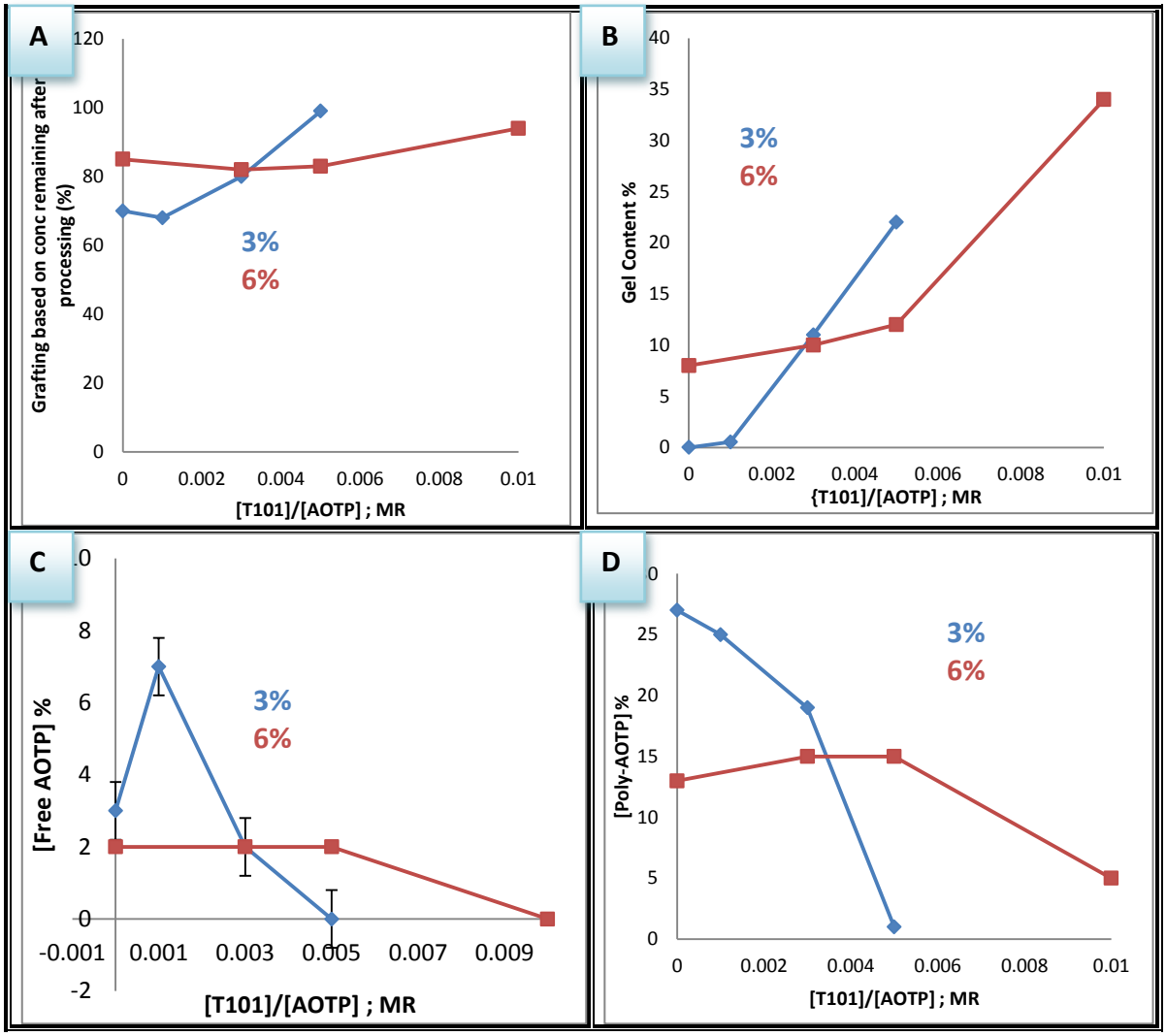


Figure 3. 16 : Effect of [T101] concentration on grafting and side reaction products of **AOTP** in PE (**180°C; 5min; 3% or 6% [AOTP]).**

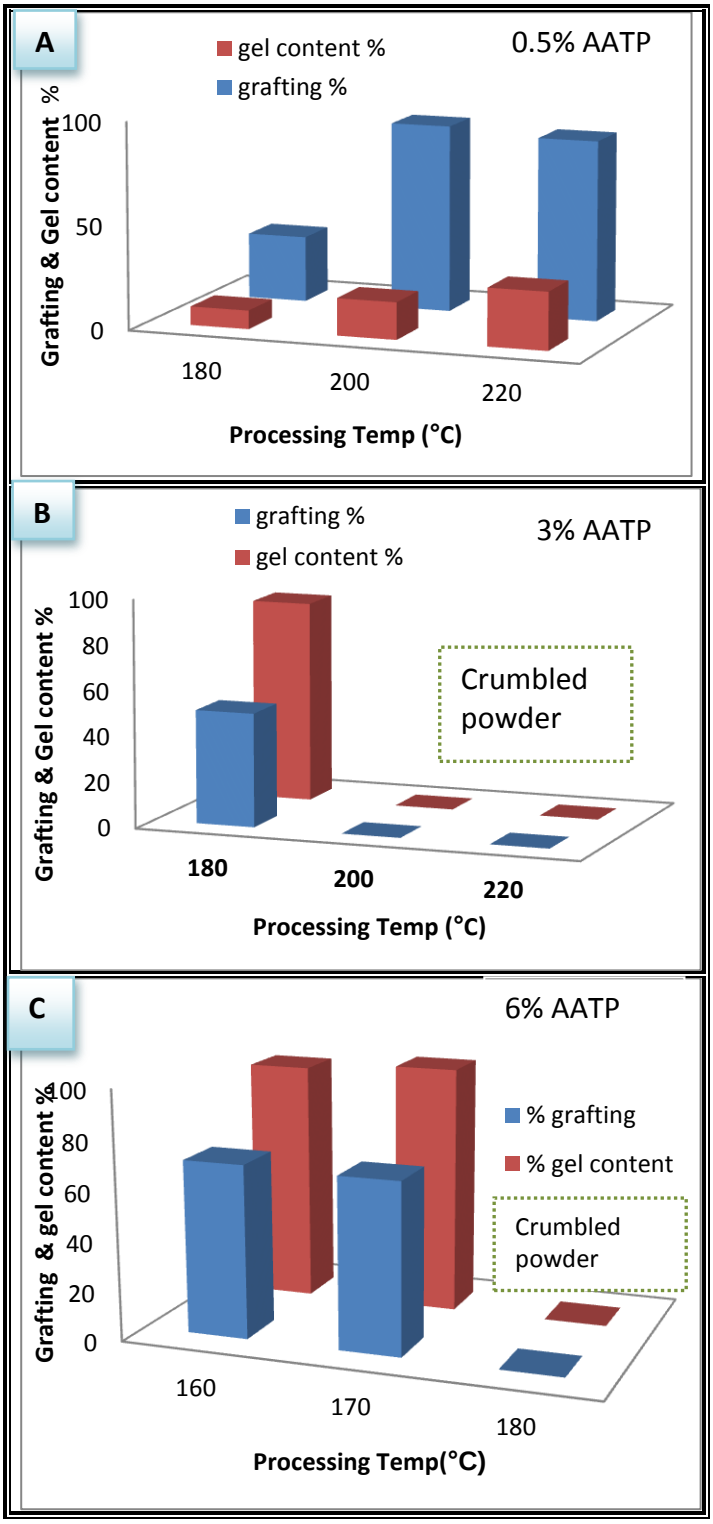


Figure 3. 17: Effect of processing temperature on grafting of **AATP** on HDPE **(5min; 0.5%, 3%, 6% [AATP])** & **[T101]/[AATP] molar ratio of 0.005.**

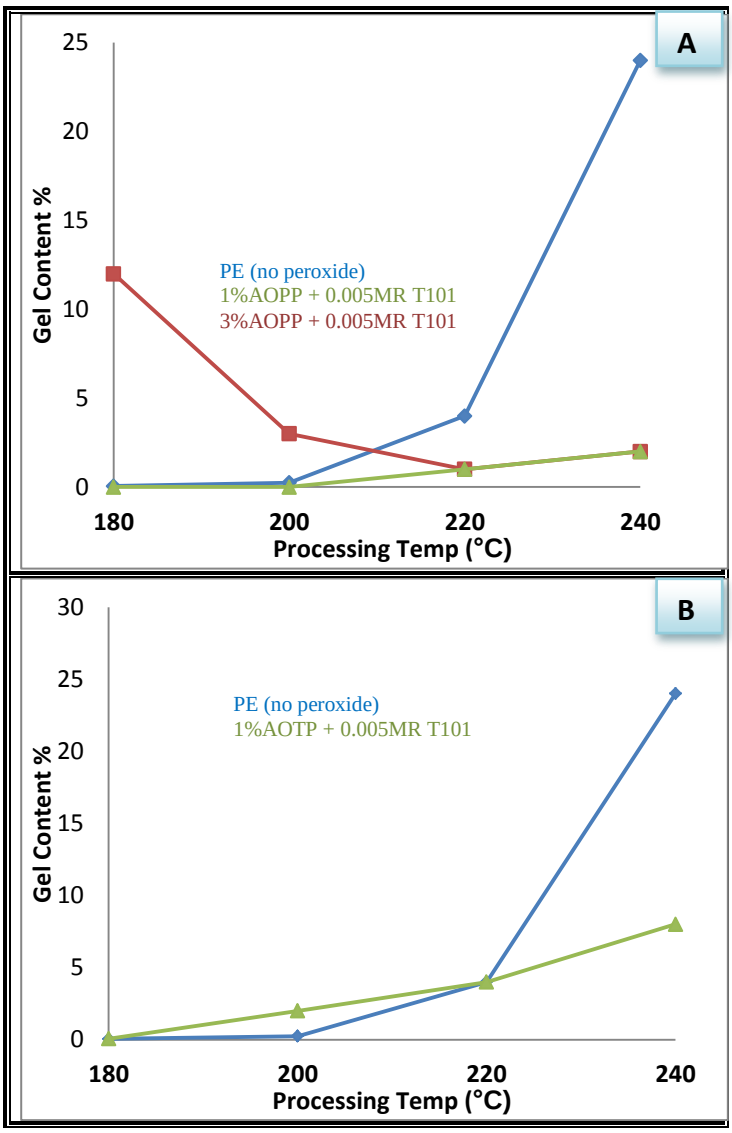


Figure 3. 18 : Effect of peroxide on PE gel formation at various processing temperature in the presence of **(A)** 1% & 3%AOPP and **(B)** 1% AOTP

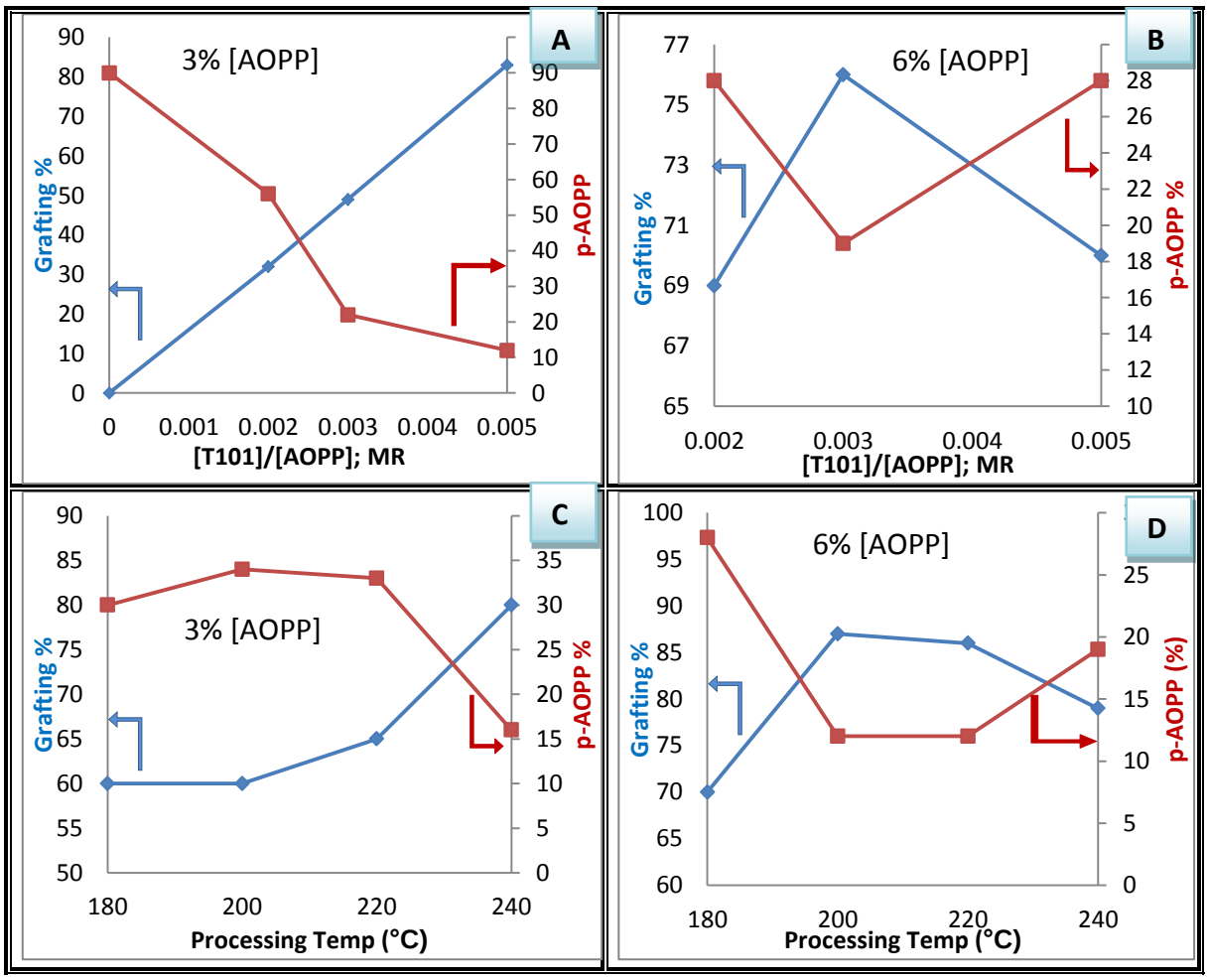


Figure 3. 19: Effect of varying Peroxide concentration at f**ixed processing temp of 180°C (A& B)** and effect of **varying processing temperature** at **Fixed peroxide concentration of 0.005MR** during processing of **3% and 6% AOPP**, on PE.

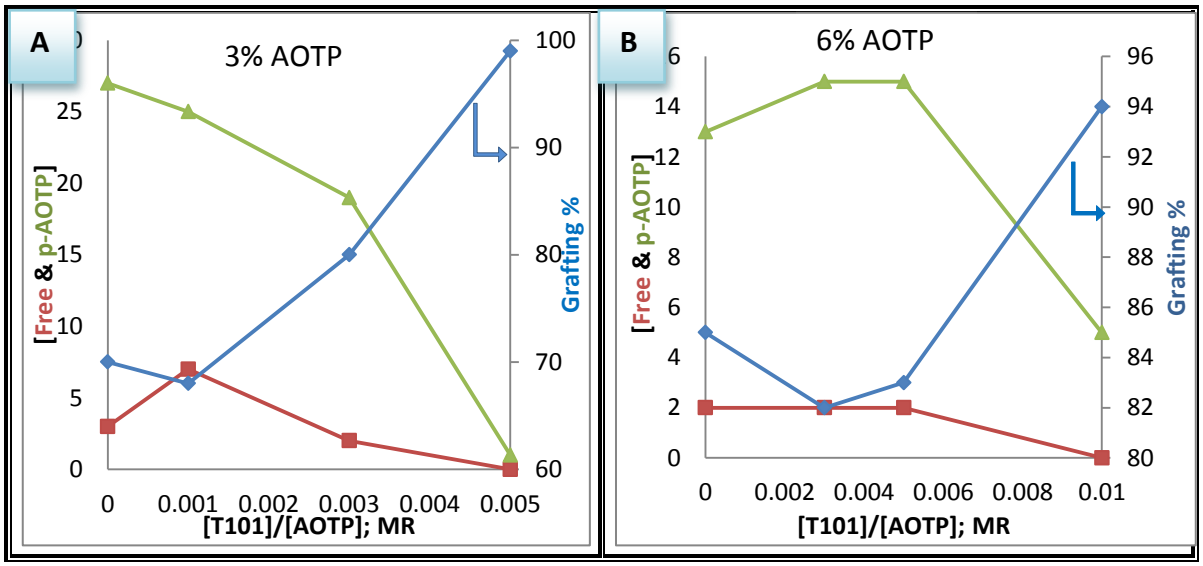


Figure 3. 20 : Effect of varying peroxide concentration at fixed **processing temperature at 180°C A &B** during processing of **3% and 6% AOTP**, on PE

Chapter 4

Stabilisation of Peroxide Crosslinked Polyethylene (PEX_a) with graftable Antioxidants

4.1 Objectives and Methodology

The main objective of the work described in this chapter was to develop an effective methodology to produce stabilised peroxide crosslinked polyethylene pipes (PEXa) using synthesised (graftable) reactive antioxidants (g-AOs), AOPP, AOTP and DBPA, (**see Table 4.1)** for structures) in order to avoid, or minimise, the loss of the AO's when in contact with extractive liquid media, e.g. potable water and solvents. This approach would overcome the expected losses of "mobile" (non-graftable) commercial AO's typically used in PEXa pipes (hindered phenols and amines). The PEXa pipes produced here were stabilised with the synthesised graftable hindered amine stabilisers used in combination with either a graftable hindered phenol (DBPA) or a conventional hindered phenol. One of three different peroxides, Trigonox B, T101 and T145, was used as the crosslinking agent.

Both PEXa pipes produced under commercial conditions, and "similarly" stabilised crosslinked samples produced in the laboratory were investigated. To produce the laboratory samples, (referred to as g-PEX, see **Table 4.2** for nomenclature) the crosslinking process was achieved using either of the peroxides TB or T101 or T145 (**see Table 4.1**) by compression moulding at 240°C for two minutes without pressure and for further 5 minutes with full pressure of 22Kg/cm^2 as described in **Section 2.4.2 i.** This process was developed in the laboratory to simulate the level of crosslinking achieved in the commercial Engel process. Lab-PEX samples were produced by one of two ways, the first was a **two-step** process, see **scheme 4.1** that involved the use of either PE-g-AO (with 0.5% AO) or an AO-masterbatch 1-6% (PE-g-AO$_{MB}$) diluted down with fresh unstablised PE (PE-g-AO$_{DMB}$) in the presence of the crosslinking peroxide TB and any other AO used. This PE-g-AO$_{DMB}$ or PE-g-AO (normal concentration of 0.5%) was then melt homogenised to mix the crosslinking peroxide and any added AOs at low temperatures of 140-150°C in a Thermo Haake Rheomix torque Rheometer. The samples were subsequently crosslinked in a second step by compression moulding to produce thin films, **see Section 2.4.2 ii, and Scheme 4.1.** Another methodology was based on a **one-step** process of crosslinking and grafting**,** i.e., the grafting and crosslinking steps were both achieved simultaneously by using compression moulding, see **Scheme 4.2**.

In addition to the lab-PEX samples (**one-step** and **two-step**), two pipe production methods were also used to produce pipes in a commercial production process. The PEXa pipe production was carried out at Uponor production plant in Virsbo, Sweden, using their commercial **Engel process** and also **High Speed Extrusion Infrared** process. The Engel process was used to produce peroxide crosslinked (PEX$_{Eng}$) pipes containing graftable

antioxidants alone and/or in combination with a conventional antioxidant. The polymer for these pipes was high density polyethylene powder-**Lupolen 5261 ZQ 456 (PE_L, MFI of 2g/10min)** containing no stabiliser (Basel). The peroxide used for the crosslinking was either TB or T145 or T101. The Engel extrusion conditions were set for a regular commercial pipe production giving 16/2-16 mm outer diameter and 2 mm wall thickness (see **Scheme 4.3** and **4.4** for the pipe production and sample preparation). A Second set of pipes was manufactured also in Virsbo, Sweden, using Uponor's commercial **High Speed Extrusion Infrared process** (PEX_{HS}). The peroxide T145-E85 was used as the crosslinking agent in this case and the polymer used was **BorPex HE1878E** (PE_B powder, MFI of 21.5kg/10min), stabilised (for transport and storage) with 700 ppm Irganox 1076. The PEX_{HS} pipes produced had the following dimension (20 mm outer diameter and 2 mm wall thickness), See **Scheme 4.5 for** their production using the method described **in sec 2.4.3.2 and scheme 4.6** for sample preparation.

The stabilised PEX_{Eng} and PEX_{HS} samples were subsequently analysed for the extent of crosslinking (using ASTM 2765 method) by Soxhlet extraction in xylene **(see Scheme 3.2 and Sec 2.6.4)**. FTIR was used to analyse the antioxidant concentration and DSC to measure the polymer crystallinity and the oxidation induction time (OIT) according to **ASTM D3895** method. Performance testing was also carried out using DSC-OIT for crosslinked samples before and after DCM, water, and xylene extractions. In order to examine the extent of antioxidant retention in pipe samples (PEX_{Eng}), films from different sections of every pipe produced by the **Engel process** (**see Scheme 4.4**) were extracted in DCM and with oxygenated deionised water. During the water extraction, water was continuously saturated with bubbling oxygen at the rate of 100ml /min, whereas DCM extraction was carried out for 48hr but oxygen was not used in this system (**See Scheme 4.4).** After these extractions, films were dried and an FTIR analysis and OIT measurements were carried out at least three times repeats for each sample. Thermal aging test was carried out using Wallace air-circulating oven at 125°C for pipe sample. Coefficient of variation was calculated as described in **Sec 2.6.2**.

Sequential solvent extraction using Accelerated Solvent Extraction process (ASE) with DCM (ASE-DCM) followed by xylene reflux extraction (xylene completely dissolves PE) was used in order to analyse the extent of antioxidant retention in the PEX_{HS} pipes **(see Scheme 4.7).** Accelerated solvent extraction (ASE) was also used to extract microtomed pipe films using deionised water in the absence of oxygen to determine the extent of antioxidant retention in pipes after water extraction and the water extract was also analysed using HPLC-MS, **see**

scheme 4.8 and Sec 2.7.7 for methodology. DCM was also used as a solvent in accelerated solvent extraction process to analyse the antioxidant retention in the PEX_{HS} pipes and to remove any free (unreacted) and polymerised antioxidant that are completely soluble in DCM, the DCM extracts were subsequently analysed by HPLC-MS **(see Scheme 4.8).**

The ultimate objective of this work was therefore to have pipe formulations containing graftable antioxidants that give rise to minimum losses when in contact with extractive media, mainly potable water or solvents. HPLC-MS analysis methods were developed in order to identify compounds found in the extracted media, i.e. in water or DCM, and to analyse the extents for antioxidant retention in the pipes after exhaustive solvent extractions. **Table 4.5 and 4.6** show the formulations of all pipes produced and some of their characteristics. **Table 4.1** gives the structures of the antioxidants & the peroxide used in the formulations.

Table 4. 1: structure and some characteristics of AOs and peroxide

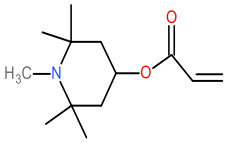
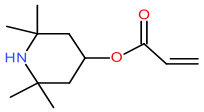
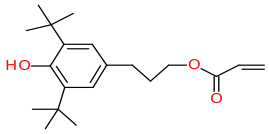
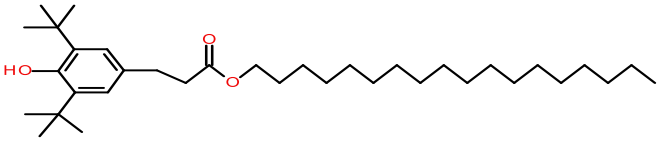
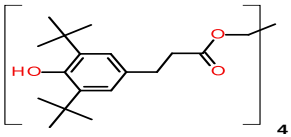
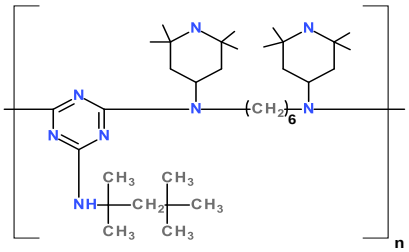
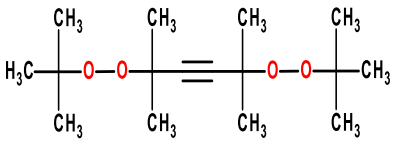
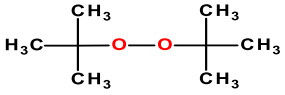
Antioxidant	Structure & Chemical Name	Mass g/mol	UV λmax =nm
AOPP	 4-acryloylloxy 1,2,2,6,6-pentamethyl piperidine	$C_{13}H_{23}NO_2$ **225**	**205**
AOTP	 4-acryloyloxy 2,2,6,6-tetramethyl piperdine	$C_{12}H_{21}NO_2$ **211**	**205**
DBPA	 3-(3,5-tert-butyl-4-hydroxy phenyl)propyl-1-acrylate	$C_{20}H_{30}O_3$ **318**	278
Irganox 1076	 octadecyl-3,5-di-tert-butyl-4hydroxyhydrocinnamate	$C_{35}H_{62}O_3$ **531**	**282**
Irganox 1010	 Pentaerythritol-tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)	$C_{73}H_{108}O_{12}$ **1178**	**278**
Chimasorb 944	 Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]	$(C_{35}H_{66}N_8)n$ **2000-3100**	
T145-E85	 2,5-Dimethyl-2,5-di (tert-butylperoxy)hexane	$C_{16}H_{30}O_4$ **286**	-
TB	 2-tert-butylperoxy-2-methyl-propane	$C_8H_{18}O_2$ **146**	

Table 4. 2 : Explanation codes and numbering for samples described in this chapter

Code	Explanation
CA	Conventional Antioxidant
PE_L	HDPE: Lupolen 5261-Unstablised powder and MFI =2g/10min
PE_B	HDPE: BorPEx1878E- stabilised powder with 700ppm Irganox 1076 & MFI=10g/10min
g1-PEX	One-step crosslinked samples containing g-AO's at 0.5%
g2-PEX	Two-step crosslinked sample containing g-AO's
g_{2DMB}-PEX	Two-step crosslinked sample with g-AO diluted from master batch
PEXa	Peroxide crosslinked PE
PEX-$_{Eng}$	Crosslinked pipe produced by Engel Process
PEX-$_{HS}$	Crosslinked pipe produced by High Speed Extrusion Infrared Process

Table 4. 3: Composition and processing conditions used in **two-step grafting** and **crosslinking** lab-produced PE_L samples, containing g-HAS with commercial Hindered phenols and with g-DBPA, see **Scheme 4.1.**

MB CODE See scheme 3.1	Composition and processing conditions							Crosslinking		Analysis			
	MB (3%) or g-AO 'Normal' conc (0.5%) Grafting peroxide T101					DMB or g-AO, Normal (0.5% actual g-AO conc.)		g_2-PEX		g_{2DMB}-PEX			
	[T101] /[HAS] MR	[HAS] %	Temp (°C)	Other AO's (%)	Grafting level (%) #	Code Grafted samples	Additional AO (%) Remarks	CODE ## XL samples	TB %	OIT CV (%) †	* OIT, min After XL	*OIT, min After DCM extraction	extent of XL%
PE-g-AOPP- 3	0	3	180	-	0	PE-g-AOPP- 3	None	**g_{2DMB}-PEX-3**	0.5				86
				-		PE-g-AOPP- 3	Irganox 1076 (0.5%)	**g_{2DMB}-PEX-3CA**	0.5				70
PE-g-AOPP -1	0.005	3	180	-	83	PE-g-AOPP -1	None	**g_{2DMB} -PEX-1**	0.5				84
				-		PE-g-AOPP -1	Irganox 1076 (0.5%)	**g_{2DMB} -PEX-1CA**	0.5				75
				-			Irganox 1010 (0.5%)						
PE-g-AOPP-8	0.003	3	180	-		PE-g-AOPP -2	None	**g_{2DMB} -PEX-8**	0.5		5	5	79
				-		PE-g-AOPP -2	Irganox 1076 (0.5%)	**g_{2DMB} -PEX-8CA**	0.5	53*	78	22	70
				-			Irganox 1010 (0.5%)						
PE-g-AOPP-4	0.01	3	180	-	91	PE-g-AOPP -4	None	**g_{2DMB} -PEX-4**	0.5		8	5	84
				-		PE-g-AOPP -4	Irganox 1076 (0.5%)	**g_{2DMB} -PEX-4CA**	0.5	78*	180	25	75
PE-g-DBPA-21	0.04		180	(3%) DBPA				**g_{2DMB} -PEX-21**	0.5				
PE-g-AOPP -500	0	0.5	240	0.5 DBPA	-			**g2-PEX-500**	0.5		34	34	82
PE-g-AOPP -501	0.02	0.5	240	0.5 DBPA	-			**g2-PEX-501**	0.5		71	69	79
PE-g-AOPP -502	0.04	0.5	240	0.5 DBPA	-			**g2-PEX-502**	0.5		80	80	84
PE-g-AOPP -600	0	0.5	**240**	0.5 DBPA	-			**g2-PEX-600**	0.5		-	-	86
PE-g-AOPP -601	0.02	0.5	**240**	0.5 DBPA	-			**g2-PEX-601**	0.5		54	45	88
PE-g-AOPP -602	0.04	0.5	**240**	0.5 DBPA	-			**g2-PEX-602**	0.5		125	90	82
PE_L-DBPA-1	0.04	0.5	**180**			**PE_L-g-DBPA-1**		**g2-PEX_L-1**	0.5		55		

CA: conventional antioxidant 0.5% Irganox 1076
PEX: Crosslinked polyethylene
g : grafted
XL; crosslinked
CV: Coefficient of variation see section 2. for calculation
*results based on 8 samples tested for OIT
% grafting concentration calculation based on calibration curves and is based on initial concentration

Table 4. 4: Composition and processing conditions used in **One-Step** grafted and Crosslinked HDPE containing g-HAS with a commercial Hindered phenol and, with g-DBPA, see **Scheme 4.2.**

ONE STEP Code	Normal concentration for grafting/ composition			Processing conditions		Analysis								
	TB %	HAS % *	Other AO's	Temp (°C)	Time (min)	†CI Untreated based on FTIR [AO]++	CI after DCM extraction	CI Retention % after DCM	OIT Retention %	Untreated sample OIT average (min)	OIT CV (%)	OIT extracted in DCM for 48h (temp, 39°C) Average (min) See scheme 4.2 Sample B	Extent of XL % Sample C	% crystallinity Sample E
PE_L	0	0	0	N/A	N/A									68
g_1-PEX-711	0.5	0	0	240	2+5				-	-		-	89	43
g_1-PEX -705	0.5	0	0.5 Irg 1076	240	2+5	0.36 55%	0.1	28	16	85	13	14	74	43
g_1-PEX -708	0.5	0	0.5 Irg 1010	240	2+5	0.41	0.32	78	100	400	10	400	76	43
g_1-PEX -709	0.5	0.5 AOPP	0	240	2+5	0.87	0.82	94	38	16	9	6	83	43
g_1-PEX -710	0.5	0	0.5 DBPA	240	2+5	0.80 84%	0.56	70	63	82	4	52	80	44
g_1-PEX -714	0.5	0.5 AOTP	0	240	2+5	1.15	1.04	90	82	16	6	4	92	43
g_1-PEX -700	0.5	0.5 AOPP	0.5 Irg 1076	240	2+5	1.11	0.84	75	12	180	12	23	76	44
g_1-PEX -703	0.5	0.5 AOPP	0.5 Irg 1010	240	2+5	1.07	0.94	88	100	400	6	400	68	43
g_1-PEX -704	0.5	0.5 AOPP	0.5 DBPA	240	2+5	1.32	1.21	91	70	97	7	52	84	44
g_1-PEX -713	0.5	0.5 AOTP	0.5 DBPA	240	2+5	1.76	1.49	85	65	110	10	89	78	43
g_1-PEX -712	0.5	0.5 AOTP	0.5 Irg 1010	240	2+5	2.03	1.25	61	80	400	2	400	82	44
g_1-PEX -719	0.5	0.5 AOTP	0.5 Irg 1076	240	2+5	0.92	0.83	91	-	-	12	-	80	44

*: see **Table 4.1** for AO structures
#: average of at least 3 samples in some cases up to 8 samples
†CI is carbonyl index
++[AO] remaining after crosslinking based on initial concentration calculated using calibration curve

Table 4. 5: Engel-(PEX_{Eng}) Pipe Formulation with reactive antioxidants

PEX_{Eng} Pipe No #	Composition (see Table 4.1 for structure)		AO after XL % **	OIT (min)								XL Extent %	Cryst (%)	Wallace oven ageing at 125°C, days
				Untreated samples		Extracted in water; 48hr ~100°C			Extracted in DCM; 48hrs 39°C					
	AO's	Peroxide		† Mean	CV %	† Mean	CV %	OIT Retention %	† Mean	CV %	OIT Retention %			
PE_L	0	0											62	
PEX_{Eng} -1	0.5% Irg1076	0.4% TB	50	98	5	51	10	52	14	21	14	86	48	239
PEX_{Eng} -3	0.5% Irg1076	0.45% T145	55	50	16	41	10	82	7	14	13	84	46	285
PEX_{Eng} -26	0.5% Irg1076	0.4% T101		51	10				6	17	12	54	48	229
PEX_{Eng} -13	0.5% AOPP	0.4% TB												>350
PEX_{Eng} -5	0.5% DBPA	0.4% TB	80	33	41	18	28	55	23	47	71	95	42	208
PEX_{Eng} -6	0.5% DBPA	0.45% T145	85	60	32	44	23	73	10	10	17	86	47	188
PEX_{Eng} -16	0.5% DBPA	0.4% T101		29	29				30	41	100		44	229
PEX_{Eng} -19	0.5% AOPP + 0.5% Irg1076	0.45% T145	-	270	16	222	50	82	29	31	11	84	45	>350
PEX_{Eng} -20	0.5% AOPP + 0.5% Irg1076	0.4% TB	-	237	11	107	30	45	27	50	11	94	44	>350
PEX_{Eng} -21	0.5% AOPP + 0.5% Irg1076	0.4% T101	-	230	21	188	39	81	33	33	14	84	45	>350
PEX_{Eng} -22	0.5% AOTP + 0.5% Irg 1076	0.4% TB	-	275	12	205	26	75	43	20	16	93	43	>350
PEX_{Eng} -24	0.5% AOTP + 0.5% Irg 1076	0.45% T145	-	245	7	400	0	95	22	46	5	84	46	>350
PEX_{Eng} -25	0.5% AOTP + 0.5% Irg1076	0.4% T101	-	236	28	164	16	69	44	37	19	86	45	>350
PEX_{Eng} -7R	0.5% AOPP + 0.5% DBPA	0.4% TB	-	132	57	27	22	21	133	16	100	94	41	>500
PEX_{Eng} -8R	0.5% AOPP + 0.5% DBPA	0.45% T145	-	188	23	120	30	64	145	41	77	83	48	>500
PEX_{Eng} -17	0.5% AOPP + 0.5% DBPA	0.4% T101	-	209	15	89	24	42	168	15	80	89	44	>500
PEX_{Eng} -10R	0.5% AOTP + 0.5% DBPA	0.45% T145	-	162	16	67	27	41	126	18	78	85	46	>500
PEX_{Eng} -15	0.5% AOTP + 0.5% DBPA	0.4% TB	-	77	21	27	35	35	16	27	20	90	41	-

† Mean: is a result of at least three and up to 8 samples tested for each reading
CV : is calculated as described in Ch 2 sec 2.
Pipe dimension : ϕ16mm , 2 mm wall thickness
**AO remaining after crosslinking, calculation based on calibration curve.

Table 4. 6: Formulation using reactive antioxidants for **High Speed Extrusion Infrared (PEX_{HS})** Pipes based on HDPE (BorPex- HE1878E) with 0.5 % T145.

PEX_{HS} pipe no	**Composition of AO's** (see Table 4.1 for structures)	**T145**	**OIT min #**		**XL Extent %**	**Cryst (%) By DSC**	**Pipe dimensions mm**
			XL	**NXL**			
PE_B	Borpex HE1878E	0.5				68	**pipe:ϕ20 mm 2 mm wall thickness**
PEX_{HS}-X1	0.5% Irg 1076 +0.5% HAS	0.5	47	27	85	47	
PEX_{HS}-X2	DBPA (0.5%) + AOPP (0.5%)	0.5	261	37	85	45	
PEX_{HS}-X3	DBPA (0.3%) + AOPP (0.3%)	0.5	96	15	88	45	
PEX_{HS}-X4	DBPA (0.5%) + AOTP (0.5%)	0.5	133	24	88	42	
PEX_{HS}-X6	DBPA (0.5%) + Chim 944 (0.5%)	0.5	157	30	89	38	
PEX_{HS}-X7	AOPP (0.5%) + Irg 1076 (0.5%)	0.5	110	9	91	34	
PEX_{HS}-X8	AOTP (O.5%), Irg 1076 (0.5%)	0.5	38	5	86	45	
PEX_{HS}-X11	AOPP (0.5%) + Irg1010 (0.3%)	0.5	223	36	82	42	
PEX_{HS}-SNIK3	IRG 1076 (0.2%)	0.5	N/A		87	39	**pipe:ϕ20 mm 2 mm wall thickness**
PEX_{HS}-SNIK4	IRG 1010 (0.2%)	0.5			86	42	
PEX_{HS}-SNIK12	IRG 1035 (0.2%)	0.5			85	43	
PEX_{HS}-FET1	Irg 1076 (0.5%) +Tin 622(0.5%)	0.5			81	38	
PEX_{HS}-FET2	irg1076 (0.5%) + Chim 944 (0.5%)	0.5			81	45	
PEX_{HS}-FET4	Irg 1076 (0.5%) +Irg 1035 (0.5%) +Tin 622 (0.5%)	0.5			87	39	

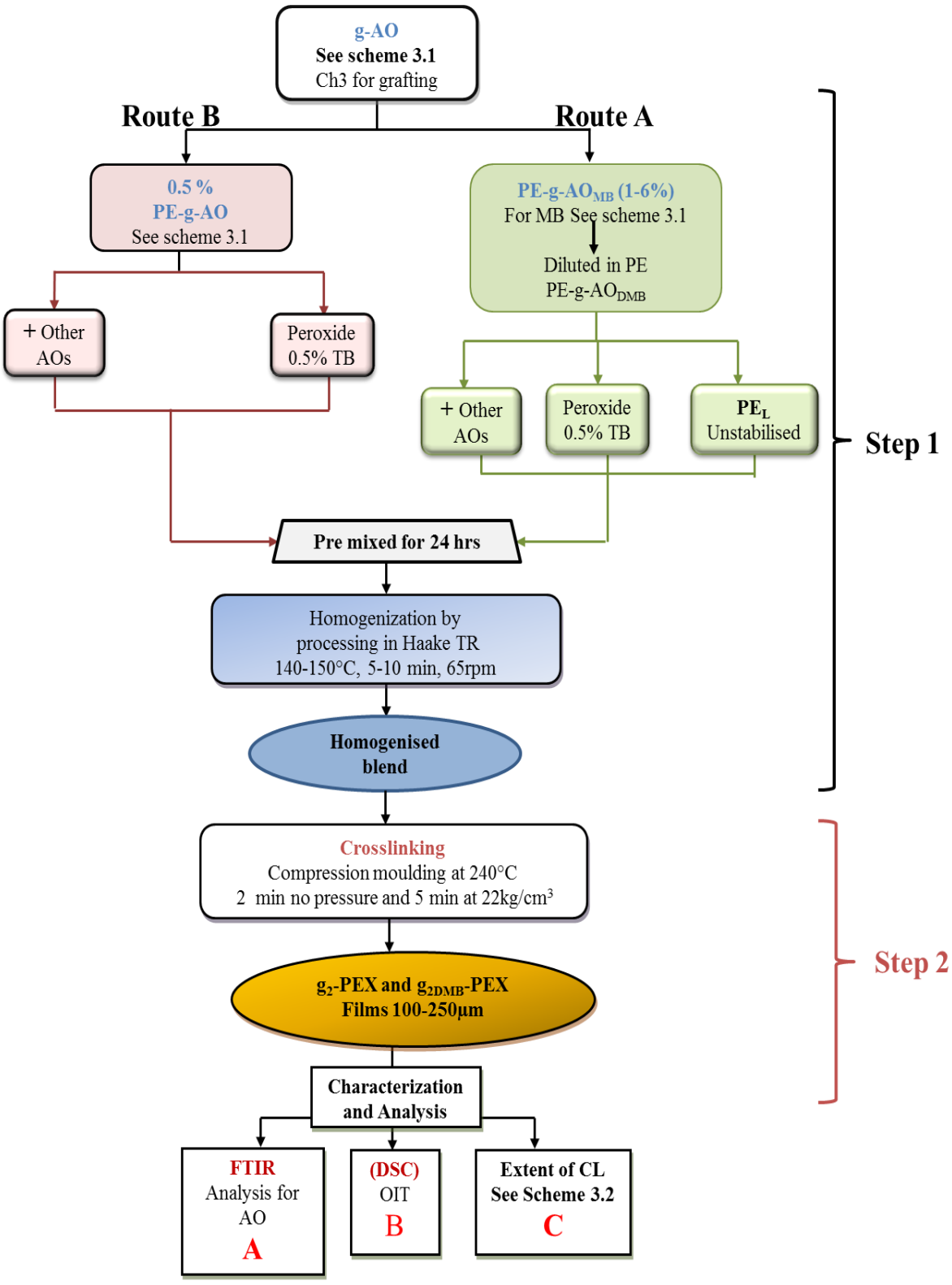
OIT results are average of triplicate or 9 samples

NXL is not crosslinked polymer, see **Scheme 4.7**

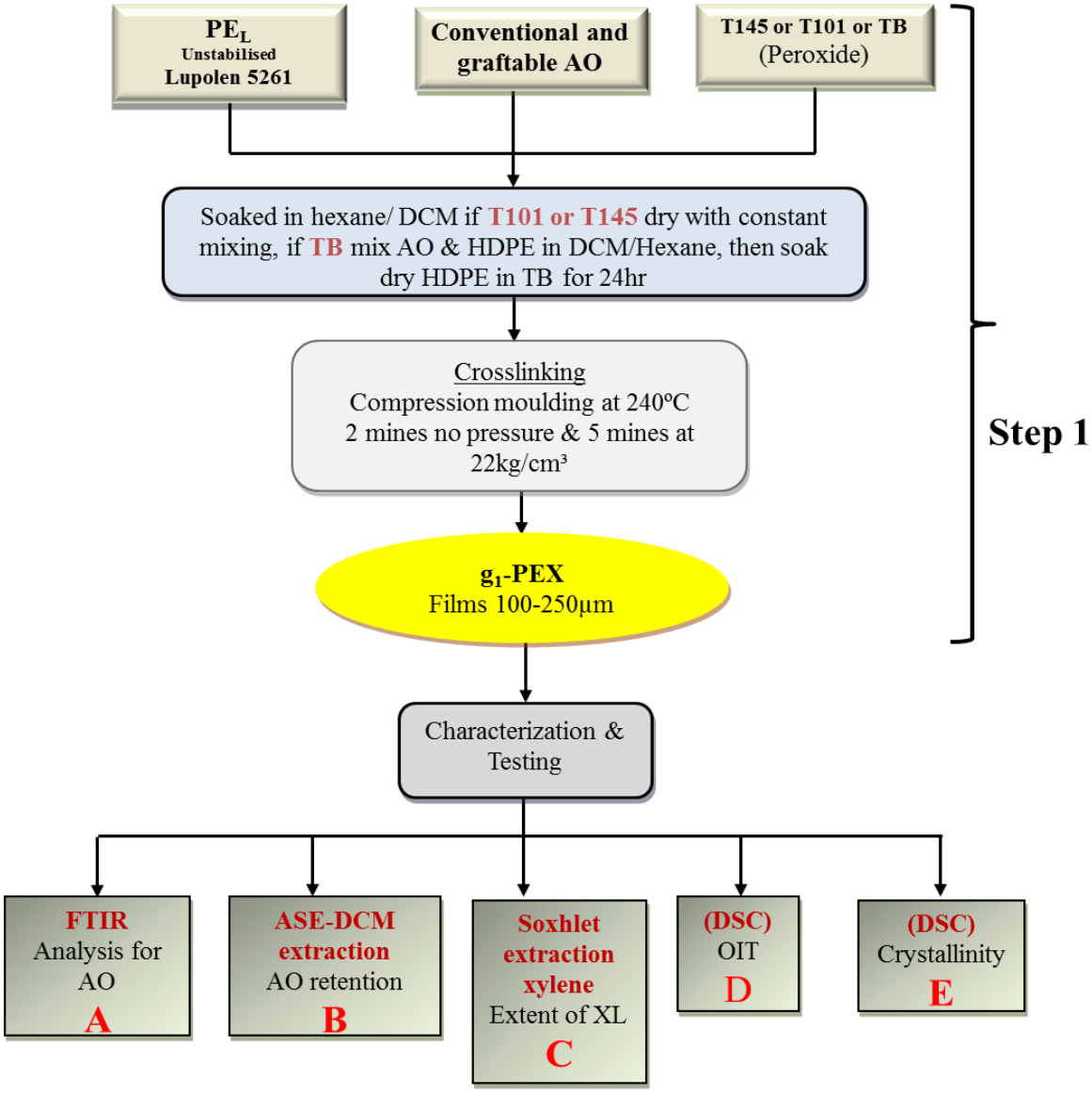
XL is crosslinked polymer, see **Scheme 4.7**

*In the text, code for these pipes will appear with their X number only (i.e X1, X2, X3….)

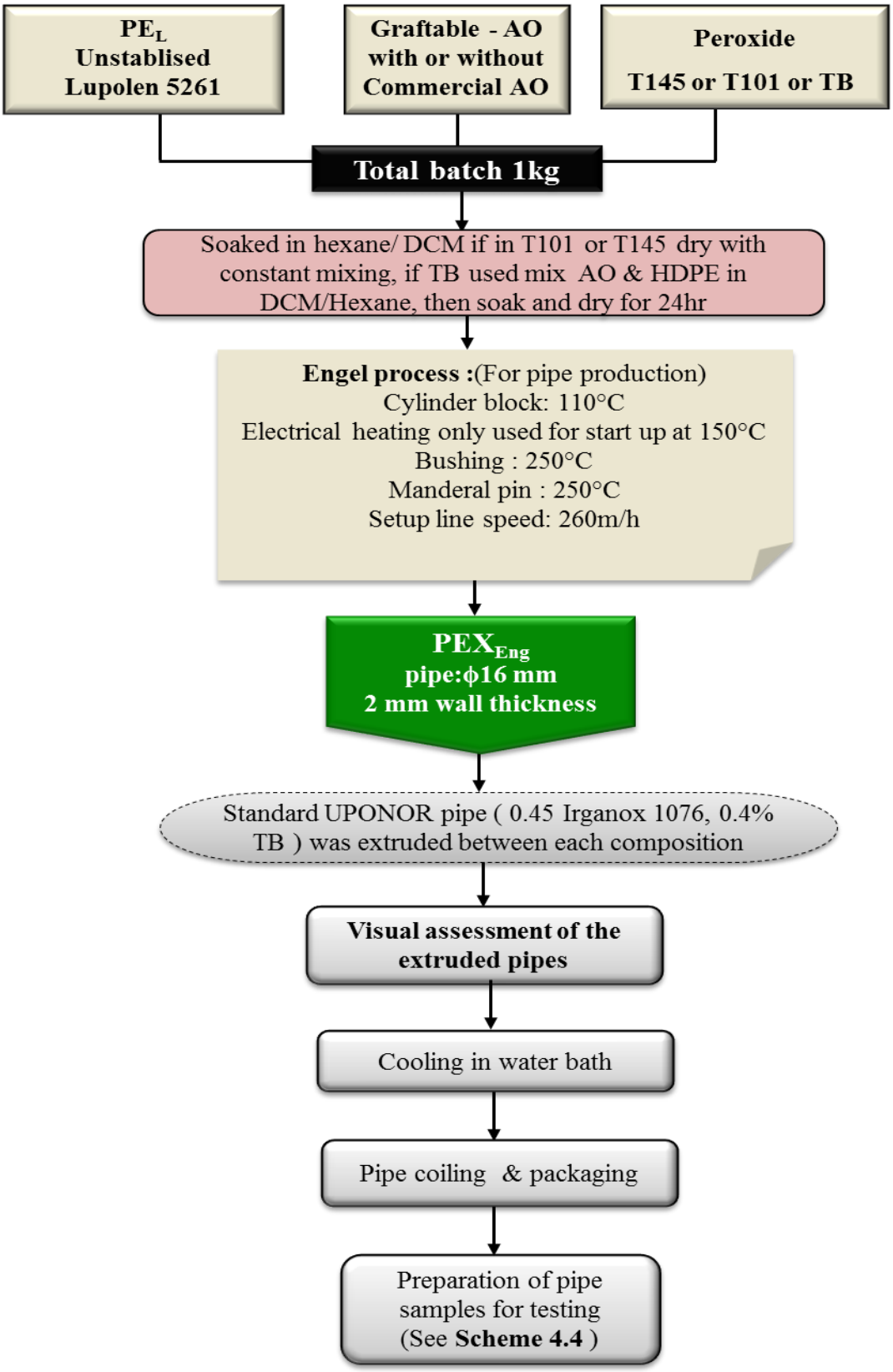
Scheme 4. 1: Methodology for **Two-step** grafting and crosslinking process



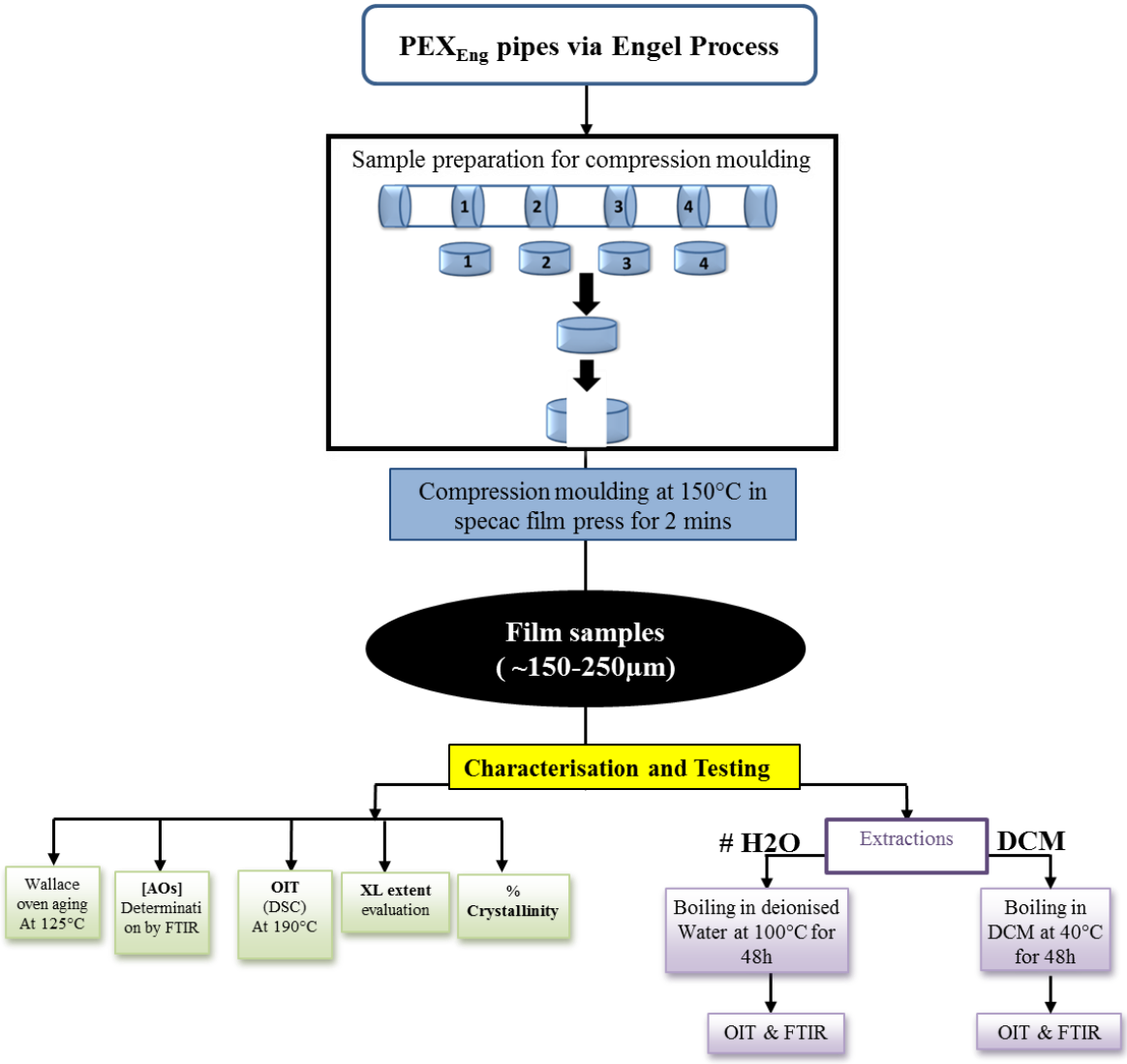
Scheme 4. 2: Methodology for **One Step** grafting and crosslinking process



Scheme 4. 3: Methodology for PEX_{Eng}- pipe production (using Engel process) carried out at Virsbo, Sweden

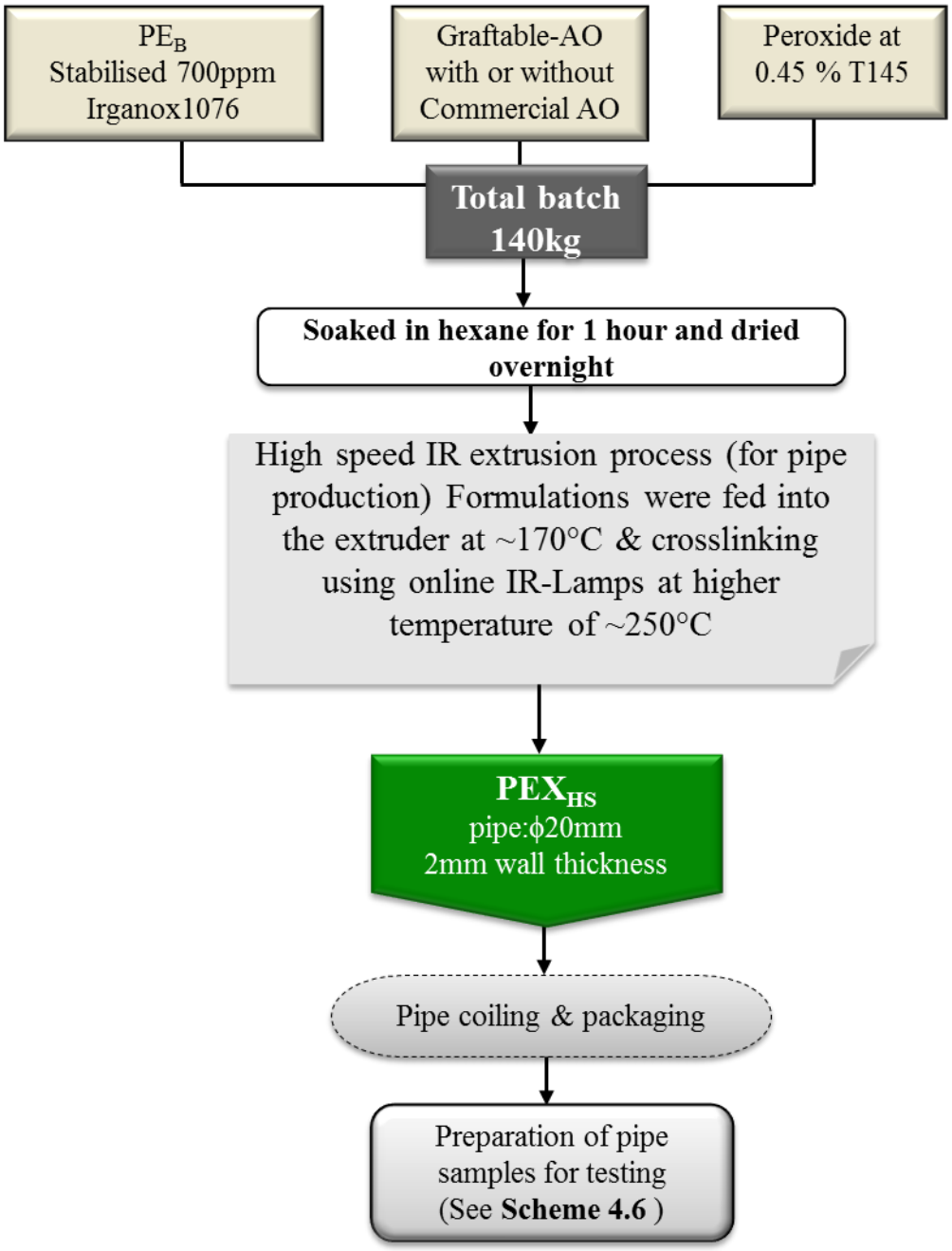


Scheme 4. 4 : Methodology of preparation of pipe samples (PEX_{Eng}) produced using Engel process for analysis

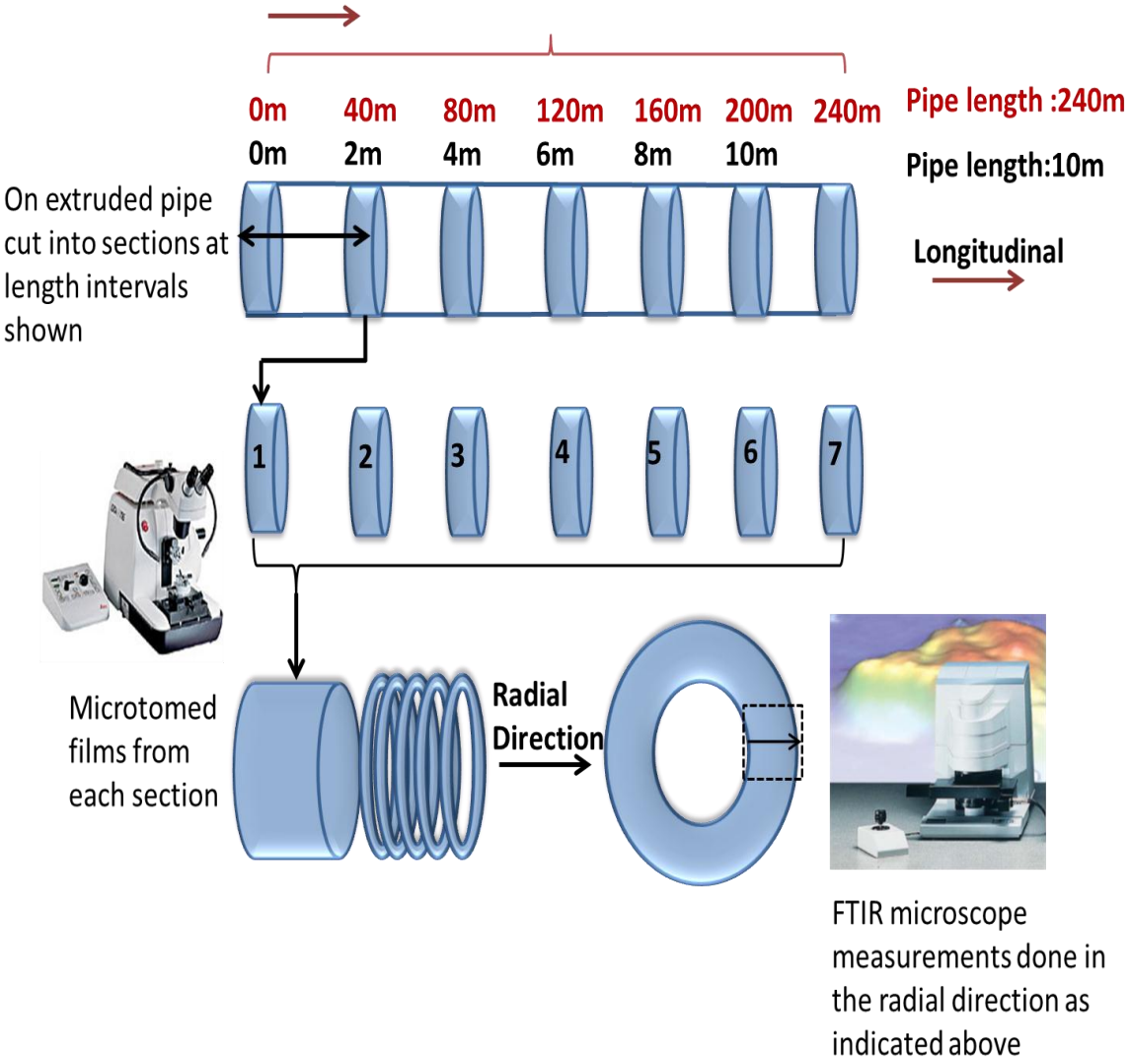


oxygenated and deionised water

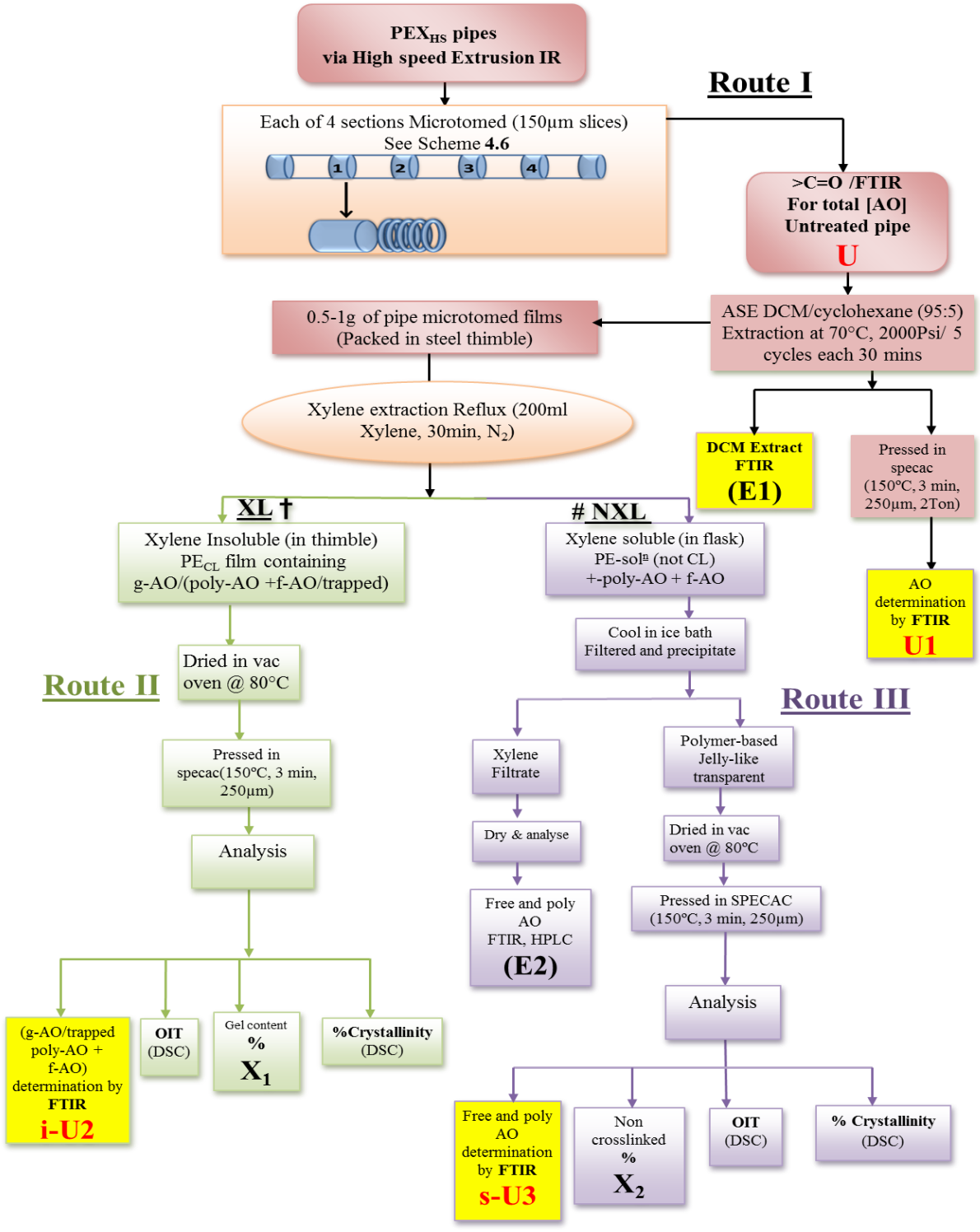
Scheme 4. 5: Methodology for PEX_{HS}-pipe process using **High speed Extrusion Infrared process** carried out at Virsbo, Sweden



Scheme 4. 6: Methodology used for Pipe Sampling **(PEX_{HS}),** (240 m & 10m length pipes) and FTIR-microscope Analysis of Samples, Produced using **High speed Extrusion Infrared process**

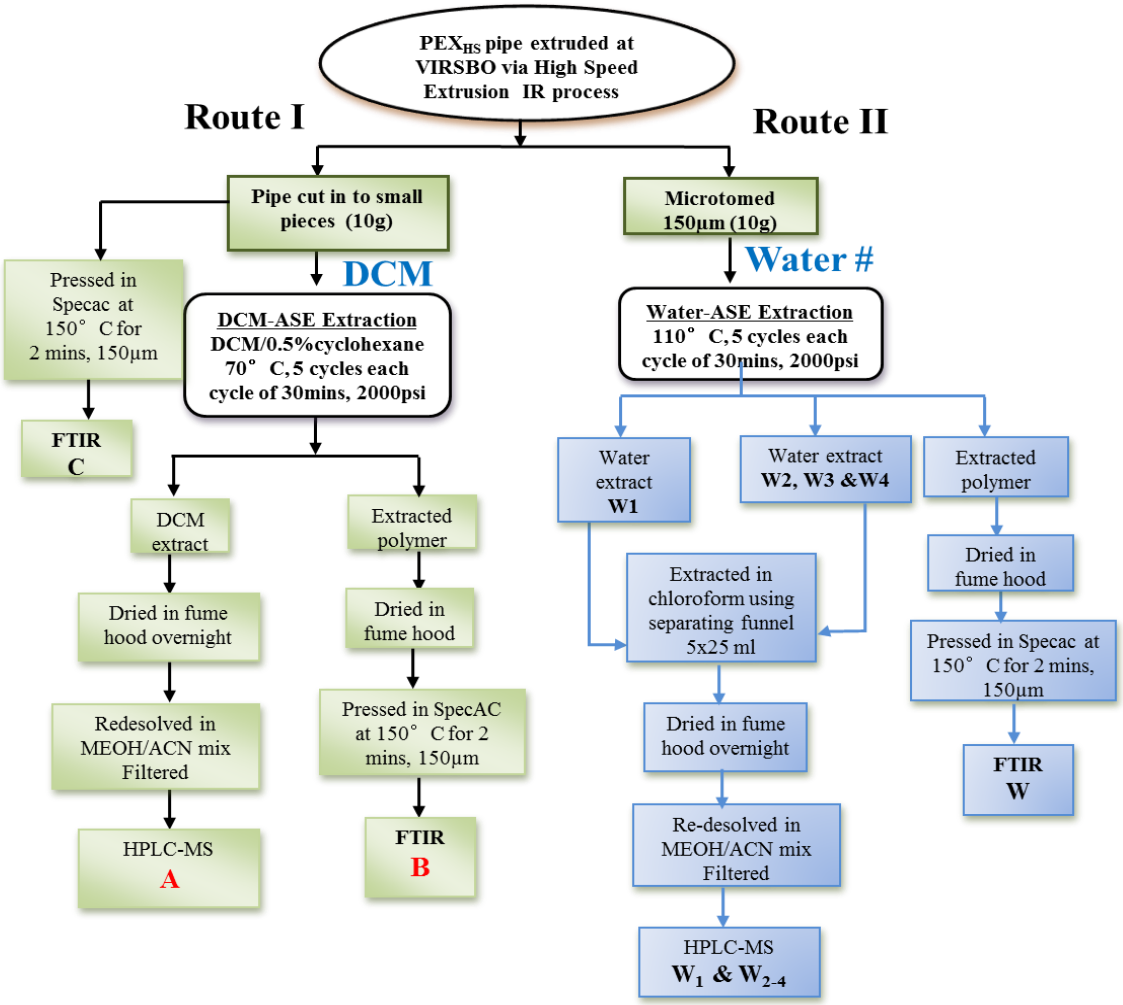


Scheme 4. 7: Sequential DCM-xylene solvent extraction: ASE-DCM(DCM: cyclohexane at 95:5 w/w) extraction (70°C, 2000psi, 5 cycle, cycle time 30 mins) followed by xylene extraction (Reflux) for **PEX_{HS} pipes**.



† XL : crosslinked, xylene insoluble fraction of polymer after DCM followed by xylene extraction
#NXL : not crosslinked, xylene soluble fraction after DCM followed by xylene extraction

Scheme 4. 8: ASE-DCM and water Extraction of **PEX_{HS}** pipes



deionised water in absence of oxygen

4.2 Results

4.2.1 PEXa Samples Stabilised with Graftable Antioxidants

(i) Crosslinking and Stability (by DSC-OIT) of Laboratory Based Samples Produced by Two-step Grafting and Crosslinking Process

In this process crosslinking of polyethylene (**PE_L**), containing graftable antioxidant (**g_2-PEX**) was either achieved by diluting AO-MB (master batches) containing 1-6% antioxidant concentration down to 0.5% concentration as described in **scheme 4.1, Route A** or directly by reactive processing the polymer using a normal AO concentration (0.5%) using the Haake Torque rheometer, in the presence of the peroxide TB, see **scheme 4.1, Route B**. These samples showed a high extent of crosslinking between 70% and 86%, see **Table 4.3 & Figure 4.1** and high level of thermal stability as determined by DSC-OIT, see **Table 4.3.**

(ii) Crosslinking and stability (DSC-OIT) of Laboratory Based Sample Produced by One-step grafting-crosslinking process

In this process the crosslinking and grafting were achieved in one step through compression moulding without the use of reactive processing step. A mixture of PE_L (Lupolen 5261Z Q456), with 0.5% antioxidant in the presence of TB were compression moulded at 240°C. Composition and analysis of the samples prepared under these conditions is given in **Table 4.4.** High level of crosslinking was achieved ranging between 68% and 92 %, **Figure 4.2 B and Table 4.4**, see also DSC-OIT results in **Table 4.4**.

4.2.2 PEX_{Eng} pipes Produced by Engel Process

(i) Analysis before any treatments

PEX_{Eng} pipes were produced using different peroxides and different antioxidant compositions, using the Engel process, see **Table 4.5 and Table 4.7.** Thin films were prepared from each pipe section as described in **Scheme 4.4**, in order to determine the extent of crosslinking, the crystallinity, the OIT, and/or the antioxidant concentration in the pipes. The percent crystallinity was also examined for the pipe-films using DSC. A high level of crosslinking was achieved ranging between 84% and 96% (**see Figure 4.3 A**). The highest level of crosslinking of >90% was found in pipes crosslinked with Trigonox B (TB). The crystallinity of the pipes was calculated using triplicate samples and it is shown to have decreased from 68% for PE_L powder (virgin untreated polymer) down to 43-48% in the crosslinked pipes (**see Figure 4.3B and Table 4.5).** Film samples of each pipe were also subjected to thermal aging in a Wallace air circulating oven with temperature maintained at 125°C. Pipes containing

Irganox 1076 (PEX_{ENG}-1, 3, 26) degraded after ~250 days, whereas all the other pipes containing a combination of Irganox 1076 with g-HAS antioxidants did not embrittle after 500 days where the test was stopped **(see Figure 4.4B).** OIT analysis, as a measure of the pipe thermal stability, was carried out on untreated pipe samples (not "purified") and showed higher stability in the pipes containing AOPP or AOTP in combination with Irganox 1076 (**see Figure 4.4A**)

(ii) Extraction of PEX_{Eng} pipes by Oxygenated water and strong organic solvent

In order to analyse the performance of PEX_{Eng} pipes in contact with extractive, two solvents were chosen, water in the presence of oxygen to simulate the end use environment, and dichloromethane (DCM) that extracts all the reactive AO-homopolymer which may be produced during the processing of the samples, **See scheme 4.4**.

Figure 4.5 shows the OIT retention after extraction in oxygenated water of PEX_{Eng} crosslinked with three different peroxides. A higher OIT retention was observed in pipes containing the conventional hindered phenol AO Irganox 1076 compared with pipes containing the g-hindered phenol (DBPA) antioxidant. Furthermore, it was shown that pipes extracted in oxygenated water gave generally much higher OIT values than when they were extracted in DCM for 48 hr **(see Figure 4.5 and 4.6).** Generally, DCM extraction (see **Figure 4.6**A) gave rise to higher OIT for pipes containing g-DBPA only (**PEX_{Eng} - 5,6 and16**) compared to pipes containing the conventional hindered phenol Irganox 1076 **PEX_{Eng} 1,3 and 26** , **Figure 4.6B** also shows that pipes containing two g-AOs (g-hindered phenol and g-HAS), generally gave higher thermal stability (OIT retention) compared to those containing a g-HAS with Irganox 1076. It is also clear from the carbonyl index of the AO (**Figure 4.6 B**) that DCM extracted PEX_{Eng} pipes containing g-HAS in combination with Irganox 1076 gave rise to a lower AO retention than when g-DBPA was used (with the g-HAS) due to the mobility and ease of the extraction of Irganox 1076.

4.2.3 PEXa pipes produced by High Speed Infrared Extrusion Process (PEX_{HS})

4.2.3.1 Antioxidant Concentration profiles in PEX_{HS} Pipes

A number of PEX_{HS} pipes were manufactured using High speed extrusion infrared process at Uponor Virsbo Sweden, in the presence of different antioxidant concentrations and formulations, see **Table 4.6 and Table 4.8**. Two different lengths of pipes were sent to Aston for analysis, pipes PEX_{HS}-X2, PEX_{HS}-X4, PEX_{HS}-X6 and PEX_{HS}-X8 were 240 meter in length, and pipes PEX_{HS}-X1 (contains Irganox 1076 and a commercial HAS "undisclosed"),

PEX_{HS}-X3, PEX_{HS}-X7 and PEX_{HS}-X11 were 10 meter in length. Pipes were separated at 40 meter intervals for the 240 meter long pipes, and at 2 m interval for the 10 m long pipes (see **Scheme 4.6).** A 1.5 cm piece was taken from each pipe, microtomed with film thickness of 150 μm using Leica Micro-systems. The microtomed films were used to examine the AO-concentration profiles across the length (longitudinal) of the extruded pipes and in the radial direction of the pipes (see **Scheme 4.6**). The carbonyl region between 1780-1710 cm^{-1} was used to determine their concentration and distribution of the antioxidants by monitoring both a line marker and a line scan using a FTIR-microscope see **section 2.6.** For the line marker**,** each FTIR spectrum was obtained in the radial direction from the inner to the outer walls of the pipes, at 100 μm intervals and the carbonyl index (area of carbonyl peak normalised to the reference peak at 2100 cm^{-1}) was measured. Line scans were also done in the radial direction and a "false" colour map with contours and wire surface projection were used to display the antioxidant (AO) distribution within the pipes. The Actual concentration of the individual antioxidants could not be measured as the pipe formulations contained combination of antioxidants all of which have a carbonyl signature peak which was used for the FTIR measurements, except for pipe PEX_{HS}-X6 which contained DBPA and Chim 944 where the latter does not have a carbonyl absorption so the concentration profile measured was in this pipe that of DBPA only.

The overall antioxidant distribution in the pipes containing all g-AO was found to be homogenous in the radial direction of the pipes, see for example, **Figure 4.7** for pipe PEX_{HS}-X4 (see also **Table 4.6**). This figure shows clear homogenous antioxidant distribution where samples were taken from different lengths of 240 m long pipe with no colour variations in the AO-carbonyl region (1780-1710 cm^{-1}) map which suggests that no changes in the antioxidant concentration occurs both across the depth of the pipe and at different lengths of the extruded pipe. In contrast, for the standard pipe containing Irganox 1076 and a commercial HAS "undisclosed", PEX_{HS}-X1, the carbonyl signature of the antioxidant showed a clear variation in the "false" colour maps with contours shown in the radial direction, see **Figure 4.8**, indicating a much less homogenous distribution of the antioxidants.

Line marker (FTIR-microscopy measurements) was also used to monitor the antioxidant distribution in the radial direction; carbonyl index was measured and plotted for all the pipes (measured in pipes of 10 m and 240 m length), see **Figures 4.9** and **4.10.** By looking at the carbonyl index in sections across the length of the pipes, small variations can be seen in all cases. Pipes PEX_{HS} -X3 pipe (0.3%AOPP +0.3% DBPA), had a lower AO-carbonyl index in the longitudinal direction in the 8 m section whereas the AO concentration (carbonyl index) in

the radial direction (across the distance from inner to outer surfaces, i.e. across the x-axis of **Figure 4.10)** remained relatively unchanged. This drop in the carbonyl index in the longer length of the X3-pipe could be due to the lower amount of antioxidant used in the formulation of this pipe, thus some of the AO could be consumed during the production or due to a poor mixing process. It is worth pointing out here that the PEX_{HS}-pipes X3 and X2 have the same antioxidant composition but pipes X3 has just over half of the antioxidant concentration of that in X2 (the higher AO concentration in pipes X2 showed a more homogenous concentration across radial direction, see **Figure 4.9)**.

4.2.3.2. Sequential extraction of PEX_{HS} Pipes using DCM by ASE followed by Reflux with Xylene

In order to investigate the antioxidant retention in PEX_{HS}-pipes, a sequential extraction method was developed using DCM (ASE) followed by Xylene (reflux) and used for microtomed pipe films (see **Scheme 4.7**). DCM extraction was performed on 10 g microtomed films to remove any unreacted and homopolymerised antioxidants from the pipes (ASE, optimised temperature of 70°C). **Figure 4.11** shows the FTIR spectra in the carbonyl region of 1800-1600cm^{-1} of untreated pipes before and after DCM extraction to monitor the changes in the AO concentration. **Figure 4.12** gives the FTIR-spectra in the carbonyl region of PEX_{HS} pipe films before (U), after DCM (U1) and after xylene (insoluble i-U2 and soluble **s-U3** fractions) extractions, see **Scheme 4.7, also See Table 4.8 and Table 4.9.** It is clear from **Figure 4.12** that the standard pipe containing Irganox 1076 and commercial HAS (undisclosed) loses more antioxidant (higher extent of decrease of >C=O peak) after DCM and xylene extractions compared to pipes with g-AOs (PEX_{HS}-X2 -X11), suggesting that the reactive antioxidants in the pipes become chemically attached to the polymer backbone.

The sequential DCM-xylene extraction followed by FTIR analysis of the fractions allowed the determination of the total amount of antioxidants present in both xylene fractions (insoluble crosslinked, and soluble non-crosslinked) of the polymer and also the percent retention of the total antioxidants (from their carbonyl signals) after the xylene extraction where the AO concentrations were calculated based on their actual concentration determined after processing. **Table 4.9** shows the analysis results and shows that in the standard pipe, PEX_{HS}-X1 containing Irganox 1076 and commercial HAS, 46% of the AO was retained after xylene extraction, (37% in the cross-linked and 9% in the non-crosslinked fractions), thus 54% of the total AO was lost after DCM and xylene extractions (see **Table 4.9, E2**) .

In contrast, PEX_{HS}-pipes containing two g-AOs (g-DBPA + either g-AOPP or g-AOTP) such as pipes PEX_{HS}-X2 and PEX_{HS}-X4, showed minimum losses of only 7% and 3%, respectively. Pipe PEX_{HS}-X6 (DBPA+ Chim 944) retained 99% of the total AO after DCM extraction (**Table 4.9**, U1), which in this case is only due to DBPA as the commercial HAS (Chimassorb 944) used here does not absorb in the carbonyl region (it has absorption in the region of 1530 cm^{-1} for the triazine rings). For this PEX_{HS}- X6 pipe, after DCM and xylene extraction, 91% of the DBPA (based on its carbonyl absorbance) was shown to be retained in the crosslinked and non crosslinked polymer (i.e, only 9% of the g-hindered phenol was lost after both xylene and DCM extractions, **Table 4.9, E2) .**

Sequential DCM-xylene extraction was also performed on other PEX_{HS}-pipe samples containing low commercial (snik samples) of and non-graftable antioxidants (both hindered phenol and HAS), see **Table 4.6 and Table 4.9**. A low antioxidant concentration (0.2%) can be expected not to be able to protect the polymer of the pipe during processing effectively, thus, the well-known thermal degradation of PE could take place more easily, and this has been confirmed from FTIR analysis, see **Figures 4.13 and 4.14.** It is clear that after DCM extraction, there appears to be a relatively small decrease in the carbonyl index (see **Figure 4.13**). However, in the xylene-soluble fraction (after sequential DCM-xylene extraction and fraction separation), pipes PEX_{HS}-SNIK 3, 4 and 12 (each with one hindered phenol only; Irg 1076, Irg 1010, Irg 1035, at 0.3, 0.2 & 0.2%, respectively), showed some major changes in the carbonyl region in their xylene-soluble fractions (**Figures 4.14)** suggesting some melt thermal degradation of the polymer has taken place (ketone formation at 1720 cm^{-1} and unsaturation at 1640 cm^{-1}). This is almost certainly due to the AO concentration present in these pipes being low and is unable to give full protection to the polymer from thermal degradation during processing.

Another set of PEX_{HS}-pipes (PEX_{HS}-**FET1,** PEX_{HS}-**FET2,** PEX_{HS}-**FET4**), which had a higher (0.5% each AO) concentrations of a combination of commercial (non-graftable) antioxidants of different formulations were also produced by the High speed extrusion IR process. Pipe **PEX_{HS}-FET2** (Irganox 1076 + Chimasorb 944) lost 10 % of its antioxidants after DCM extraction (based on the >C=O index, see also **Figure 4.14 and Table 4.9**) after ASE-DCM extraction which is the same as the level of AO loss in the standard X1 pipe (containing Irganox 1076 and commercial HAS), **Table 4.9.** After DCM and xylene extractions, PEX_{HS}-FET2 lost only 8% of its antioxidant, whereas pipe PEX_{HS}-FET1 (Irganox 1076 + Tinuvin 622) and the standard pipe PEX_{HS}-X1(containing Irganox1076 and a commercial HAS) had an AO loss in xylene of 51% and 54%, respectively (**Table 4.9, E2**).

A **hydrostatic test** with water inside and air outside the PEX_{HS}-pipes was also done and conducted at Uponor , Virsbo Sweden, under 2.5 MPa pressure at elevated temperature according to ISO-**1167-1973** standard test, whereas failure time greater than a year (8500hr) has to be achieved for the pipes to be considered to be commercially sound. Pipe PEX_{HS}-X6 containing g-hind phenol (DBPA) and the commercial HAS (Chim 944) failed in the hydrostatic test (during 2600 and 4200hr), see **Table 4.10** and this is supported by IR results, **Figure 4.13** which shows a clear polymer degradation causing formation of ketones ($1720cm^{-1}$) and unsaturation ($1640cm^{-1}$) in the polymer-xylene-soluble fractions and the disappearance of the Chim 944 from the xylene fraction (disappearance of the $1530cm^{-1}$ triazine peak). It is interesting to note that this pipe showed similar fingerprint in its carbonyl and unsaturation regions in the xylene-soluble fraction (see 1720 and 1640 cm^{-1} peaks) to that of the SNIK samples (see **Figures 4.12 & 4.14**). Also, pipes PEX_{HS}-X2 and PEX_{HS}-X6 both had a yellow brown discolouration initially after processing in comparison to the other extruded pipes (**see Table 4.8**).

DSC-OIT measurement was also performed on the pipe films (results were in triplicates or in some cases on 9 samples) before and after DCM Extraction but the onset could not be determined for pipes containing the reactive antioxidants (g-AO), see **Figure 4.15**, whereas for pipe X1 the onset was clear see **Figure 4.16** . DSC-OIT Measurements were also done on the crosslinked (i-U2) and non-crosslinked (s-U3) fractions of the PEX_{HS}-pipes (see **Scheme 4.7**) the onset of the DSC curves for these fractions of the PEX_{HS}-pipes containing graftable antioxidants could be determined and showed a much higher OIT for the xylene insoluble fraction, see **Figure 4.17**.

4.2.3.3 Analysis of hydrostatically tested failed pipes

Hydrostatic test was conducted on all pipes at Uponor, Virsbo (done in triplicates), at two different temperatures **110°C** (**Hydrostatic test 2**) and 115°C (**Hydrostatic Test 1**), as described in the previous section, see **Table 4.10**). Hydrostatic test at 110°C showed that the PEX_{HS}-pipe sample X3, X6 and X4, have failed and have not met the **ISO-standard** (pipes should last over ~8500hr under these test conditions), whereas the other samples for this test are still on-going during the writing up period of this thesis.

Hydrostatic test 1 was done at high temperature of 115°C for PEX_{HS}-pipe samples, since both samples tested under these conditions (X3 and X6) had failed at 500h, thus the test was abandoned and repeated at lower temp of 110°C. Pipe X3 (failed at 2023hr) and pipe X6 (failed at 4228hr) were sent to Aston for analysis. Visual inspection of the failed pipes

showed localized failure with inhomogeneous discoloration. **Figure 4.18** shows pictures of the hydrostatically failed pipes X3 and X6. The section labelled Section "1" of pipe X3 (0.3% DBPA and 0.3% AOPP) is shown to have little visual changes, whereas in section "2", of the pipe darker brown discoloration is observed with powdered deposit on the internal surface of the pipe. The Section labelled "3" has undergone **stage-three type** failure **[109, 137-139]** and the surface has cracked. Pipe X6 with antioxidant formulation of 0.5%DBPA and 0.5% chimasorb 944, has failed at **4228hr** (~178days) and underwent homogenous discoloration throughout the pipe (unlike X3) see **Figure 4.18**.

FTIR-ATR analysis was carried out directly on the external and internal surface of X3 and X6 pipes for both untreated and the hydrostatically failed pipe sections. **Figure 4.19** shows the ATR spectra of pipe the untreated internal surfaces in the light (Section1) and dark (Section 2) parts of the failed X3 pipe sections. It is clear that for the inner surfaces exposed to water, a low level of ketones (at1717cm^{-1}) and esters (at1738cm^{-1}) were formed in both the light and the dark sections of the pipe. In contrast, in the outer surfaces which were exposed to air (oxygen), a significant change in the carbonyl region can clearly be seen (**Figure 4.20**) with the formation of ɣ-lactones (1768cm^{-1}), ketones (1717cm^{-1}), esters (1737cm^{-1}) and carboxylic acid (1697cm^{-1}), see **Figure 4.19**. Furthermore, a significant amount of double bond-containing oxidation products of the polymer are also formed, particularly in the darker section of the pipe (both in inner and outer surfaces) including the formation of vinylidene (872 cm^{-1}), and a broad bond formation for the C-O-C absorption at 1021 cm^{-1} ,see **Figure 4.20**.

The failed Pipe X6 (0.5% DBPA + 0.5 Chim944) which has shown a more homogenous discoloration, gave rise to similar changes in the carbonyl and double bond regions to that observed in pipe X3. The carbonyl region for the hydrostatic-failed outer surface of the pipe formed more carbonyl transformation products than that formed in its inner surface, see **Figures 4.21 & 4.22**. A substantial amount of C-O-C- absorption at (1026cm^{-1}) and vinylidene (874cm^{-1}) were formed in both inner and outer surfaces of the failed pipe 6 and these are known oxidation products of PE.

4.2.3.4 ASE-DCM extraction for HPLC-MS Analysis of PEX_{HS} pipes

An ASE extraction method was developed (see **Scheme 4.8, Route A)** using dichloromethane (DCM) as the extraction medium, since all the antioxidants used in the PEX_{HS}-pipes as well as the AO-homopolymer by-products that may have formed during processing are soluble in DCM. HPLC-MS method was then developed to analyse the neat antioxidants used in the

pipes after the pipe extraction (see **section 2.7**). All the antioxidants were found to elute at different retention times (**see Figures 4.23, 4.24 and 4.25**) according to the method developed in this work (see **Section 2.),** and each antioxidant did not interfere with the other when two antioxidants were used in the pipe formulations. This method was used to analyse the DCM extracts obtained from ASE-DCM extractions of the PEX_{HS}-pipes. FTIR analyses, were done before and after the extraction, see **Scheme 4.8 sample B**. Dried DCM extracts (after re-dissolving in ACN/MEOH, see **Scheme 4.8, sample A**) was put through positive and negative ionisation mode HPLC-MS (using **Zorbax –RXC18,** for all conditions see **section 2.7, pg)**.

The DCM-extracts themselves were dried in a fume hood and re-dissolved in 2 ml ACN/MEOH, in order to examine their full HPLC-UV chromatograms (detected at 205 nm) see samples **A** in **Scheme 4.8 and Figure 4.26**. Each LC peak observed in the chromatograms were then subjected to MS-analysis in order to identify products formed from the hindered phenol AOs used in the pipe formulations, these will be discussed in **Section 4.3**.

4.2.3.5 ASE-water extraction of PEX_{HS}-pipes

The ultimate reason for this work was to understand the interactions of antioxidants and their extractability in water; therefore a water boiling test was carried out with a less time consuming experiment designed for this purpose. 10 gram of pipes was microtomed (150 μm thickness) and the extraction temperature and time were optimized under pressure using ASE-Dionex system, (extraction at 110°C, and 5cycles of 30 mins at 2000psi) and the procedure was repeated 4 times. The HPLC-MS method used for the DCM extracts had to be modified in the case of the water extracts. The water extracts were first ran using the DCM-HPLC-MS method, for 70 minutes but no Irganox 1076 could be detected (it eluted at ~50 minutes by this method) and all the peaks eluted in the first few minutes without a good resolution. By using a LC-MS modified method, where the MS ionisation temperature was increased from 350°C to 600°C, the peaks became more resolved. Thus, the water extracts were further ASE-extracted up to four times using HPLC-grade chloroform, dried in a fume hood overnight and re-dissolved in 2 ml HPLC-Methanol ready for LC-MS analysis. The extracted samples were repeated in the positive and negative ionisation modes of the mass spectrometer, each run was 20 minutes long.

Water Extracted microtomed PEX_{HS}-pipe films (200μm thickness) were also analysed by FTIR. The % antioxidant loss (determined via the AO-carbonyl index) was calculated, see **Table 4.12 column W (see also Scheme 4.8, route II,)** with the highest AO loss found to be

in the standard X1 pipe of 14%, compared to a range of 3-8% loss in the pipes containing graftable AO's (pipes X2-X11).

Scheme 4.8 shows that the pipe film samples were analysed by HPLC-MS, both after one water-ASE extraction (samples W_1) and after cumulative extractions collected (2^{nd}, 3^{rd} and 4^{th} extraction cycles), samples W_{2-4}. As can be expected W_1 samples had less species extracted in water compared to samples W_{2-4} and, see **Figure 4.27** for full chromatograms for all pipes (samples W_{2-4}) and **Figure 4.28** for comparison of chromatogram of W_1 and W_{2-4} of all pipes. The separated LC-peaks were subjected to MS-analysis and the possible structure for products formed from water extraction will be discussed in **Section 4.3**.

4.3 Discussion

4.3.1 Laboratory production of stabilised- crosslinked PE using peroxide (PEXa) samples containing graftable AOs using one-step or two-step processes and their thermal stability

At the early stage of this work, laboratory methods were developed that could simulate the stabilised and crosslinked pipes produced by the commercial Engel process. The laboratory methods used were challenging as it involved the requirement of first achieving a high level of grafting of reactive AOs on the HDPE polymer and then utilising the same peroxide to give rise to a high extent of crosslinking of over 75%, typical of the crosslinked PE used in the PEXa pipes and without the grafting reaction interfering with the crosslinking process. This is why two methods were developed for this purpose, a **one-step** grafting and crosslinking and a **two-step** process. In the latter process, first the grafting is achieved either directly using the normal AO concentration of 0.5% g-AO-MB or via the use of an g-AO-MB (1-6% AO), diluted down to the required concentration of 0.5 %, (see **Scheme 4.1 and 4.2)** then in a second step, the polymer containing the g-AO was crosslinked using either the same or different peroxide initiator used for grafting process

A good antioxidant distribution in the lab-produced from PEXa samples is important if a good stabilisation is to be achieved. To check the homogeneity of the antioxidant distribution in the two-step process, the coefficient of variation (CV) of the OIT measurements was examined for two samples (OIT was used here to give an indication of the polymer stability). The results showed a very large variation (% CV of OIT) suggesting a poor distribution of the antioxidants in the two-step process, see **Table 4.3**. In addition to OIT measurements, results from FTIR-microscopy-mapping analysis of the carbonyl signature of the AO in PEXa samples showed also clearly that in the **two-step** process, the route of the direct AO grafting using a low concentration **(0.5%)** followed by crosslinking (sample g_2-PEX)gave rise to a dramatic improvement in the antioxidant distribution compared to the two-step route where the grafting was carried out first in a MB (3% AO) diluted down to 0.5% concentration followed by crosslinking, sample g_{2DMB}-PEX (see **Figure 4.29 B &D**). One of the reasons that may contribute towards the observed poor distribution of g-antioxidants could be the due to the fact the MB samples had to be granulated first before dilution and this may limit the homogenisation of the PE-g-AO in polymer during dilution with fresh polymer and subsequently with the crosslinking peroxide (TB).

The one-step grafting and crosslinking process gave rise to a better g-AO distribution compared to that achieved by the two-step process, based on FTIR-mapping of the AO distribution (**Figure 4.29**). This is reflected also by a much smaller calculated percentage of the coefficient of variation in OIT values of these PEXa samples of ~2-13% (see **Figure 4.30**) compared to ~ 50% for the two samples examined in the two-step process, results in **Table 4.2**. Purifying the polymer in the two step process by extraction of the f-DBPA and p-DBPA (from g_{2DMB}-PEX sample) and leaving just the g-DBPA and examining the AO distribution again, **figure 4.29A** shows that once the ungrafted antioxidants are removed, a significant improvement in the g-AO distribution is achieved which is similar to the AO distribution in one-step suggesting that the g-AO is well melt distributed within the polymer chains.

The thermoxidative stability of the samples have been assessed by examining their DSC-OIT which is one of the most practical and commonly used methods for obtaining information on polymer stability, antioxidant effectiveness, life predication of polymer, degree of polymer degradation and determination of antioxidant level remaining in the polymer [115, 140-143]. However, the OIT data obtained from DSC needs to be interpreted cautiously when it is being related to long term thermal stability performance of polymers in service in the solid state as OIT obtained in the polymer melt at temperatures above the melting point of the polymer [144]. The OIT retention after DCM extraction of the **one-step** PEXa samples containing the grafted hindered phenol DBPA when used as the only AO is shown to be higher than samples containing the corresponding non-graftable hindered phenol Irg 1076 alone, see **Figure 4.30**. This was also confirmed by the observed retention of the carbonyl index of the AO in these samples, **see Figure 4.31.** It was found that it takes more than 48h extraction with DCM to remove Irganox 1010 from the polymer matrix, whereas 48 hours DCM extraction was enough to remove all the Irganox 1076 available along with any unreacted graftable antioxidants, thus the fact that **Figure 4.30B** shows 100% OIT retention for samples containing Irg 1010 may be due to incomplete extraction of Irg 1010 (i.e, longer time of extraction would have been needed for this sample).

4.3.2 Characterisation and Thermal Stability of Pipes Produced by the Engel Process (PEX_{Eng}-pipes) Containing Graftable AOS in the Presence or Absence of Conventional AOs

Commercial PEXa pipe production with formulation containing chain breaking (CB) AOs and a peroxide used as the crosslinking initiator is the subject of a similar challenges to the one highlighted earlier for the lab produced PEXa samples. The major concern here is the interference of the crosslinking peroxide initiator with the polymer stabilisation by

conventional hindered phenol antioxidants (or in the presence of g-AO with conventional CB- hindered phenol AO), such as Irganox 1076 and Irganox 1010, since CB-AOs are known to function by reacting with radicals produced by the peroxide initiator, mainly alkyl peroxyl radicals, as well as with alkyl radicals via their oxidative transformation products [41, 86]. The use of a peroxide initiator for the crosslinking reaction of PEXa pipes, would therefore, also give rise to the consumption of the hindered phenol AOs in the systems, thus can be expected to reduce the overall in-service lifetime of the pipes used typically in contact with water environment. It is for this reason that all the work described in this thesis has been based on the use of a more "permanent" graftable antioxidants (g-AO) instead of the mobile conventional antioxidants with the overall aim of investigating whether this approach would overcome the problems highlighted above i.e. grafting of AOs in contact with a solvent and lower extent of interference of the crosslinking process with the stabilisation reaction of PEXa-pipes that are produced under a commercial setting. Based on the knowledge gained from the lab-experiments for producing PEXa material containing g-AOs, PEX_{Eng} pipes were produced using some specific formulations composed of a combination of HAS-AOs and hindered phenols (graftable or conventional) in the presence of three different peroxides used for the purpose of the AO grafting (when g-AOs were used) and for the polymer crosslinking reactions, **see Table 4.5 and 4.7**. It is important to note here that the chemical compositions chosen for the PEX_{Eng}-pipe production were not optimised due to time limitations. The challenge here was to achieve both grafting and crosslinking together in a one-step process during the Engel production where there is very little sheer mixing in the Engel "extruder".

Overall, all of the PEX_{Eng} pipes gave high level of crosslinking of over 80% (except for the pipe containing Irganox 1076 crosslinked with the peroxide T101) which gave much lower crosslinking level of ~54% (see **Table 4.5** and **Figure 4.3A**). Typically for the Engel process, the peroxide TB is used and indeed the results shown in **Figure 4.3A (see also Table 4.5)** confirm that the highest extent of crosslinking was achieved when TB was used. The reason for the use of the other two other peroxides (T145 and T101) was to try to achieve a high level of AO grafting as these peroxides were shown, both in the lab-produced one step and two-step PEXa production as well as in previous work in the PPP group [101], to give a high level of grafting of reactive AOs on polyolefins.

The crystallinity of all the pipes was shown to be between 40-48% (see **Figure 4.3B**) compared to 62% for the virgin polymer. This reduction in crystallinity can be expected due to the high level of the crosslinking of the polymer. The thermal stability of the PEX_{Eng}-pipes

was examined using both DSC-OIT and embrittlement time after oven aging in an air-circulating single cell Wallace oven at 125°C.

It is clear from **Figure 4.4**, that the overall thermal stability of the **untreated** pipes containing a combination of a g-HAS and Irganox 1076 is much higher than for pipes containing one AO, either Irganox 1076 or the g-hindered phenol DBPA. However PEX_{Eng} pipe extraction with **DCM**, a solvent in which all the AOs and the homopolymers of g-AO are soluble, had resulted in a major reduction in their thermal stability (from DSC-OIT),**see Figure 4.4A vs 4.6A**. For example all the pipes containing a combination of Irganox 1076 and g-HAS had shown a drastic reduction in their thermal stability (OIT of 11-19mins), compared to the values before extraction of 230-270min. In contrast, combinations of two graftable AOs (AOPP +DBPA or AOTP +DBPA) in the extracted pipes are shown to retain a much higher level of their thermal stability after extraction (see **Figure 4.6A**). The extent of the retention of the AOs in the PEX_{Eng}-pipes after processing was determined based on the reduction in the AO-carbonyl peak (from FTIR) of the AO after DCM extraction. All pipes containing one or two graftable AOs had shown AO-retention of over 70-90% compared to 55% only when Irganox 1076 was used, see **Figure 4.6**. Calculation of the actual AO concentration remaining in the polymer after DCM extraction using calibration curves (i.e. not based on the AO-carbonyl index) showed that Irg 1076 resulted in 55% retention (after DCM) whereas the graftable hindered phenol DBPA results in up to ~85% retention (see **Table 4.5**) confirming the advantages of using graftable AOs in the PEX_{Eng} pipes (see also Figure 4.6B for AO amount based on their carbonyl index).

The formation of polymer oxidation products (ketone, aldehydes acids and lactones) during oven aging at 125°C of PEX_{Eng}-pipes revealed a much higher extent of oxidation (lower thermal stability) in pipes containing the g-HAS AOTP (**Figure 4.32 F,G and H**) compared to the g-HAS AOPP, **see Figure 4.32 C,D and E**. **Figure 4.4 A and B** shows also that PEX_{Eng} pipe containing the graftable hindered phenol DBPA (5,6 ,16) alone had the lowest thermal stability; whereas when DBPA was combined with a graftable-HAS (samples 7R, 8R and 17) the thermal stability (aging and OIT) of the pipes had increased significantly, however, the percent coefficient of variation for the OIT of these pipe samples containing (g-DBPA +g-HAS, e.g., samples) was a high suggesting a poor distribution of the antioxidants or the peroxide used for achieving the AO grafting in the pipes **(see Table 4.5);** this is most likely due to the lack of mixing in the Engel Extrusion Process.

Water (oxygenated) extraction at boiling temperature for PEX_{Eng} pipe samples containing two graftable antioxidants showed a reduction in the extent of OIT retention down to 35-70% (see **Figure 4.5**) suggesting that hydrolysis of the ester group of the grafted antioxidants may have occurred resulting in their partial leachability and loss in water. However, samples containing the g-AOs in combination with the conventional AO Irganox 1076, have shown a higher extent of retention of OIT (70-90%) upon water extraction (**Figure 4.5**). When the PEX_{Eng} untreated pipes were subjected to long-term thermal stability in an air circulating oven at 125°C, no significant decrease in the AO-carbonyl peak (at 1738cm^{-1}) was observed (**Figure 4.32**), which confirms that the lower thermal stability performance of PEX_{Eng} pipes in boiled water must be caused by hydrolysis of the AO ester bond and their consequent loss through leaching. The effect of the type of peroxide used for the production of PEX_{Eng} pipes on their extent of retention in their thermal stability (via OIT) after water extraction is also shown in **Figure 4.5**. It is interesting to note from **Figure 4.5 (& Table 4.5)** that the use of the peroxide T145 in almost all the pipes (PEX_{Eng} 3, 6, 19, 24) has resulted in a much higher extent of retention of OIT after water extraction compared to PEX_{Eng} pipes produced (up to 8 samples were used OIT measurement to get the mean values) for using the other two peroxides (TB and T101).

4.3.3 Characterisation and thermal stability of Pipes produced by commercial High Speed Extrusion IR process (PEX_{HS}-pipes) containing graftable AOS in the presence or absence of conventional AOs

Uponor Ltd has more recently started producing pipes by a different process to the Engel process. The pipes in this process are first extruded in a twin screw extruder (formulations containing a peroxide and antioxidants) and are then crosslinked using IR-light. Since this process was introduced (half way through the programme), it was decided to produce PEX_{HS} pipes that contain formulations similar to those used in the earlier production by the Engel process in the presence of the peroxide T145. Overall, all the PEX_{HS} pipes formulations for this study (see **Table 4.8 and 4.6)** gave high level of crosslinking of over 80% and with the expected reduction in their crystallinity down to 34-47% (see **Table 4.6**) compared to 68% for the virgin polymer.

Different formulations containing combination of g-AO (DBPA, AOPP, and AOTP) and convectional AOs (Irg 1076, Irg 1010, Tin 622 and Chim 944) used at different concentrations were extruded. A minimum of 0.5% of AO concentration is typically required to produce commercially useful PEXa pipes, to allow for substantial amount of AO to remain

in the pipes after production to protect the polymer from oxidative degradation during processing and subsequently in service.

Examination of the extent of oxidation of the produced PEX_{HS} pipes (through microtomed films) was assessed by subjecting the samples to sequential extraction process, See **scheme 4.7** (DCM followed by Xylene) and the different stages of the polymer samples obtained from this process (untreated polymer, the DCM extracted polymer, the xylene soluble (i.e. non crosslinked component) and (i.e. crosslinked fractions) xylene-insoluble) were examined by FTIR analysis in order to assess the extent of the polymer oxidation in the different fractions. A PEX_{HS} pipe containing a small concentration (0.2%) of Irganox 1076 only (PEX_{HS} Snik3) showed a major oxidation in the more oxidation vulnerable xylene soluble (non-crosslinked) fraction, see **Figure 4.14**. This is clearly illustrated by the observed large increase in the extent of formation of esters (1739cm^{-1}), ketones (1719cm^{-1}) and double bonds (1641 cm^{-1}). In contrast when the Irganox 1076 was used at higher concentration of 0.5% and in combination with the conventional HAS (chim 944 also used at 0.5%) a much lower extent of oxidation was observed (see **Figure 4.18**, sample FET2) with extent of formation of ketones in all the fractions and much of the Irganox 1076 was preserved (carbonyl absorption). However, it is important to note here that the HAS used, in this FET2 pipe, which has a signature IR-absorptions at 1530cm^{-1} and 1568cm^{-1} (due to C-N absorbance of the triazine), seem to have been completely depleted in both the xylene soluble and insoluble fractions (complete disappearance of the 1530cm^{-1} band in **Figure 4.14,** sample FET2).

It is interesting to compare the behaviour of sample PEX_{HS}-Fet2 (Irg 1076 + chim 944) with that of the PEX_{HS}-X6 (g-DBPA +chim944) by examining their FTIR spectra after sequential DCM-xylene extraction. Pipe X6 showed less change in the amount of the g-DBPA (compared to Irg 1076 in pipe FET2) in all the fractions (absorbance 1740cm^{-1}, **Figure 4.12**, X6) but has shown some oxidation-ketone products (1720cm^{-1}) to be formed in the non-crosslinked (xylene-soluble) fraction of the polymer, along with some double bonds (1640cm^{-1}). However the difference here (compared to pipe Fet2) is that the chimasorb 944 (HAS) was retained in the xylene-soluble fraction to a large extent was lost (see IR absorptions at 1568 and 1530cm^{-1}), but a large amount was lost in the xylene-insoluble (XL) fraction. The distribution of the g-DBPA in this (X6) pipe is quiet uniform, (see **Figure 4.9-X6**); the distribution of chim 944 was not examined here. The crosslinked part of this X6-pipe seems to have been protected, to a large extent, by g-DBPA (most of the chim944 was lost in this fraction, **Figure 4.12**), as observed from both the high OIT values (**Figure 4.17**) and the

retention of the g-DBPA via its measured carbonyl (**Figure 4.33**, sample i-U2). It is also interesting to see here that the more oxidation vulnerable non-crosslinked fraction has undergone a much larger extent of deterioration, evident by a drastic reduction in its OIT and the amount of g-DBPA present in this fraction (**Figure4.17 and 4.33**, sample iU2).

Further, results of the hydrostatic stabilisation test, both at 115°C and 110°C, confirmed the poor stability of this pipe as it had failed at a very early stage of this test, see **Table 4.10** and **Figure 4.18**. A closer examination of the inner and outer surfaces of the fractured (hydrostatic test) X6 pipe (**Figure 4.21 and 4.22**) shows clearly outer fractured surface which was exposed to air in this test resulted in the formation of a large amount of C-O-C absorbance at 1026cm^{-1} and ketone absorbance at 1716 cm^{-1} with much less chim-944 retained (1567/1533cm^{-1}) on its outer fracture surfaces, **Figure 4.22 B &C**. Furthermore, this X6 pipes was the only PEX_{HS} pipe that showed visibly a high extent of discolouration after processing (yellow to brown in colour, see **Table 4.8**) suggesting a higher extent of oxidation that must have taken place in this pipe during production compared to the others produced in the same process. This may be attributed, at least in part, to a less well distribution of the high molecular weight HAS (chim 944) used in the system which may have, to a certain extent, also phase-separated in the polymer and come out (migrated) from the inner surface to the outer fractured pipe surface, that was exposed to air causing its premature fracture under the hydrostatic pressure conditions.

Hydrostatic test that was performed at 115°C showed also that pipe PEX_{HS}-X3 has failed prematurely (see **Table 4.10**). The X3 pipe which had a low AO concentration of 0.3% for each of the g-DBPA and g-AOPP, exhibited highly oxidized and embrittled wall surfaces (dark oxidation region that reached half the thickness of the original pipe, see **Figure 4.18. Figure 4.19.** These figures show clearly that for the inner fractured surface of the X3 pipe that was exposed to water, a low level of oxidation products were formed such as ketones (at1717cm^{-1}) and esters (at1738cm^{-1}) in both the light and the dark sections of the pipe. However, in the outer surfaces which were exposed to air (oxygen), see **Figure 4.20B**, a significant change in the carbonyl region can be seen with the formation of much higher amount of γ-lactones (1768 cm^{-1}), ketones (1717 cm^{-1}) ، esters (1737 cm^{-1}) and carboxylic acid (1697cm^{-1}), accompanied by very large C-O-C absorption at 1026 cm^{-1}, see **Figure 4.20C.** Furthermore, a significant amount of double bond-containing oxidation products of the polymer [113, 145] were also formed, particularly in the darker section of the pipe (both in inner and outer surfaces) including the formation of 1412cm^{-1} and vinylidene at 872 cm^{-1}),

see **Figure 4.20**. For both Pipe samples (X3 and X6) that had failed under hydrostatic test at 115°C, results from FTIR-ATR compared with those of the corresponding untreated pipes suggest that the oxidation process is highly accelerated by possible hydrolysis (in presence of water) leaching, migration and loss of the mobile-AOs (low g-AO present at low concentration in pipe X3) from the pipe internal surfaces at the high temperature of the test. In the case of pipe X3 which contained g-AOs, these must have undergone hydrolysis during the test and thus became mobile and vulnerable to water leaching and loss, thus the pipe fracture through a clear chemical degradation by what is known as a stage III failure [4, 109]. The discoloration, particularly in the inner surface of X3 pipe, has occurred selectively at the point of contact with the air–water interface, and is most likely to be due to a combination of polymer oxidation, as well as, accumulation of transformation/oxidation products of the phenolic AO on the surface. This type of discoloration could also be a consequence of interaction of the different AOs and/or their transformation products in the formulation. In the presence of phenolic AOs, polymer discoloration is typically a consequence of a sacrificial consumption of phenols during the stabilization process and can be ascribed principally to transformation products having coloured quinonoid structures **[68, 69].**

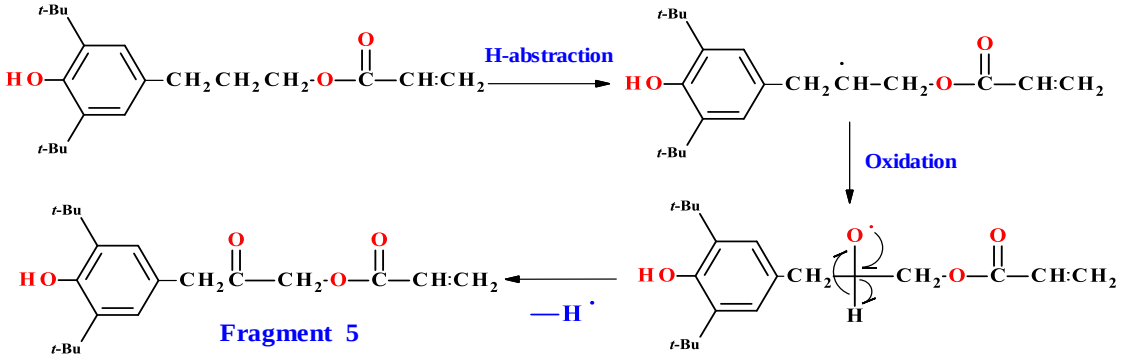
4.3.4 Examination of Oxidative Transformation products formed during the high speed extrusion IR production of the PEX_{HS}-pipes using HPLC-MS Analysis

The aim of the work on producing PEX_{HS} pipes containing g-AOs was mainly for their use in potable water systems. Hence it was important to examine the degradation of PEX_{HS} pipes through the study of the amount of AOs physically lost (previous sections) and the nature of the oxidation products of the antioxidants (chemical consumption) [114, 137, 146-148]. It has been reported in the literature that physical loss of antioxidants from PEXa potable water pipes would not only affect the stability of the pipe material but would also play a role in the possible deterioration of the quality of the transported water. In order to examine the interaction of contact media (water and a solvent DCM) with the stabilising system in PEX_{HS}-Pipes, the pipes were treated with either non-oxygenated boiling water under pressure (13 MPa or 2000 psi) using ASE Dionex system for thin films microtomed from the pipes (150μm) when exposed to DCM extraction under pressure using also ASE-Dionex cells to accelerate the extraction of the additives (e.g. through hydrolysis) , including the free, grafted (if hydrolysed) or the polymerised AO (as well as their transformation products that may be formed during the pipe processing). In order to monitor the migrants from the water and DCM extraction process, the extracts were analysed and products identified using HPLC-MS analysis.

FTIR analysis of the pipe samples after DCM extraction showed low level of AOs in the DCM extraction with minimum loss observed in the g-DBPA hindered phenol level in the pipe X6 (note in this pipe, the C=O peak measured corresponds only to g-DBPA as the HAS used here does not absorb in this region, see column B in **Table 4.11)**. It is clear from **Table 4.11** that pipes which contained Irganox 1076 along with a graftable HAS (X7 and X8) have lost more of their antioxidants after DCM extraction than pipes which have two graftable antioxidants (X2 & X4).

HPLC-MS analysis was carried out on all the DCM and water extracts of PEX_{HS} pipe to examine the nature of the products (AOs themselves and their oxidative transformation products) present in the extracts. Each peak observed in the chromatograms was subjected to MS analysis in order to identify the AO-based extracted products from the pipes. Since the polymer used for all pipes contained a small amount (750 ppm) of the thermal stabilising antioxidant (Irganox 1076), all pipe extracts showed the presence of the same concentration of Irganox 1076 (from HPLC), except for Pipes X1, X7 and X8 where Irg 1076 was present at much higher concentrations and this is because the pipes have in addition, an added 0.5% Irganox1076 in their formulations. All the HPLC separated peaks identified by mass spectroscopy are labelled and summarised in **Table 4.11** along with their UV and masses. The first Peak in the chromatograms which eluted at 3.08 mins and had a mass of 263 m/z and UV- λ max at 278 nm (see **Figure 4.34 & Table 4.10**) was present in all the PEX_{HS}-pipe extracts containing DBPA (X2, X3, X4 and X6).

The structures for compounds responsible for the HPLC peaks that had eluted at retention times of 3.08 and 3.36 (see **Figure 4.34**) and 3.95 (see **Figure 4.35**) corresponded most likely to hindered phenol based structures **1-5** (**Structure Scheme 4.1**) which correspond to DBPA and some of its different oxidation products. The presence of the peak that had eluted at 3.95 min with a mass of 333 (**fragment 5)** can be explained by the formation of a ketonic group (additional oxygen). The formation of this extra ketonic group must have occurred through oxidation of methylene group in DBPA, see **Reaction 4.1** below.

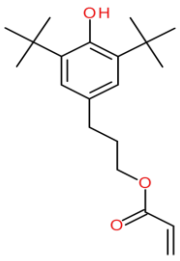


Reaction 4. 1: Formation of Ketonic group on DBPA through Oxidation

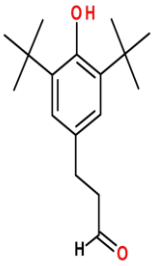
In **Figure 4.34**, the mass spectra of the HPLC peak that had eluted at 3.08mins had m/z at the beginning, middle and end of the HPLC peak of 263, 317 and 233, suggests that this is mainly the aldehyde of DBPA, **fragment 2** (see **structure Scheme 4.1**) eluted with small amount of DBPA (**structure 1** m/s of 317) and ethyl hindered phenol, **structure 2** at m/z of 233, see **structure Scheme 4.**1. **Figure 4.36** shows that for pipes containing DBPA (X2, X3, X4 and X6) a peak eluted at 5.05 min with a mass of 623 m/z. This suggests a structure corresponding to a dimer of DBPA, see **structure (6) in Structure Scheme 1 (See also Table 4.11).**

Peaks that had eluted at 29.91, 33.8, 51.92 and 63.31 mins (see **Figure 4.37 and 4.38**) were found to be present in all the pipe extracts and belong to Irganox 1076 (as the parent molecule) or to its oxidative transformation products produced during the stabilisation process in the polymer matrix. The peak that had eluted 29.91 minutes corresponding to m/z of 473 (see **Figure 4.37**) is assigned to **structure 7 in Scheme 4.1** where one of the tertiary butyl groups of Irganox 1076 had split-off **[149].** Irganox 1076 was extracted by DCM from all the pipes and this was confirmed by the observed peak in all pipes at 51.92 minutes with a strong absorbance at 278 nm and a mass of 529 (**Figure 4.38**) corresponding to Irganox 1076 itself, This peak was much more intense in pipes PEX_{HS}-X7 and PEX_{HS}-X8 because Irganox 1076 was added in the formulations of these pipes (see **Figure 4.38**, structure **9** in reaction **Scheme 4.1** and **Table 4.11. [149, 150]**). There is another fragment of Irganox 1076 (**Figure 4.38)** which is also present in all the pipe extracts having UV absorbance at longer wavelength of 312 nm and a mass of 527, which suggests that the hydroxyl group here had oxidized to the corresponding stilbene Quinone, **See Str.10** (see **Structure Scheme 4.1** & **Table 4.11**) **[68, 149].See Str.10** (see **Structure Scheme 4.1** & **Table 4.11**) **[68, 149]**. Whereas the peak eluting at 33.8 minutes corresponding to m/z of 545 **see Figure 4.37**, can be explained by the formation of a ketonic group within the Irganox 1076 structure in a similar way to the ketonic group formed in the DBPA structure (**structure 5**) discussed above (see **structure 8, Scheme 4.1**) **[68, 149].**

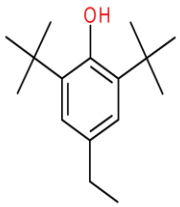
Structure Scheme 4.1: Structures of Identified compounds in DCM Extracts of PEXHS-pipes analysis by HPLC-MS



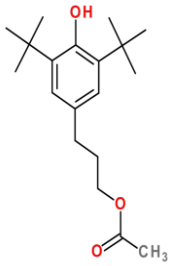
317m/z
RT: 3.08
Figure:4.34
1



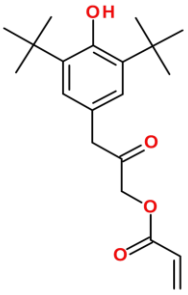
263m/z
RT:3.08
Figure:4.34
2



233m/z
RT:3.08
Figure:4.34
3

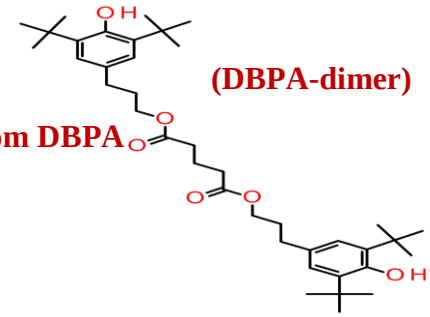


305m/z
RT:3.36
Figure:4.34
4

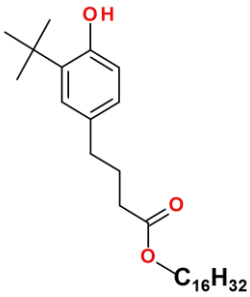


333m/z
RT:3.95
Figure:4.35
5

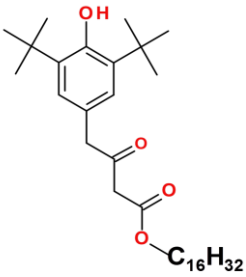
From DBPA



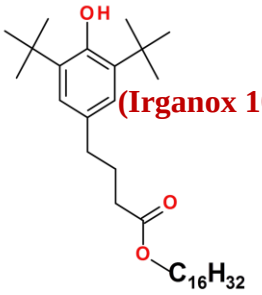
(DBPA-dimer)
623m/z
RT:5.05
Figure:4.36
6



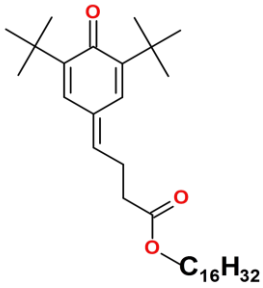
473m/z
RT:29.91
Figure:4.37
7



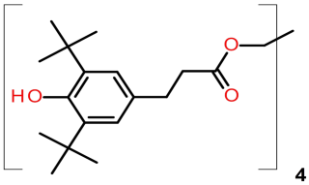
545m/z
RT: 34.11
Figure: 4.37
8



(Irganox 1076)
529m/z
RT: 51.92
Figure: 4.38
9



527m/z
RT: 63.68
Figure: 4.38
10



1175m/z
RT: 11.47
Figure: 4.39
11

(Irganox 1010)

In Pipe PEX_{HS}-X11 which contains Irganox 1010 in combination with AOPP a peak which only appeared in this pipe eluted at 11.47 mins with UV absorbance of 278 nm and a mass of 1198 m/z (run in positive mode at 600°C), This peak corresponded to Irg 1010 itself indicating that some of it was extracted in DCM (see **Figure 4.39**, **Table 4.11).** All the above HPLC-MS runs were done on both negative and positive ionisation mode, with the latter being run with would be the aim of detecting nitrogen compound but unfortunately none of the nitrogen compounds could be detected under the conditions used.

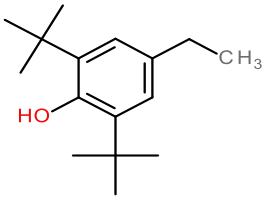
The PEX_{HS}-pipes which were subjected to water extraction, **Scheme 4.8**, were also analysed by HPLC-MS (analysis for their water extracts). Pipe PEX_{HS}-X2, PEX_{HS}-X3, PEX_{HS}-X4 and PEX_{HS}-X6 which contained DBPA, have shown more fragments present in their extracts compared to pipes containing Irganox 1076 (see **Figure 4.40**). This suggests that Irganox 1076 in these pipes is more stable in water than the graftable hindered phenol DBPA. This may be because g-DBPA had undergone higher extent of hydrolysis resulting in the breakdown in its ester bond which leads to the loss of more of the AO from the polymer during the water extraction process.

Figure 4.40 shows an HPLC peaks that had eluted, at 3.03 minutes having m/z of 231 and a strong absorbance at 276 nm. This peak was shown to be present only in pipes X2, X3, X4 and X6, all containing DBPA, suggesting that it is most likely a fragment of DBPA, where some of the "tail" becomes cleaved off under heat and pressure and the suggested structure for this compound is **Structure 12 (see also Rn in Scheme 4.2) and Figure 4.40 [9, 149]**). This compound 12 may also have formed from Irg 1076 or 1010, but if this was the case then a much lower amount is formed from pipes containing Irg 1076 or 1010 (X1, X7, X8, X11) which had shown a much smaller peak eluting at this retention time of 3.03min.These undesirable splitting-off reactions would reduce the antioxidant efficiency of the stabilizers without contributing to the protection of the polymer.

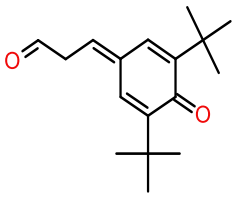
Another fragment which was also present in the same pipes (containing DBPA) eluted at 3.41 min with a m/z of 261 and with a strong UV absorbance of 237 nm, see **Figure 4.41.** A structure suggested for this compound is **structure 13 (**3-(3,5-ditert-butyl-4-oxo-cyclohexa-2,5-dien-1-ylidene) propanal)**, see Structure Scheme 4.2**. At 3.5 minutes there appeared a peak which was present in pipe X6 and was also present as a slight shoulder in pipe X3 having a strong UV absorbance at 281 nm and a mass of 247 m/z. The structure suggested for

this compound is structure **14 (**2,6-ditert-butyl-4-(1-hydroxyethylidene)cyclohexa-2,5-dien-1-one), **Figure 4.41**. Compounds 13 and 14 must have formed during the stabilisation mechanism of DBPA and were extracted in water.

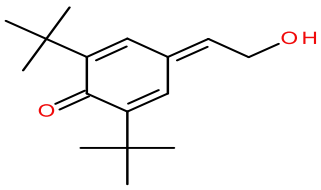
Structure Scheme 4.2: Structures of Identified compounds in water Extracts of PEX_{HS}-pipe analysis by HPLC-MS



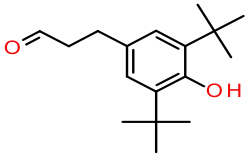
231m/z
Rt: 3.03 min
Figure: 4. 40
12



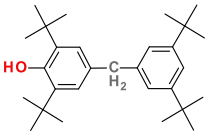
261m/z
Rt: 3.41
Figure: 4.41
13



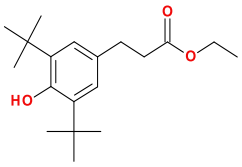
247m/z
Rt: 3.59
Figure:4.41
14



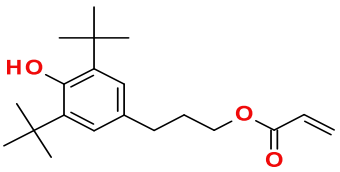
263m/z
Rt: 4.49
Figure: 4.42
15



408m/z
Rt: 6.04
Figure:4.42
16



299m/z
Rt: 9.32
Figure: 4.43
17



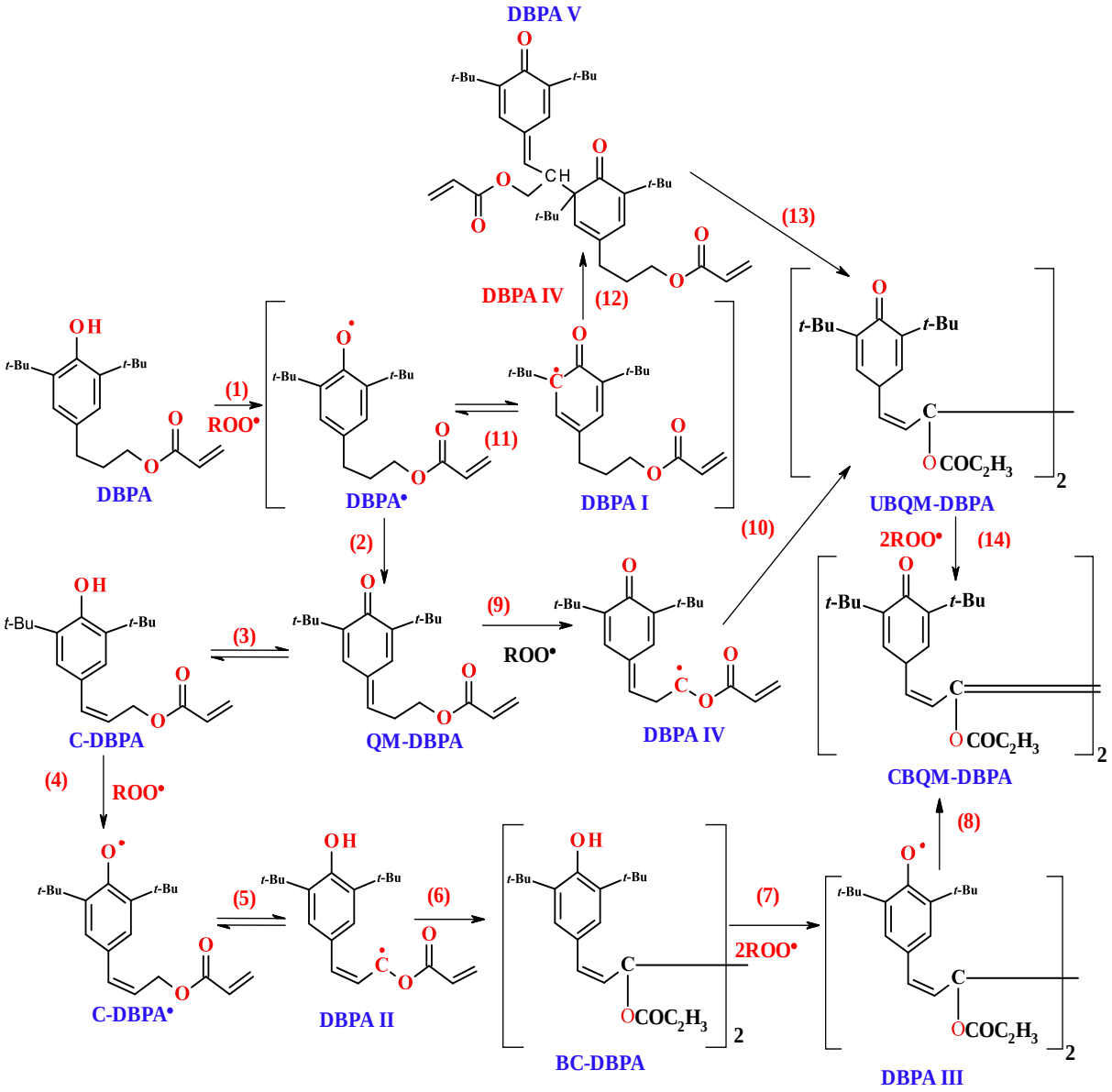
(DBPA)

317m/z
Rt: 10.73
Figure: 4.45
18

Figure 4.42 shows a fragment from water extraction that eluted at retention time 4.49 minutes having a UV absorbance of 277 nm and m/z of 263. The peak is suggested to correspond to compound with, **structure 15** (3-(3,5-ditert-butyl-4-hydroxy-phenyl) propanal) which is present in the pipes containing DBPA (X2, X3, X4, X6) and may result from cleavage of the carbonyl from the DBPA, see **structure 15, in Structure Scheme 4.2 [9, 149]** . **Figure 4.43** shows that in pipe X4 a fragment elutes at 10.73 minutes with m/z of 317 and UV absorbance of 278 nm, which is DBPA itself (**structure 18**).

In pipe PEX_{HS}-X1 containing Irganox 1076 and a commercial HAS there were few additional peaks present only in this pipe, including a fragment eluted at 6.04 minutes with UV absorbance of 274 nm and molecular weight of 408 (see **Figure 4.42**), and another fragment eluted at 9:32 minutes with m/z of 299 and absorbance of 269 nm, see **Figure 4.41**, UV and MS-spectra suggest structures based on Irganox 1076 with some of its tail being cleaved off, which is possible at high temperature. Another fragment was also present in pipe X1 only which eluted at 17.5 minute having UV absorbance of 308 nm but there was no fingerprint for this compound in the mass spectra, See **Figure 4.44**.

DBPA, like other hindered phenol antioxidants, is expected to act as an effective chain breaking donor (CB-D) antioxidant. The antioxidant mechanism of DBPA used for the stabilisation of PEXa pipes in this work is suggested here and is shown in **Mechanism scheme 4.1.**DBPA reacts with alkyl peroxyl radical to give the corresponding phenoxyl radical, DBPA$^{\bullet}$ (see **Rn 1 in Mechanism Scheme 4.1**). The latter would lead to formation of QM- DBPA (**Rn 2**), which can isomerise to the more stable C-DBPA (**Rn 3**). The latter can also react as chain breaking antioxidant to form C-DBPA$^{\bullet}$ (**Rn 4**) and through hydrogen atom abstraction gives rise to the carbon radical, DBPA II (**Rn 5**) followed by dimerization to give rise to the formation of BC-DBPA (**Rn 6**). The BC-DBPA can also act as CB-D by giving away its phenolic hydrogen atom to from DBPA III (**Rn 7**) which in turn gives the CBQM-DBPA (**Rn 8**). Alternatively, the latter can be formed from the oxidation of **UCBM-DBPA** (**Rn 14**). **UBQM-DBPA** which itself can be formed from the quinone methide radical **DBPA IV** (**Rn 10**) that is obtained from further oxidation of QM-DBPA (**Rn 9**). Dimer **DBPA V** is formed via radical coupling of DBPA I and DBPA IV (**Rn 12**). The Quinone methide (QM), cinnamate (C), biscinnamate (BC), benzoquinone methide (BQM) all have quite distinct UV/visible spectra.



Scheme 4. 1: suggested mechanism of melt Stabilisation action of DBPA in HDPE where QM: quinone methide, C:cinnamate , BC: biscinnamate , UBQM: unconjugated bisquinonemethide , CBQM: conjugated bisquinonemethide

Table 4. 7: composition and processing conditions of **PEX_{Eng}-pipes** extruded in Uponor-Virsbo, Sweden using the Engel process

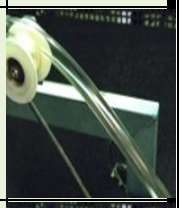
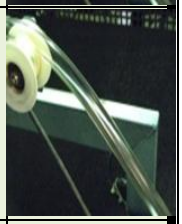
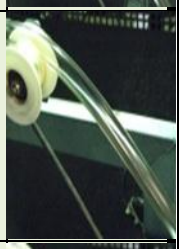
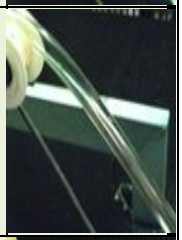
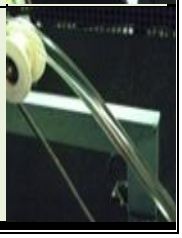
Trial pipe no	Composition		Preparation of the formulation	Conditions	Observation during processing	Pictures
	AO's	Peroxide				
PEX_{Eng}-1	0.5% Irg1076	0.4% TB	Standard composition	Set temperature: cylinder block; 110°C Electric heating (only used for start-up): 150°C Bushing:250°C Mandrel/pin:250°C Set line speed :260m/h	Standard composition no changes	
PEX_{Eng} -19	0.5%AOPP: 0.5% Irg1076,	0.45%T145-E85	All soaked in hexane, dried in fume hood overnight		Transparent no changes, good quality pipe	
PEX_{Eng} -20	0.5%AOPP: 0.5% Irg1076	0.4%TB	HDPE soaked in hexane, dried under fume hood overnight; TB added and soaked in a sealed container over night		Transparent no changes, good quality pipe	
PEX_{Eng} -21	0.5%AOPP: 0.5% Irg1076,	0.4%T101	All soaked in hexane, dried in fume hood overnight		Transparent no changes, good quality pipe	
PEX_{Eng} -22	0.5%AOTP: 0.5%Irg 1076,	0.4% TB	HDPE soaked in hexane, dried under fume hood overnight; TB added and soaked in a sealed container over night		Transparent no changes, good quality pipe	
PEX_{Eng} -24	0.5%AOTP: 0.5%Irg 1076,	0.45% T145-E85	All soaked in hexane, dried in fume hood overnight		Transparent no changes, good quality pipe	
PEX_{Eng} -25	0.5%AOTP: 0.5% Irg1076,	0.4%T101	All soaked in hexane, dried in fume hood overnight		Transparent no changes, good quality pipe	

Table 4. 8: Composition and processing conditions of **PEX_{HS}-pipes** produced in **Uponor-Virsbo Sweden** via **High-Speed Extrusion IR process**.

Trial pipe no	Composition		Preparation of the formulation	Conditions	Observation during processing	Pictures
	AO's	Peroxide				
PEX_{HS-} X1	Irganox 1076, + HAS	**T145**	**The formulations were prepared by first soaking the polymer & AO's in hexane for 1hour and drying in fume hood over night before feeding in to the extruder**	**Extruding the mixture using twin extruder at extremely low temperature, followed by crosslinking by heating with high temperature short wavelength infrared radiation (170-250°C for curing, IR lamp 4Kw)**	Good visual pipe quality no changes	
PEX_{HS-} X2	DBPA 0.5% + AOPP0.5%	**T145**			Yellowish in colour	
PEX_{HS-} X3	DBPA 0.3% + AOPP 0.3%	**T145**			No change	
PEX_{HS-} X4	DBPA 0.5% + AOTP 0.5%	**T145**			No change	
PEX_{HS-} X6	DBPA 0.5% + Chimasorb 944 0.5%	**T145**			Yellow to brown in colour	
PEX_{HS-} X7	AOPP 0.5% + Irganox 1076 0.5%	**T145**			No change	
PEX_{HS-} X8	AOTP 0.5% + Irganox 1076 0.5%	**T145**			No change	
PEX_{HS-} X11	AOPP 0.5% + Irganox 1010 0.3%	**T145**			No change	

Table 4. 9: Sequential ASE-DCM extraction followed by xylene reflux (see Scheme 4.7) for PEX_{HS}-pipe films

Pipe film Samples PEX_{HS}	FORMULATION	Extent of crosslinking See scheme 4.7 Route II & III		Relative amount of AO's based on >C=O index from FTIR (N^{o} are >C=O index, also presented as % of total based on actual amount, U1, in pipes after processing)						
		% Xylene Insol polymer XL	% Xylene Soluble polymer NXL	Untreated Actual [AO] (100%)	Remaining After DCM Ext	[AO] Lost in DCM (inferred)	[AO] Remaining in Polymer after Sequential DCM & Xylene Extr Based on the actual concentration			Total [AO] Lost (in Xylene) (inferred)
				See Scheme 4.7					Total AO remaining	
		% (X_1)	% (X_2)	U **[AO]%	U1 U1X100/U	E1 100-U1	i-U2 iU2x100/U1	s-U3 sU3X100/U	i-U2+s-U3	E2 (total lost) 100-(i-U2+s-U3)
X1	Irganox 1076+ commercial HALS "undisclosed"Uponor standard	85	15	0.84 66%	0.75 90%	10%	0.28 37%	0.07 9%	0.35 46%	54%
X2	DBPA (0.5%) + AOPP (0.5%) + T145	85	15	1.26	1.17 93%	7%	0.88 75%	0.21 18%	1.09 93%	7%
X3	DBPA (0.3%) + AOPP (0.3%) +T145	88	12	0.82	0.82 100%	0%	0.54 65%	0.12 14%	0.65 79%	21%
X4	DBPA (0.5%) + AOTP (0.5%), T145	88	12	1.39	1.37 99%	1%	1.17 85%	0.18 13%	1.35 97%	3%
X6	DBPA (0.5%) + Chimasorb 944 (0.5%) +T145	89	11	0.65 82%	0.64 99%	1%	0.49 77%	0.09 14%	0.58 91%	9%
X7	AOPP (0.5%) + Irganox 1076 (0.5%) +T145	91	9	1.11	0.90 81%	19%	0.67 75%	0.10 11%	0.77 86%	14%
X8	AOTP(0.5), Irganox 1076(0.5)	86	14	1.29	1.14 88%	12%	0.83 73%	0.22 19%	1.04 92%	8%
X11	AOPP (0.5%) + Irganox 1010(0.3%)	82	18	1.08	1.06 98%	2%	0.79 75%	0.24 23%	1.05 98%	2%
SNIK3	Irganox1076 (0.2%)+T145	87	13	0.27 38%	0.24 89%	11%	0.15 63%	0.08 33%	0.23 96%	4%
SNIK4	Irganox 1010 (0.2%)+T145	86	14	0.30	0.37 123%	0%	0.25 67%	0.09 13%	0.34 80%	20%
SNIK12	Irganox 1035(0.2%)+T145	85	15	0.29	0.29 100%	0%	0.21 72%	0.10 34%	0.31 106%	0%
FET1	Irganox 1076 (0.5%) + Tinuvin 622(0.5%)+T145	81	19	2.10	2.09 99%	1%	0.77 37%	0.25 12%	1.01 49%	51%
FET2	Irganox 1076 (0.5%) + Chimm944(0.5%)+T145	81	19	1.05 60%	0.95 90%	10%	0.65 68%	0.23 24%	0.88 92%	8%
FET4	Irganox 1076 (0.5%) +Irganox 1035 (0.5%) TINUVIN 622(0.5%)	87	13	2.34	2.04 87%	13%	0.62 30%	0.14 6%	0.77 36%	64%

**[AO]% : Antioxidant concentration calculated using calibration curves

Table 4. 10 : Results of **hydrostatic tests of PEX_{HS}- pipes** conducted in **Uponor Virsbo, Sweden**

Sample ID	FORMULATION	Hydrostatic Test 1 @ 115°C, 2.5 MPa failed pipe sent to Aston For Analysis	Hydrostatic test 2 @ 110°C Hydrostatic test water inside and air circulating outside under 2.5MPa, 110°C (20-01-2014) #		
			Sample 1	Sample 2	Sample 3
PEX_{HS}- X1	0.5% Irg 1076+ 0.5% commercial HAS "undisclosed" Uponor standard		9,663	11,486	>14,835
PEX_{HS}- X2	DBPA (0.5%) + AOPP (0.5%)+ T145		11,646	>13,609	>16,566
PEX_{HS}- X3	DBPA (0.3%) + AOPP (0.3%)+ T145	**2023**	8,095	8,966	10,166
PEX_{HS}- X4	DBPA (0.5%) +AOTP (0.5%)+ T145		6,837	4,694	8,702
PEX_{HS}- X6	DBPA(0.5%)+Chim 944(0.5%)+ T145	**4228**	3,158	3,438	2,614
PEX_{HS}- X7	AOPP (0.5%) + Irg 1076 (0.5%)+ T145		11,646	11,646	>16,566
PEX_{HS}- X8	AOTP(O.5%), Irg 1076 (0.5%)+ T145		9,614	10,094	11,438
PEX_{HS}- X11	AOPP (0.5%) + Irg1010 (0.3%)+ T145		5,294	>11,949	>11,949

For commercially sound test results, time to failure must be > one year = 8500 h

Orange : Not fulfilling the requirements in the PEX –**ISO 1167-1973** Standard

Green: fulfils the requirements

: failed pipe samples sent to Aston for analysis

Table 4. 11: Summary of FTIR analysis of DCM extracts and HPLC retention times and suggested structures based UV and Mass of **DCM extracts** of PEX_{HS}-pipes (See **Scheme 4.8**)

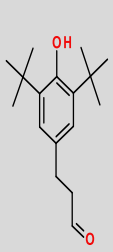
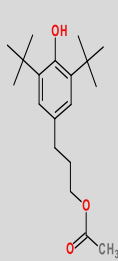
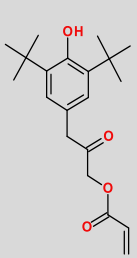
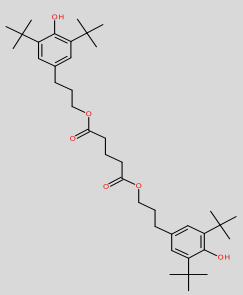
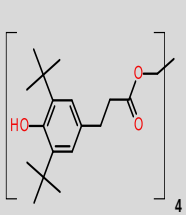
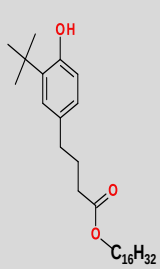
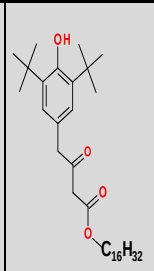
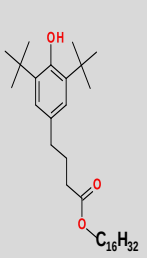
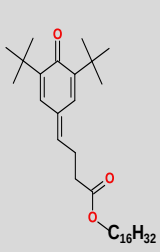
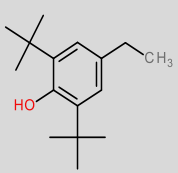
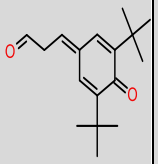
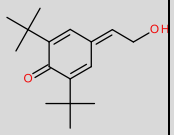
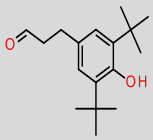
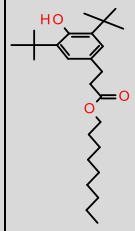
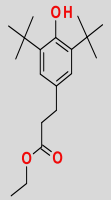
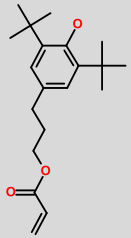
See Figure			Fig 4.32	Fig 4.32	Fig 4.33	Fig 4.34	Fig 4.38	Fig 4.35	Fig 4.35	Fig 4.36	Fig 4.36
RT(min)			3.08	3.38	3.95	5.05	11.47	29.91	34.11	50.77	63.31
UV λmax, nm			**282**	**277**	**276**	**278**		**278**	**282**	**278**	**312**
Mass m/z			**263**	**305**	**333**	**623**	**1175**	**473**	**545**	**529**	**527**
Suggested structures from Mass spectra Structure numbers see structure Scheme 4.1Page		**B** *Amount of AO lost in DCM (based on carbonyl index)* **%** **See scheme 4.8**				 Dimmer of DBPA	 Irganox1010			 Irganox 1076	 stilbene Quinone
Code	**Composition**		**2**	**4**	**5**	**6**	**11**	**7**	**8**	**9**	**10**
X1	0.5% Irganox1076 + 0.5% HAS	**7**	**NO**	**No**	**No**	**No**	**No**	**Yes**	**Yes**	**Yes**	**Yes**
X2	0.5%AOPP,0.5%DBPA	**5**	**Yes**	**Yes**	**Yes**	**Yes**	**No**	**Yes**	**Yes**	**Yes**	**Yes**
X3	0.3%AOPP,0.3DBPA	**8**	**Yes**	**Yes**	**Yes**	**Yes**	**No**	**Yes**	**Yes**	**Yes**	**Yes**
X4	0.5%AOTP,0.5%DBPA	**5**	**Yes**	**Yes**	**Yes**	**Yes**	**No**	**Yes**	**Yes**	**Yes**	**Yes**
X6	0.5%DBPA,0.5%Chim944	**1**	**Yes**	**Yes**	**Yes**	**Yes**	**No**	**Yes**	**Yes**	**Yes**	**Yes**
X7	0.5%AOPP,0.5%Irg1076	**11**	**NO**	**No**	**No**	**No**	**No**	**Yes**	**Yes**	**Yes**	**Yes**
X8	0.5AOTP,0.5%irg1076	**10**	**NO**	**No**	**No**	**No**	**No**	**Yes**	**Yes**	**Yes**	**Yes**
X11	0.5%AOPP,0.5%Irg1010	**6**	**NO**	**No**	**No**	**NO**	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**

Table 4. 12: Summary of retention times and suggested structures based upon UV and Mass for **<u>water extracts</u>** of PEX_{HS}-pipes **(See Scheme 4.8)**

See Figure			Fig 4.40	Fig 4.41	Fig 4.41	Fig 4.42	Fig 4.42	Fig 4.43	Fig 4.43	Fig 4.44
UV-RT(min)			**3.03**	**3.41**	**3.59**	**4.49**	**6.04**	**9.32**	**10.73**	**17.5**
UV(nm)			**276**	**237**	**281**	**278**	**273**	**270**	**278**	**307**
Mass			231	261	247	263	408	299	317	--
Suggested structures from Mass spec **Structure no see structure Scheme 4.2 Page**		**W %** **AO lost in water % (based on carbonyl index)** **See Scheme 4.8 Sample** **W_{2-4}**	 2,6-ditert-butyl-4-ethyl-phenol **12**	 3-(3,5-ditert-butyl-4-oxo-cyclohexa-2,5-dien-1-ylidene) propanal **13**	 2,6-ditert-butyl-4-(1-hydroxyethylidene)cyclohexa-2,5-dien-1-one **14**	 3-(3,5-ditert-butyl-4-hydroxy-phenyl)propanal **15**	 nonyl 3-(3,5-ditert-butyl-4-hydroxy-phenyl)propanoate **16**	 ethyl 3-(3,5-ditert-butyl-4-hydroxy-phenyl)propanoate **17**	 DBPA **18**	
Code	**Composition**									
X1	Irganox1076+ 0.5% HAS	**14**	**NO**	**NO**	**NO**	**NO**	**YES**	**YES**	**NO**	**Yes**
X2	0.5%AOPP,0.5%DBPA	**8**	**YES**	**NO**	**YES**	**YES**	**NO**	**NO**	**NO**	**NO**
X3	0.3%AOPP,0.3DBPA	**5**	**YES**	**NO**	**NO**	**YES**	**NO**	**NO**	**NO**	**NO**
X4	0.5%AOTP,0.5%DBPA	**7**	**YES**	**NO**	**YES**	**YES**	**NO**	**NO**	**YES**	**NO**
X6	0.5%DBPA,0.5%Chim944	**4**	**YES**	**YES**	**YES**	**YES**	**NO**	**NO**	**NO**	**NO**
X7	0.5%AOPP,0.5%Irg1076	**4**	**NO**	**NO**	**NO**	**NO**	**NO**	**NO**	**NO**	**NO**
X8	0.5AOTP,0.5%Irg1076	**5**	**NO**	**NO**	**NO**	**NO**	**NO**	**NO**	**NO**	**NO**
X11	0.5%AOPP,0.5%Irg1010	**3**	**NO**	**NO**	**NO**	**NO**	**NO**	**NO**	**NO**	**NO**

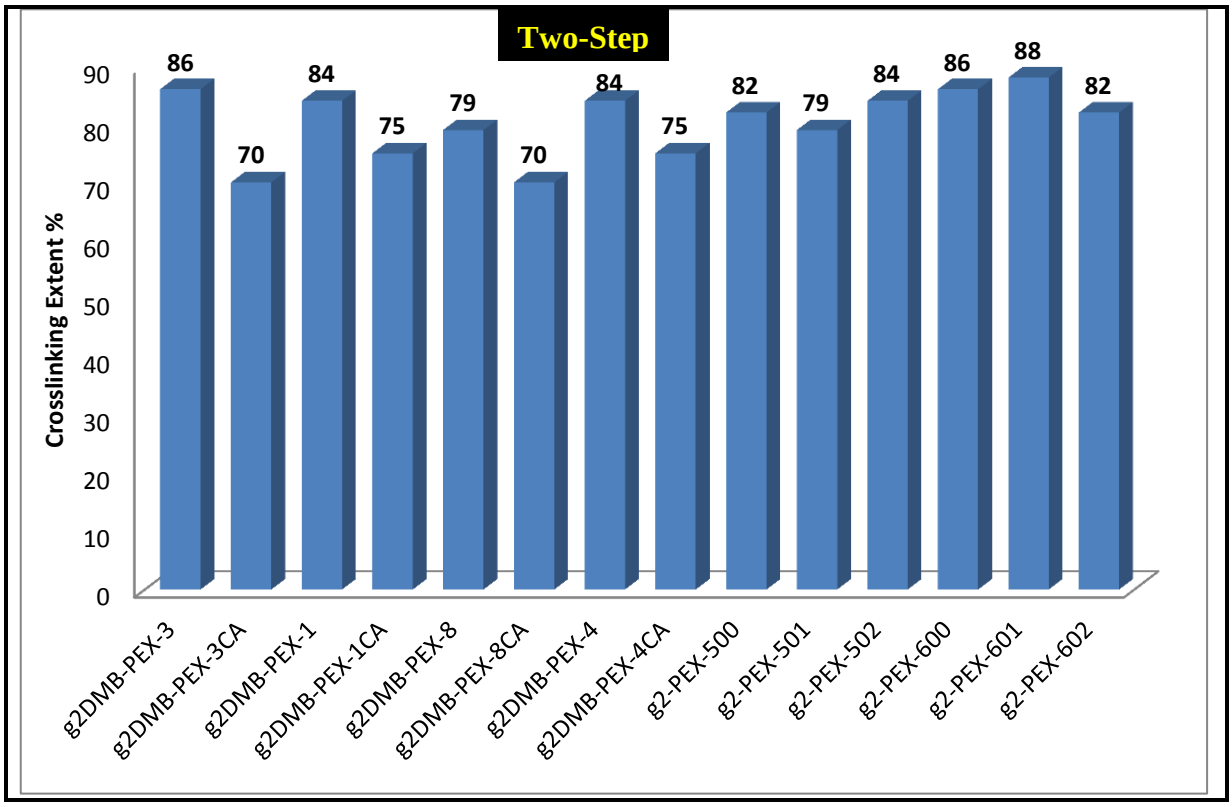


Figure 4. 1: crosslinking extent of PEX_a produced using two-step methodology**, see also Table 4.3 and see scheme 4.1 C.**

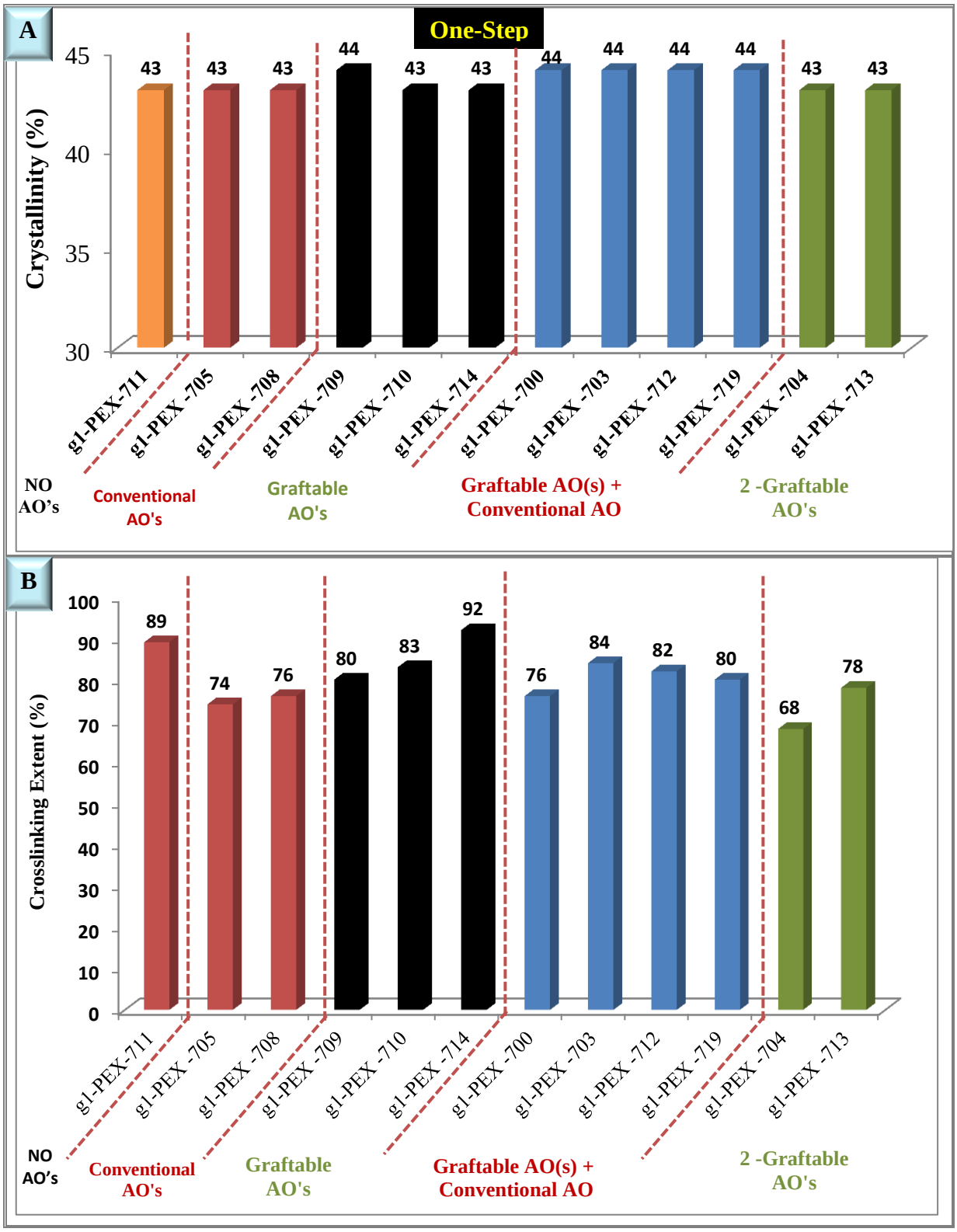


Figure 4. 2 : Analysis of **One-Step grafting and crosslinking process** of PE_L**, see Scheme 4.2 samples C and E**

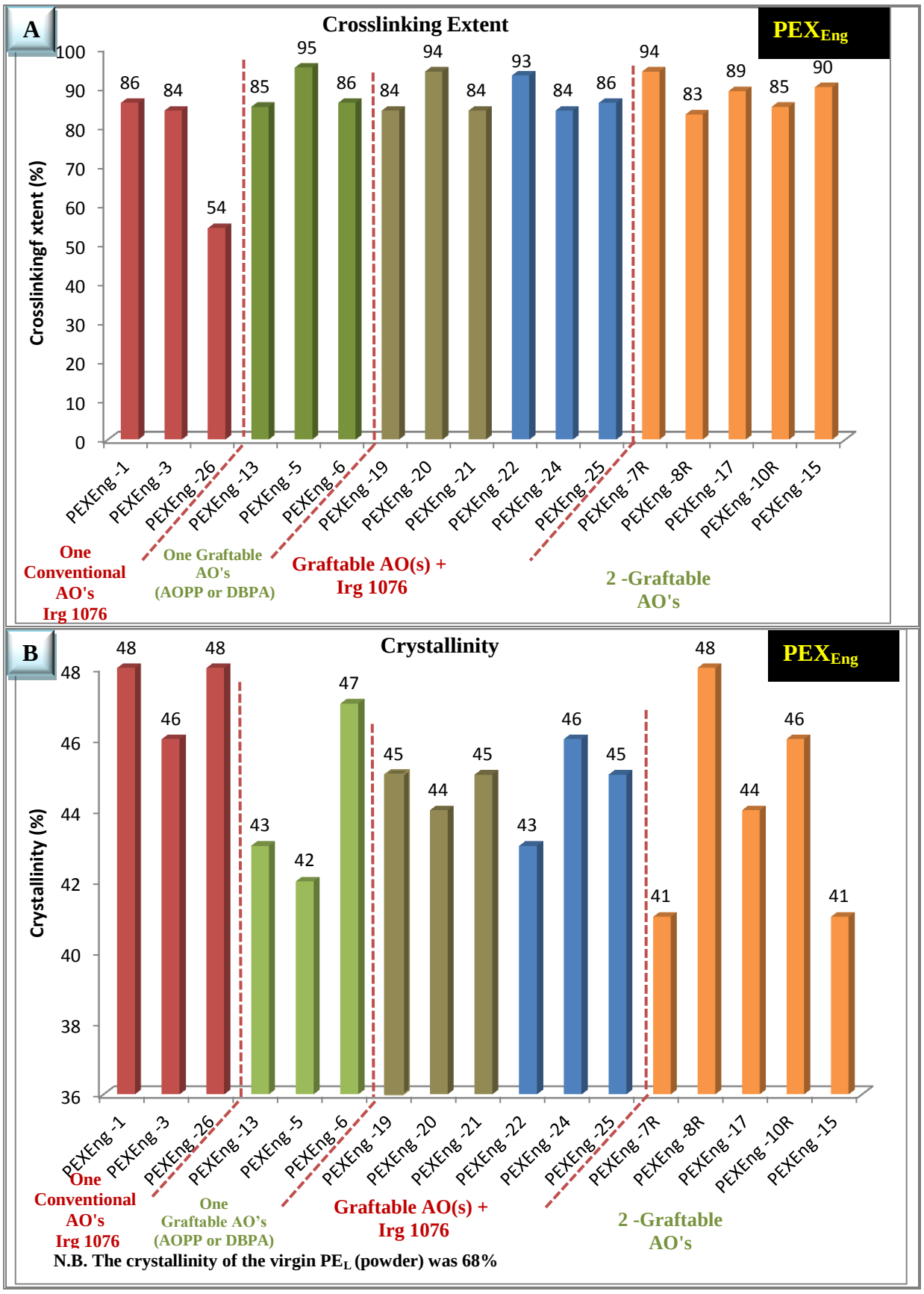


Figure 4. 3 : Crosslinking (A) and crystallinity (B) of PEX_{Eng} pipe samples (films of 150-250µm thickness), see **Scheme 4.4 and Table 4.5** for composition

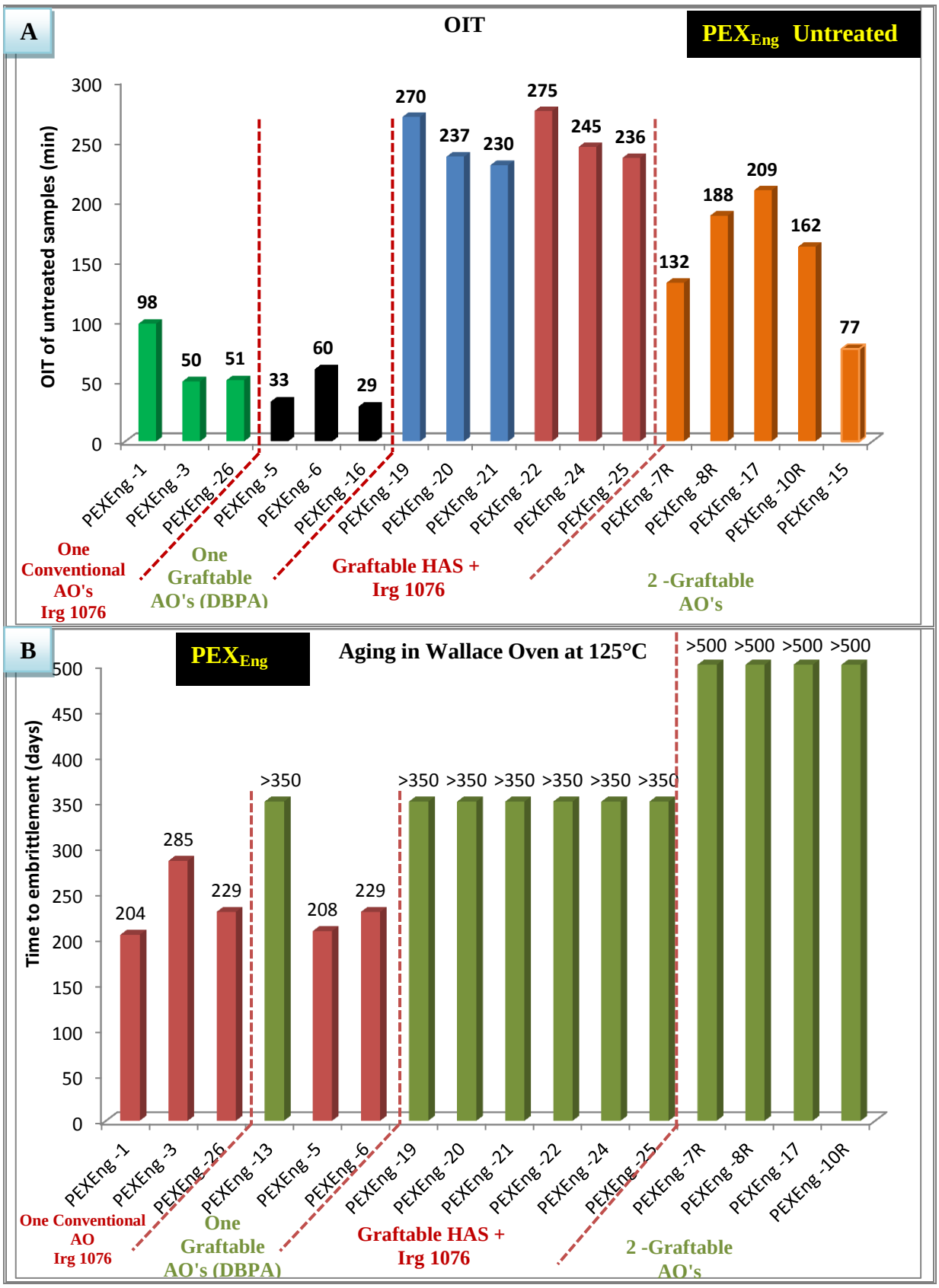


Figure 4. 4 : Thermal stability by DSC-OIT (A) and by oven aging (B) of untreated PEX_{Eng} pipes (see Table 4.5), see **Scheme 4.4.**

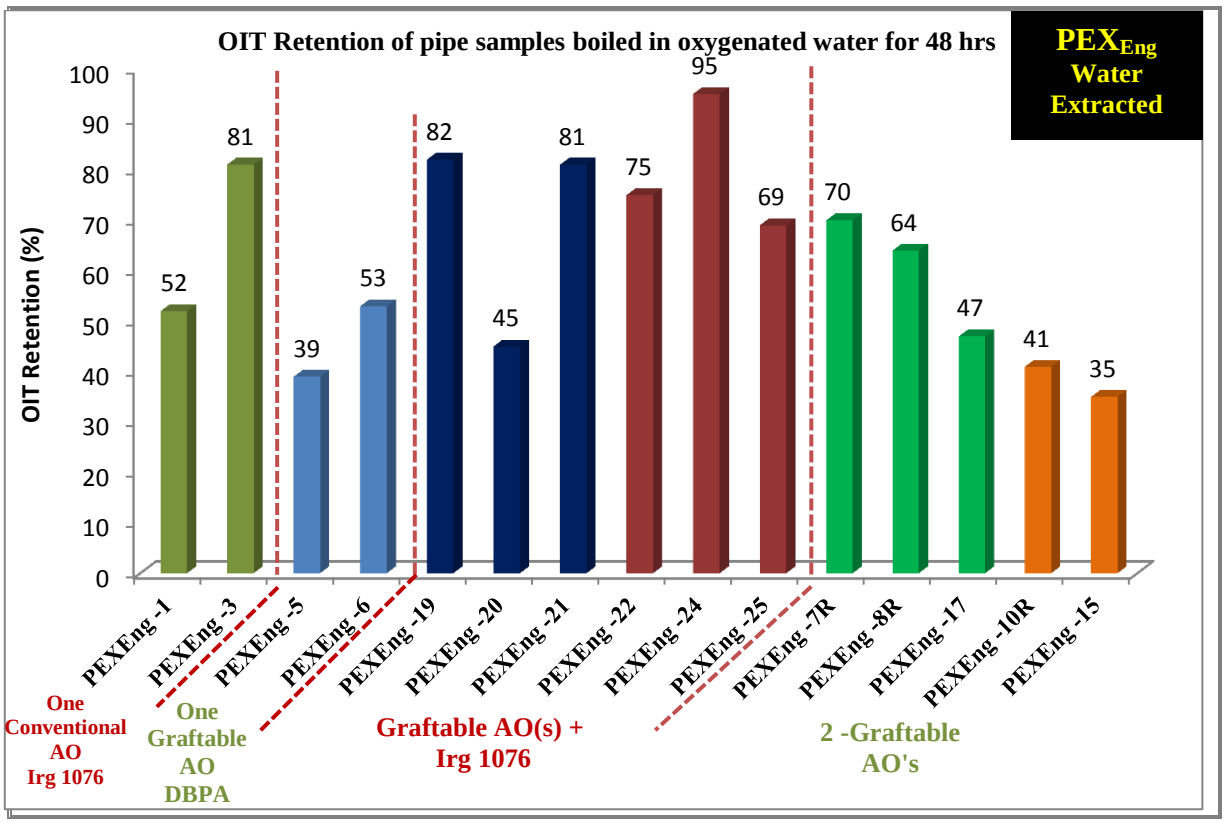


Figure 4. 5 : OIT retention in **PEX$_{Eng}$ pipes** extracted in **oxygenated water** for 48h

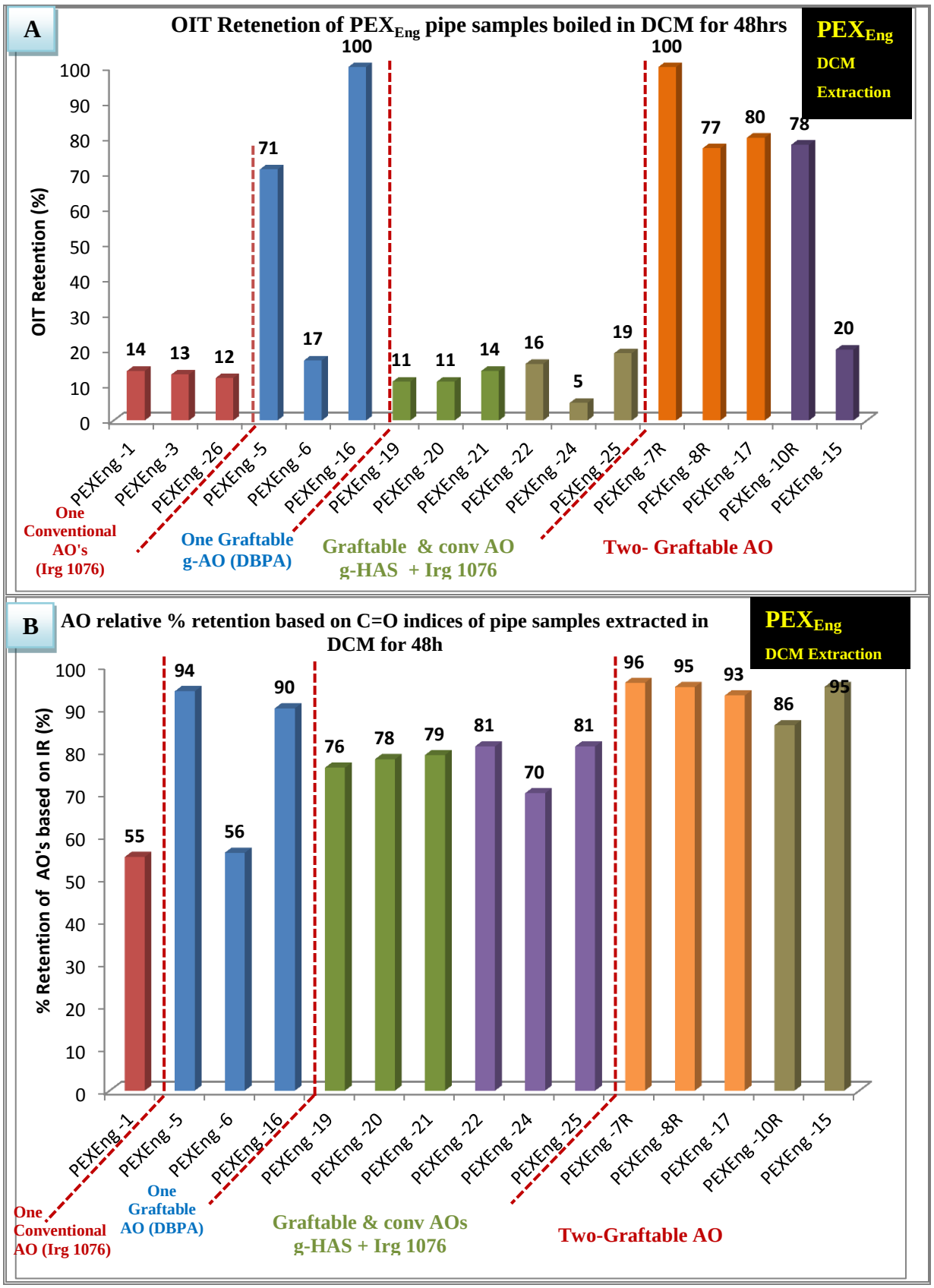


Figure 4. 6: OIT retention and AO retention based on carbonyl indices for **PEX$_{Eng}$ pipes** extracted in DCM for 48h, see Table 4.5 for composition.

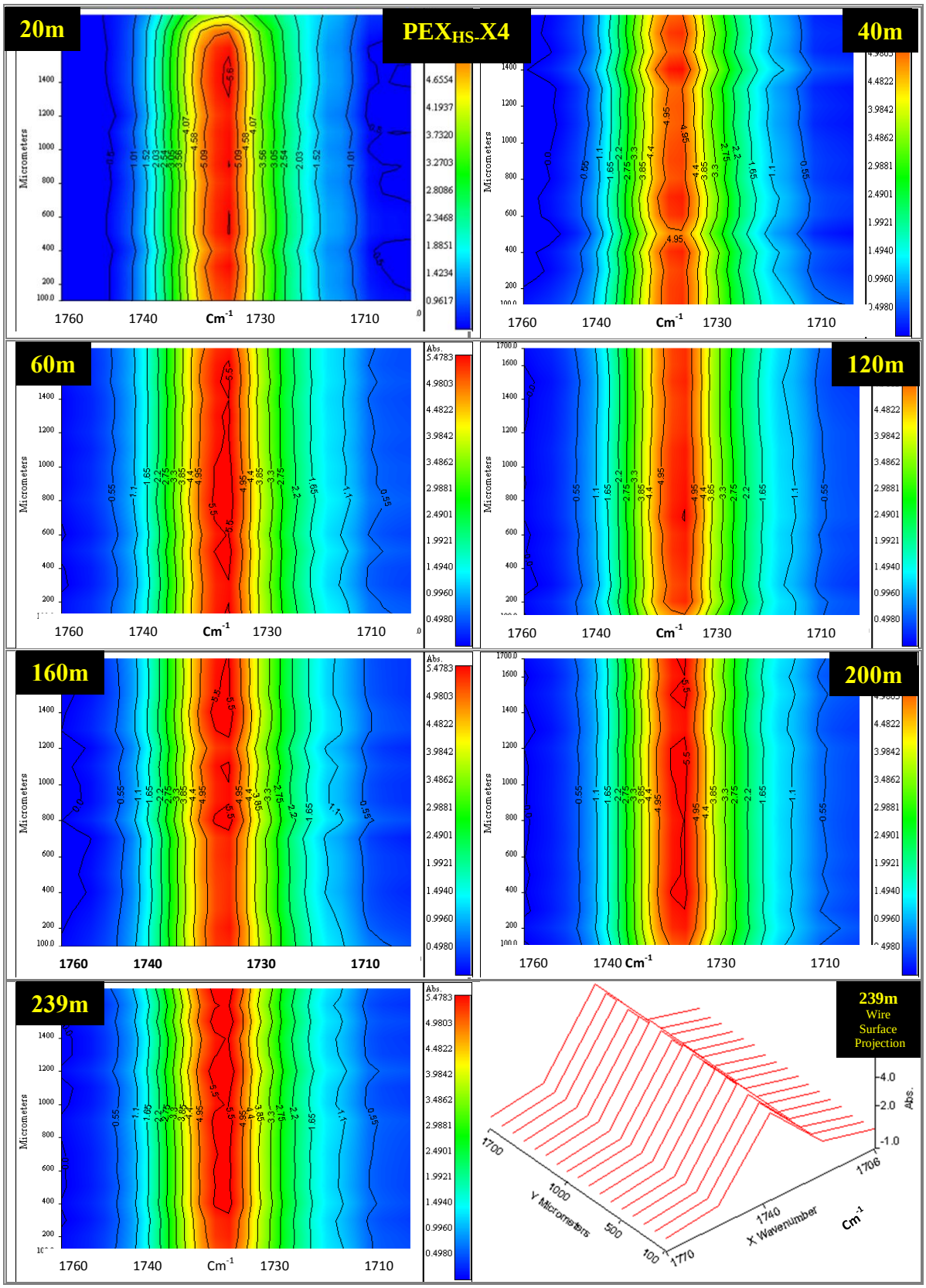


Figure 4. 7:FTIR-microscope of carbonyl region represented by false colour maps with contours (*colour denotes the intensity of >C=O peak*) -line scan in the radial direction for pipe **PEX_{HS}-X4 (DBPA + AOTP)** measured on microtomed films) using Mic-FTIR. The AO concentration (via the carbonyl index of the AO) illustrated is taken from different lengths of a 240m pipe length.

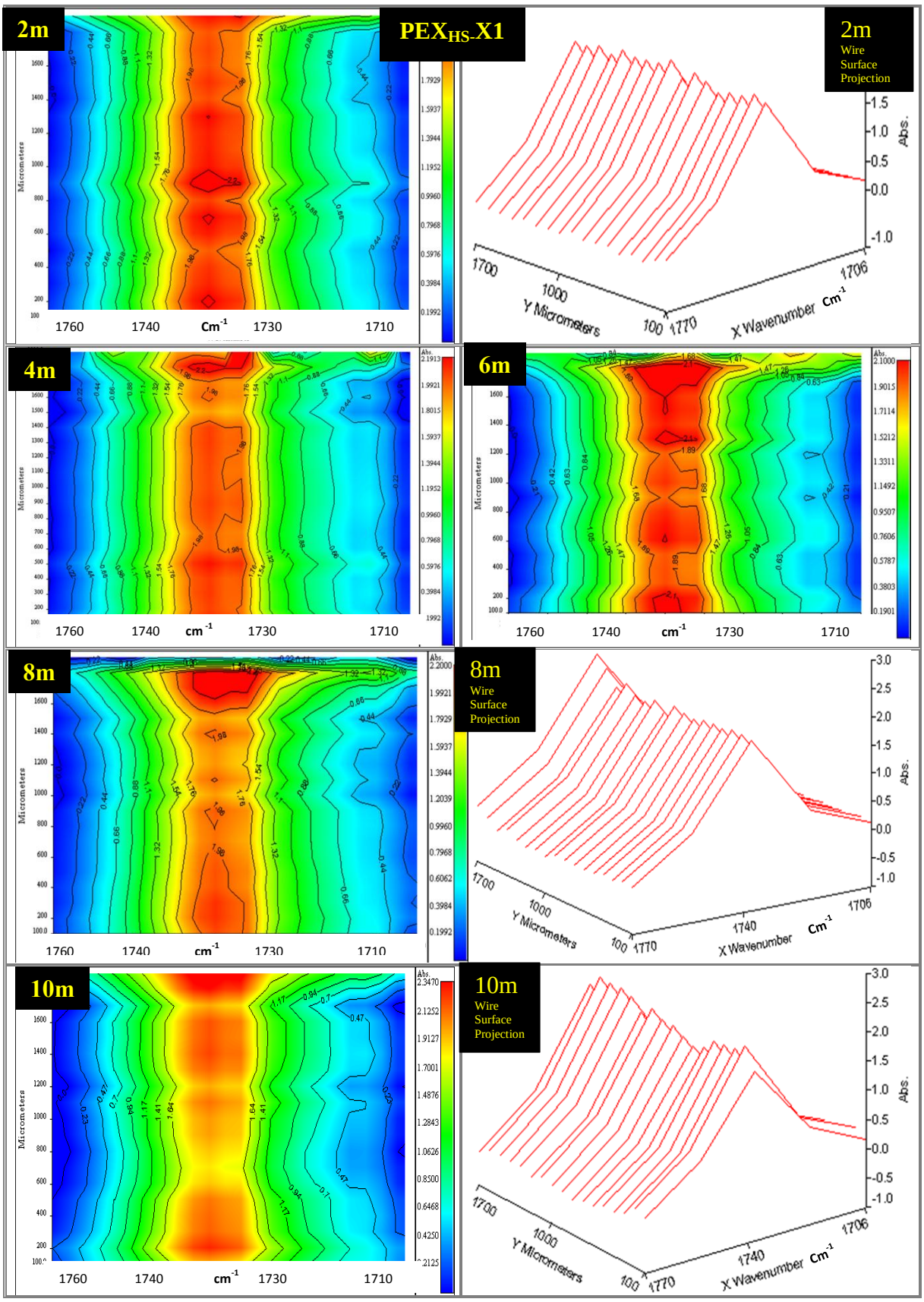


Figure 4. 8: FTIR-microscope of carbonyl region represented by false colour map with contours (*colour denotes the intensity of >C=O peak*) -line scan in the radial direction for pipe **PEX_{HS}-X1** (Irganox 1076 and commercial HAS "undisclosed") measured on microtomed films) using Mic-FTIR. The AO concentration (via the carbonyl index of the AO) illustrated is taken from a 10m pipe length

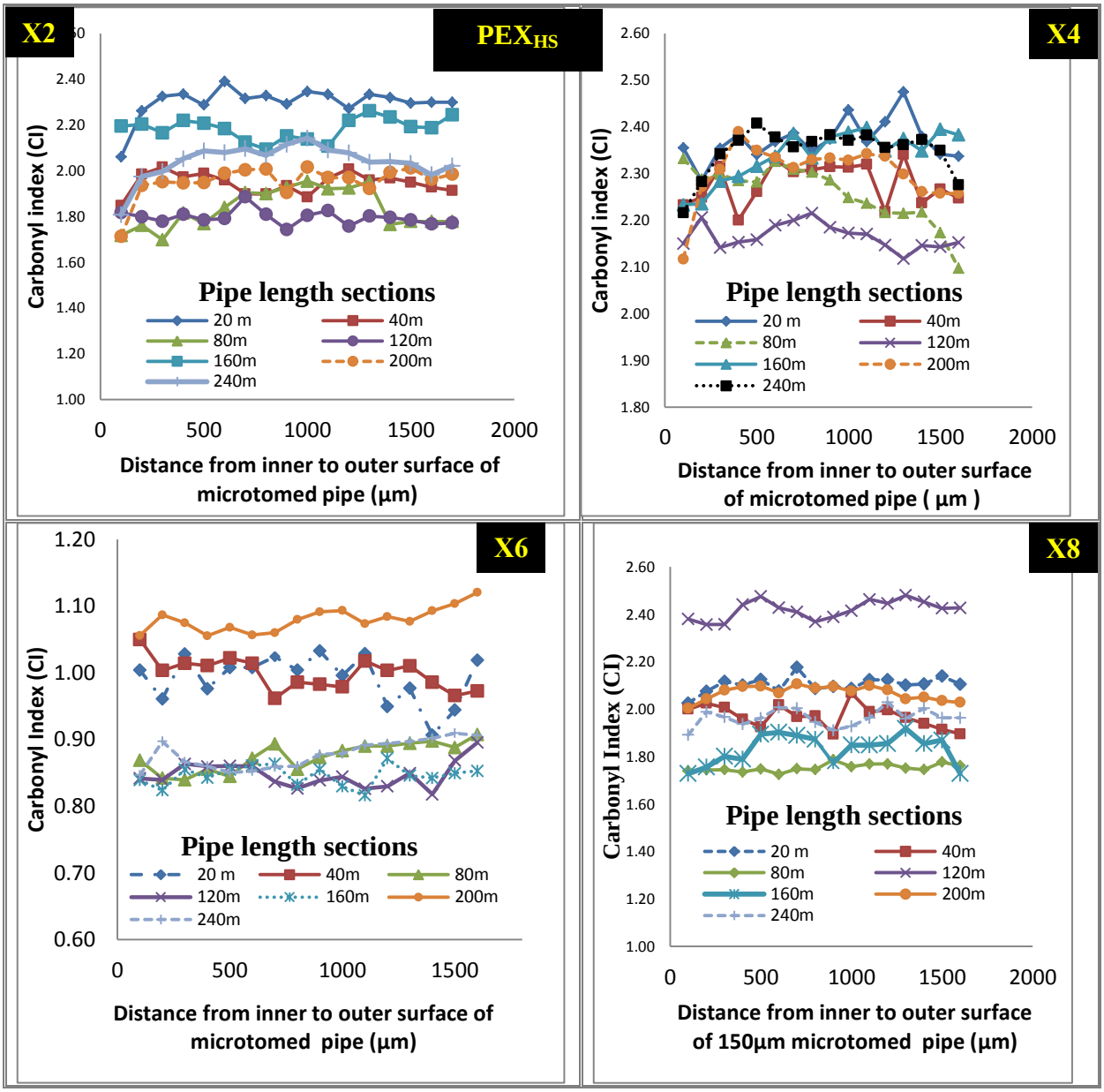


Figure 4. 9: Carbonyl index (obtained from FTIR-microscope line scans) as measurement of AO distribution across 20-240m of microtomed **PEX_{HS} pipes** in the radial direction (from inner to outer surface), of different sections taken from across a 240m pipes lengths for different pipes see **Table 4.6 and Scheme 4.6,**for pipe formulations and sampling.

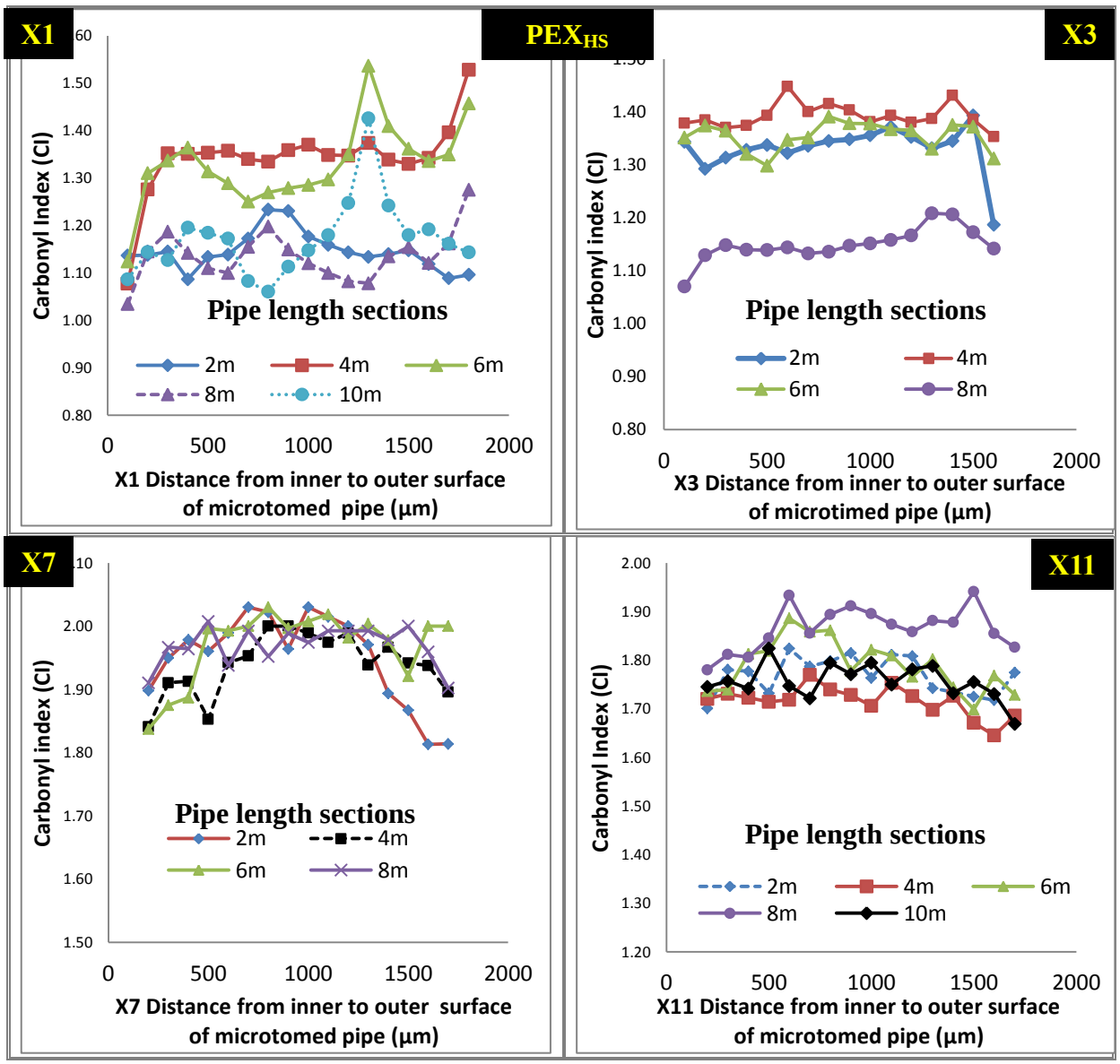


Figure 4. 10: Carbonyl index (obtained from FTIR-microscope line scans) as measurement of AO distribution across 2-10m of microtomed **PEX_{HS} pipes** in the radial direction (from inner to outer surface), of different sections taken from across a 10m pipe length for different pipes see Table 4.6 for formulations and **Scheme 4.6** for sampling.

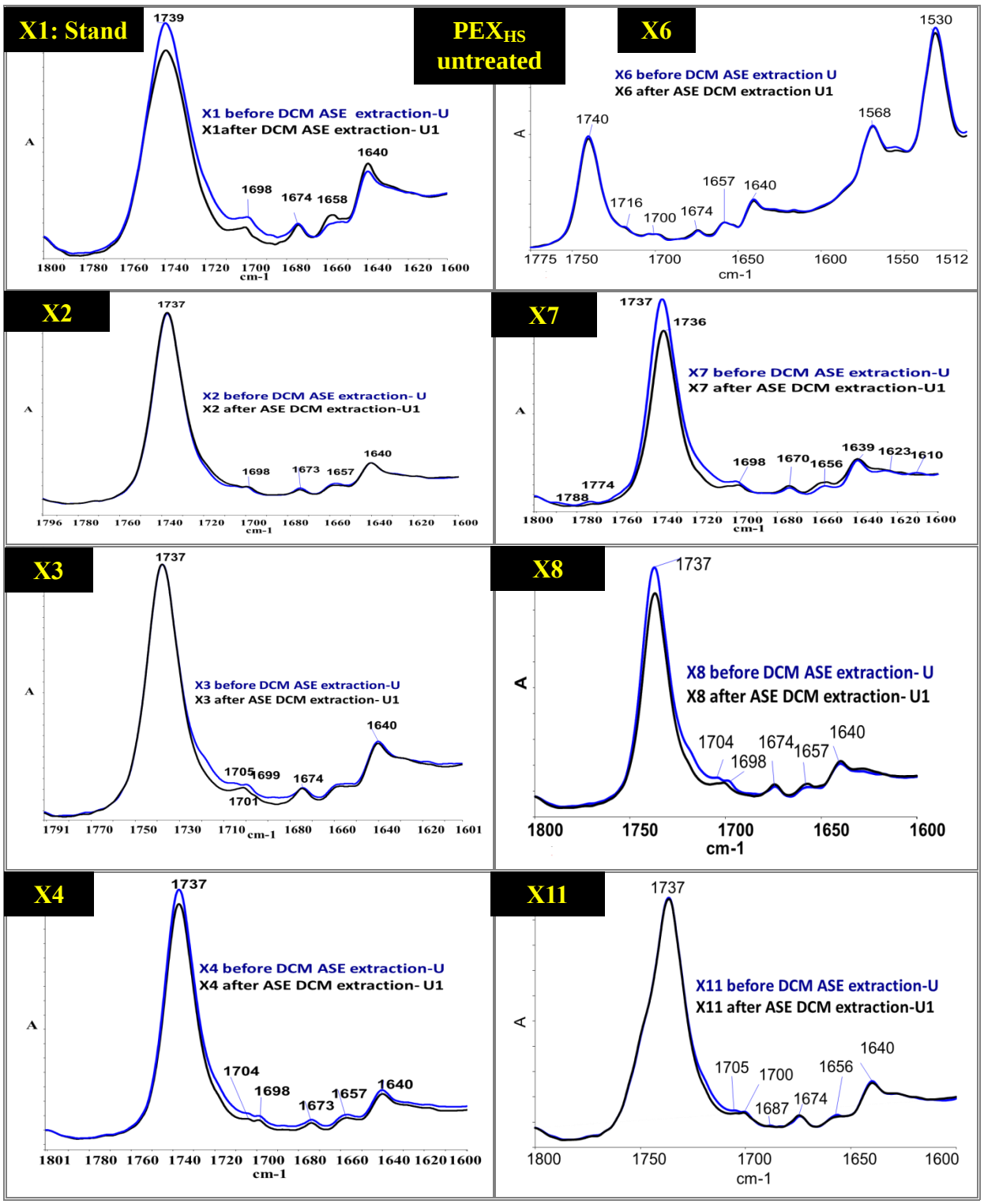


Figure 4. 11: FTIR of PEX_{HS} (~250µm) which were extracted with DCM solvent mixture by ASE (DCM:cyclohexane at 95:5 w/w: at 70°C, 2000psi,5 cycle, cycle time 30 mins) before (**blue**) and after (**black**) extraction, see **Table 4.6** for formulations and **Scheme 4.6 Route I** for samples U and U1.

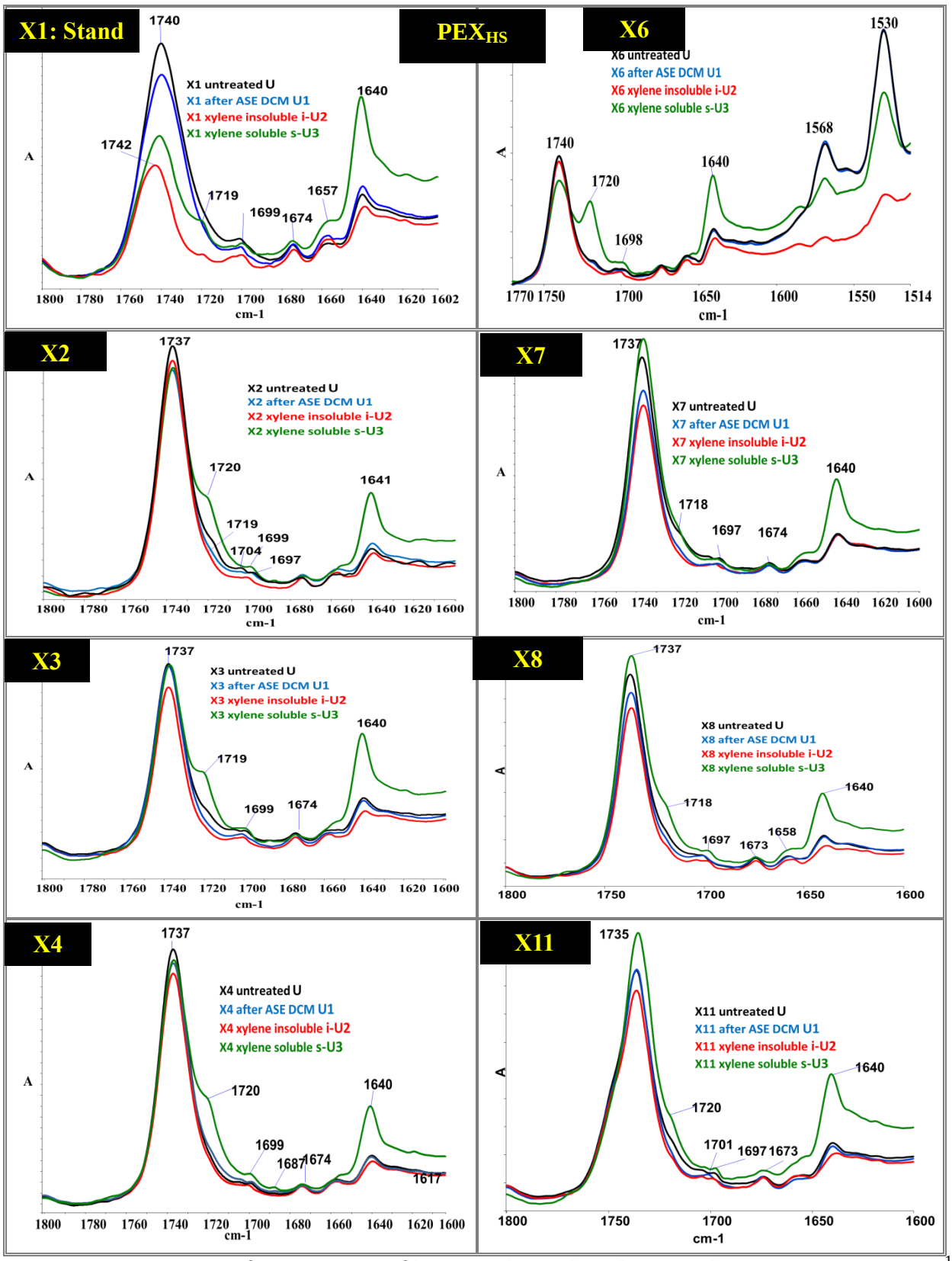


Figure 4. 12: FTIR of **PEX_{HS} pipe** films in the carbonyl region between 1800-1600cm^{-1} before (samples "**U**"), after ASE-DCM extraction system (samples "**U1**") and after subsequent xylene extraction in the sequential DCM-Xylene extraction process (samples " **i-U2"- is** xylene insoluble and **"s-U3"** is xylene soluble fractions, see **Scheme 4.7, Route II and III**)

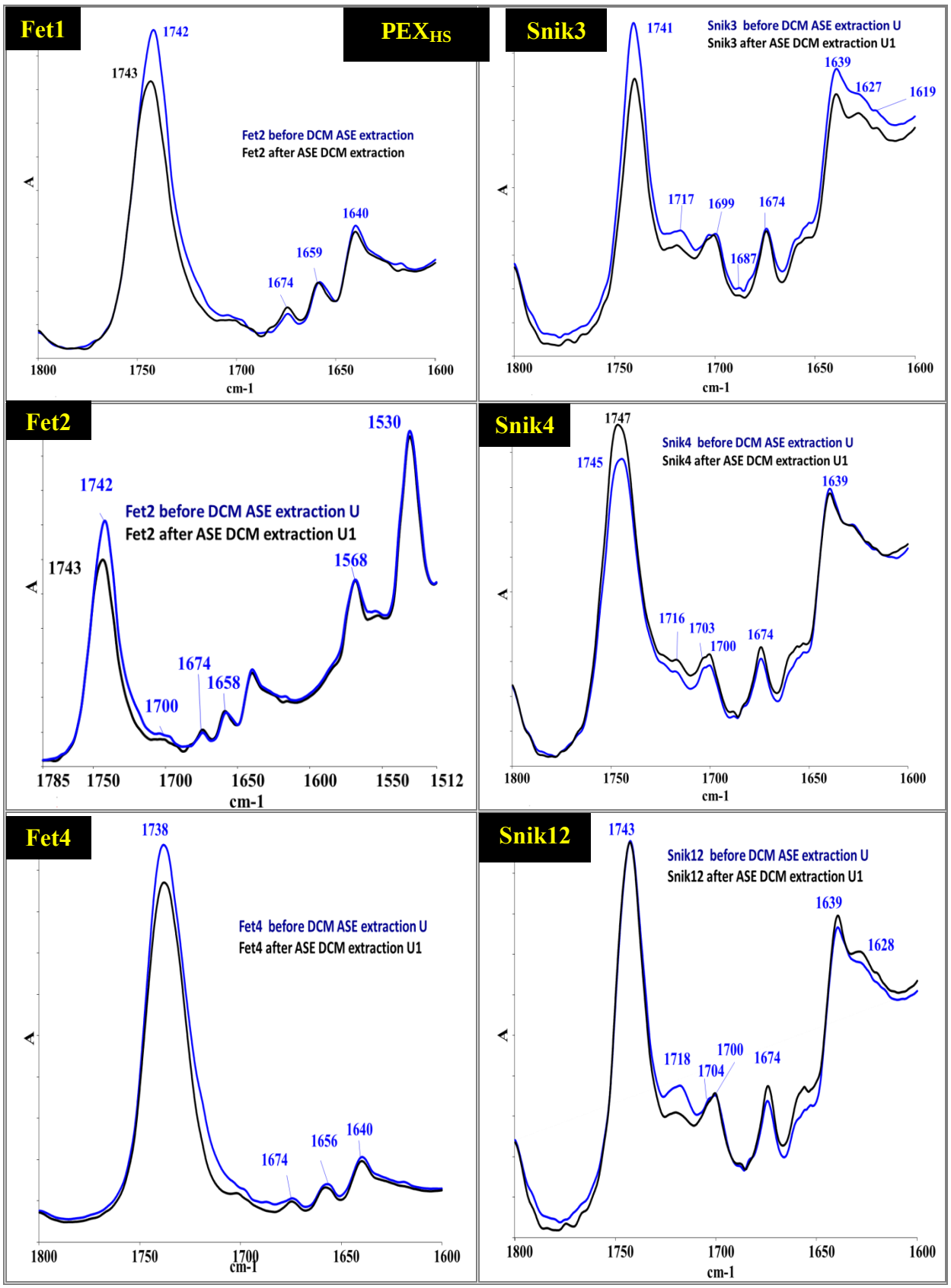


Figure 4. 13: FTIR of **PEX_{HS} pipe** films (~250µm), which were extracted with DCM solvent mixture by ASE ASE-DCM (DCM:cyclohexane at 95:5 w/w: at 70°C, 2000psi,5 cycle, cycle time 30 mins) extracted samples before (**blue**) and after (**black**)extraction in the region of 1800-1600cm^{-1}, see **Table 4.6 for** formulations and **Scheme 4.7, Route 1** for sampling.

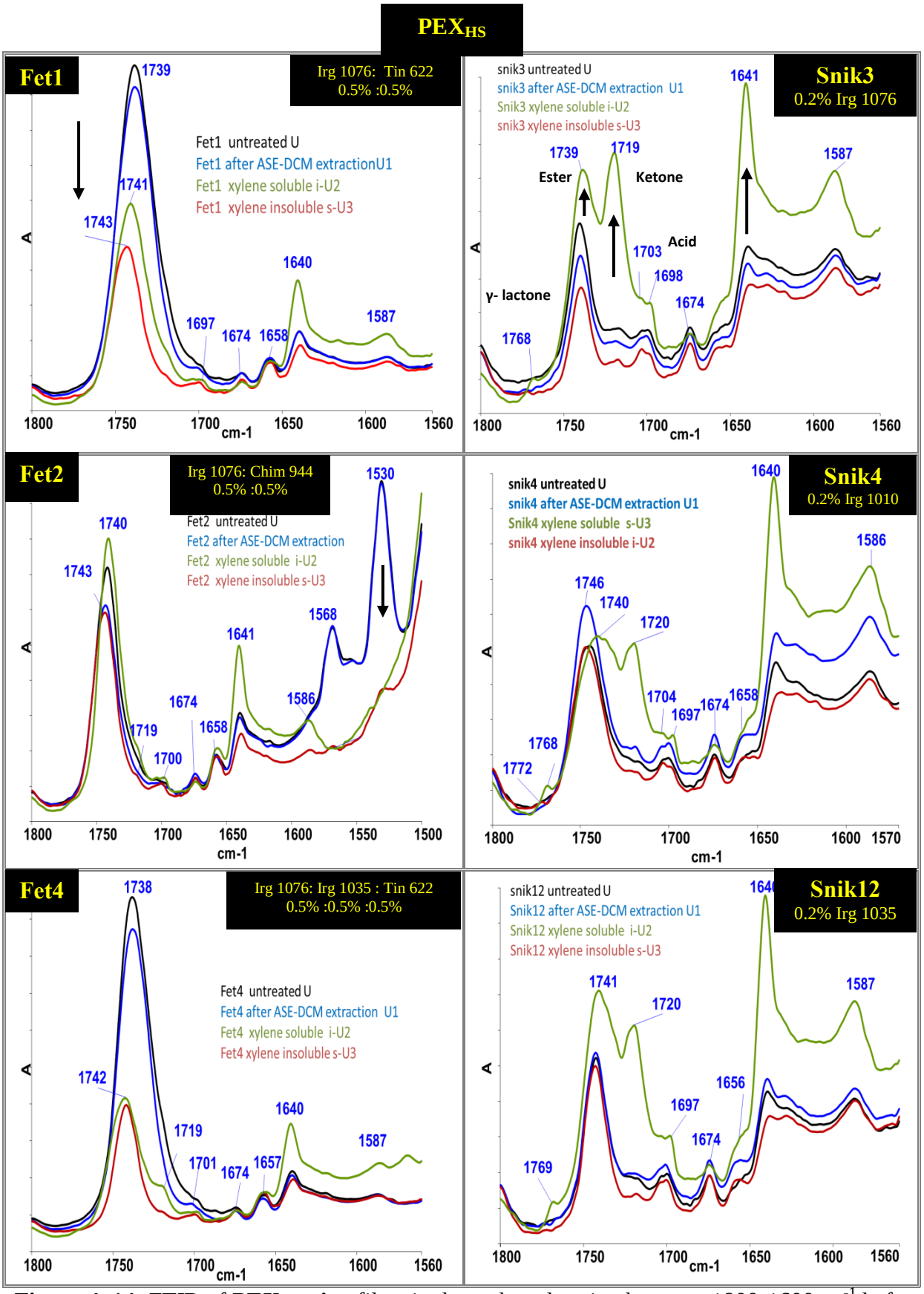


Figure 4. 14: FTIR of **PEX_{HS} pipe** films in the carbonyl region between 1800-1600cm^{-1} before (samples "**U**") and after ASE-DCM extraction (samples "**U1**") and after subsequent xylene extraction in sequential DCM-Xylene extraction process (samples **" i-U2"** - xylene insoluble and **"s-U3"** xylene soluble fraction, see **Scheme 4.7 Route II and III**

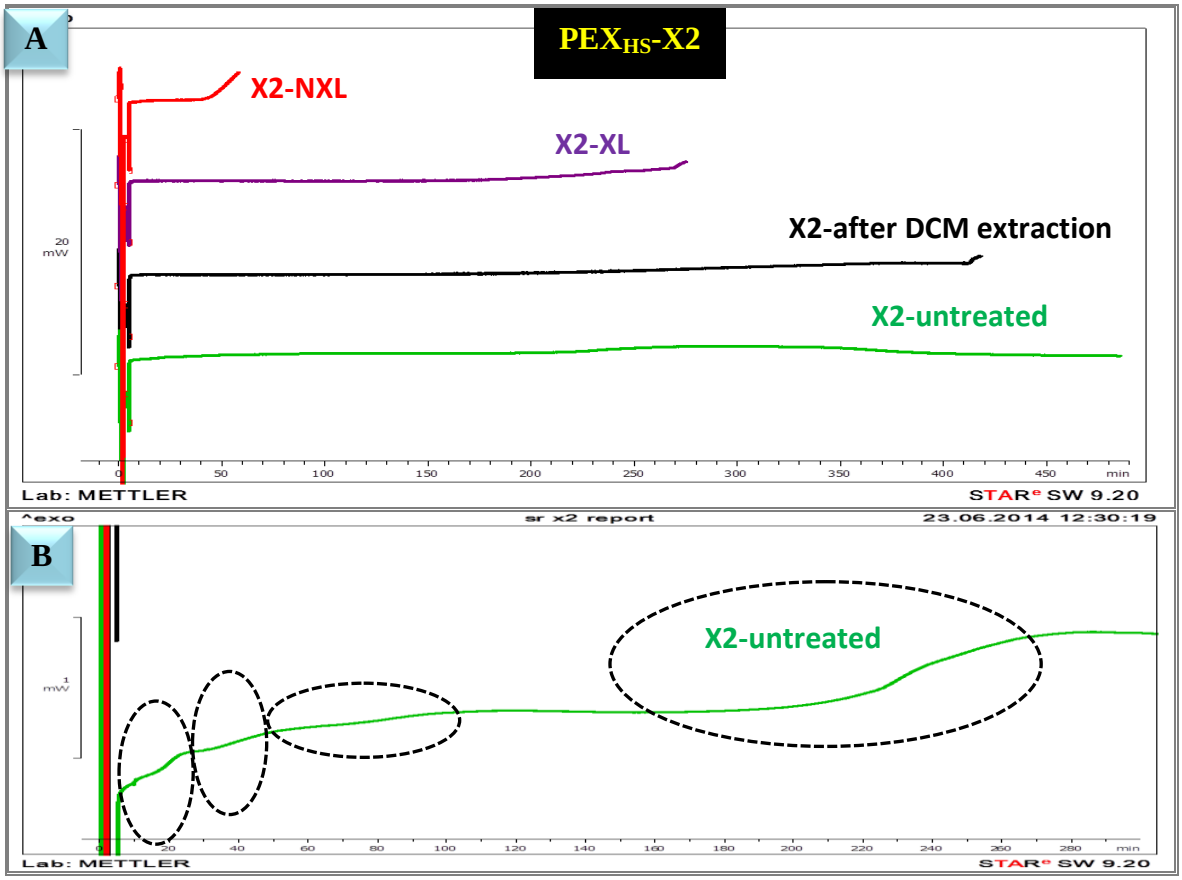


Figure 4. 15: OIT curves for Pipe **PEX_{HS}-X2** (green is untreated, **black is after DCM extraction**, **purple is crosslinked sample** and red non crosslinked sample (after xylene extraction), see **Scheme 4.7.**

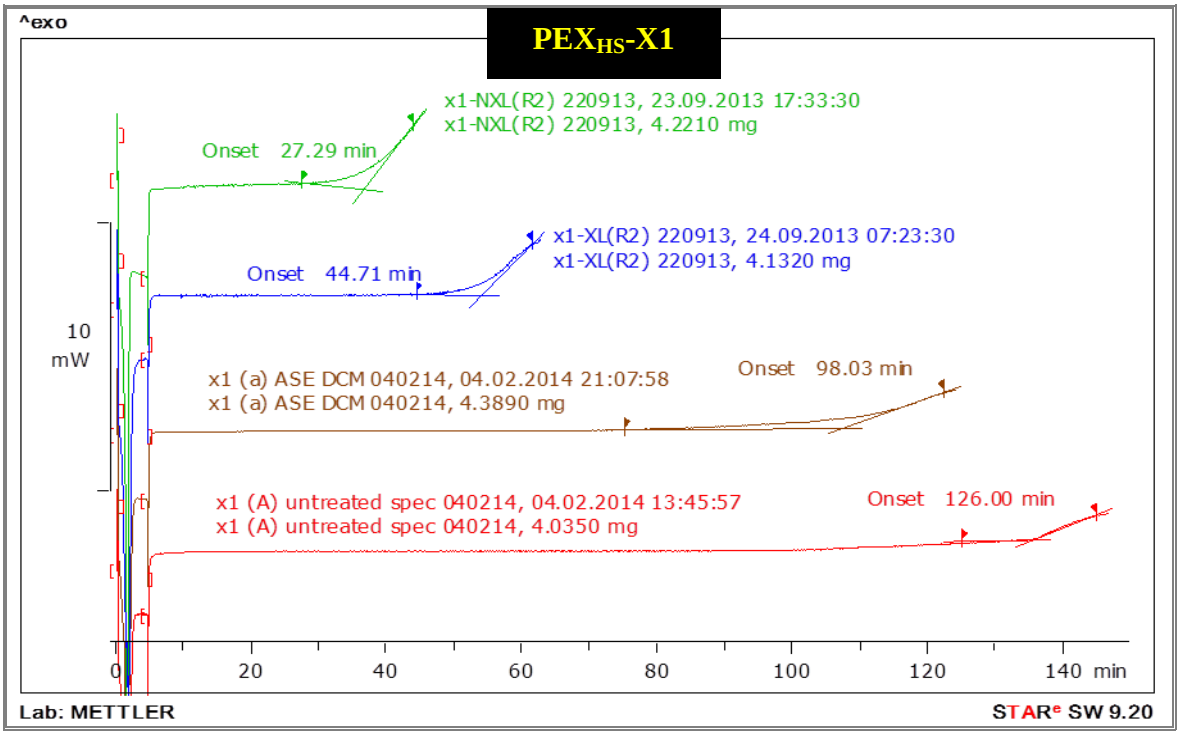


Figure 4. 16: OIT curves for Pipe PEX_{HS}-X1(red is untreated, brown is after DCM extraction, blue is crosslinked sample and green is non crosslinked sample (after xylene extraction) **see Scheme 4.7**.

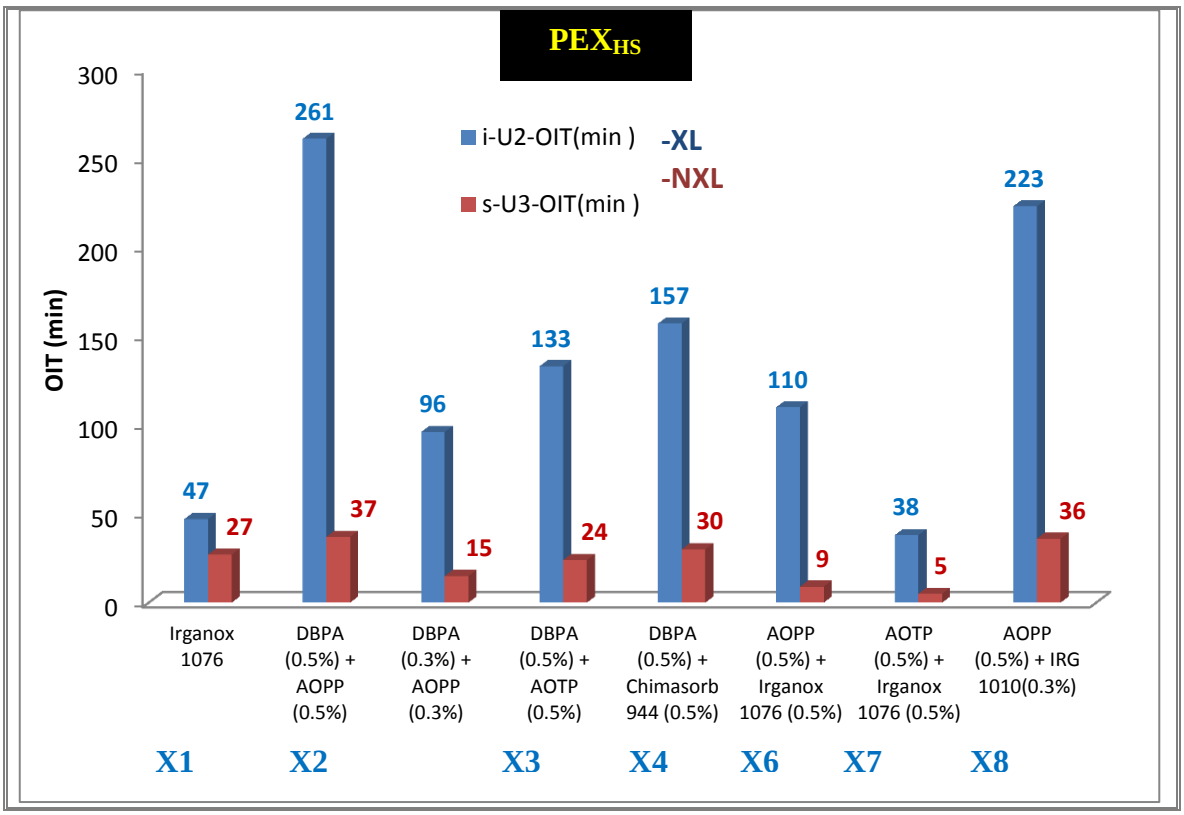


Figure 4. 17: OIT of crosslinked (XL) and non-Crosslinked (NXL) films of **PEX_{HS} pipes** after xylene extraction, see **Scheme 4.7**.

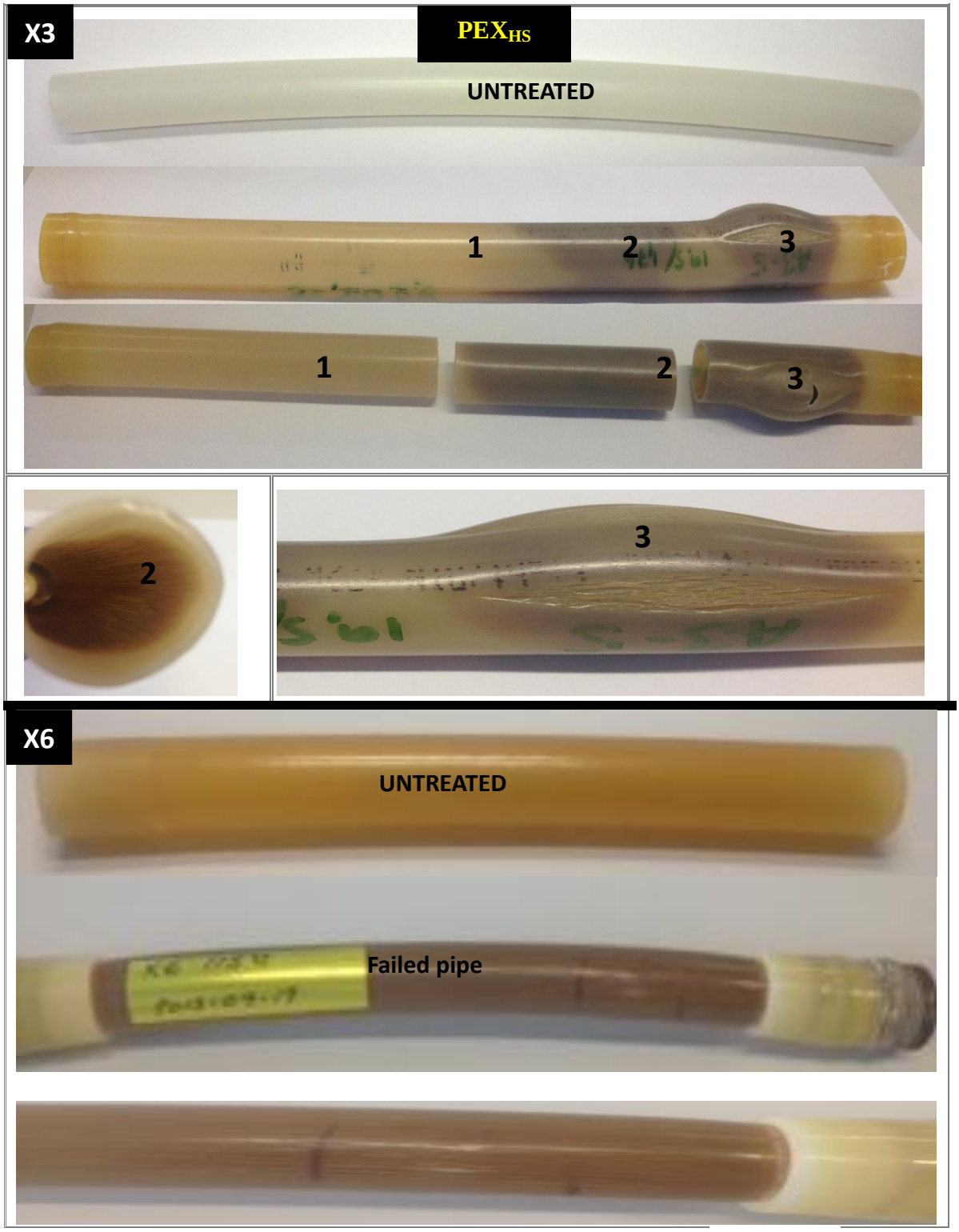


Figure 4. 18: Picture of untreated **PEX_{HS}-X3** pipe and **PEX_{HS}-X6** failed under hydrostatic pressure tested at 115°C at 2023hr and 4228hr, respectively

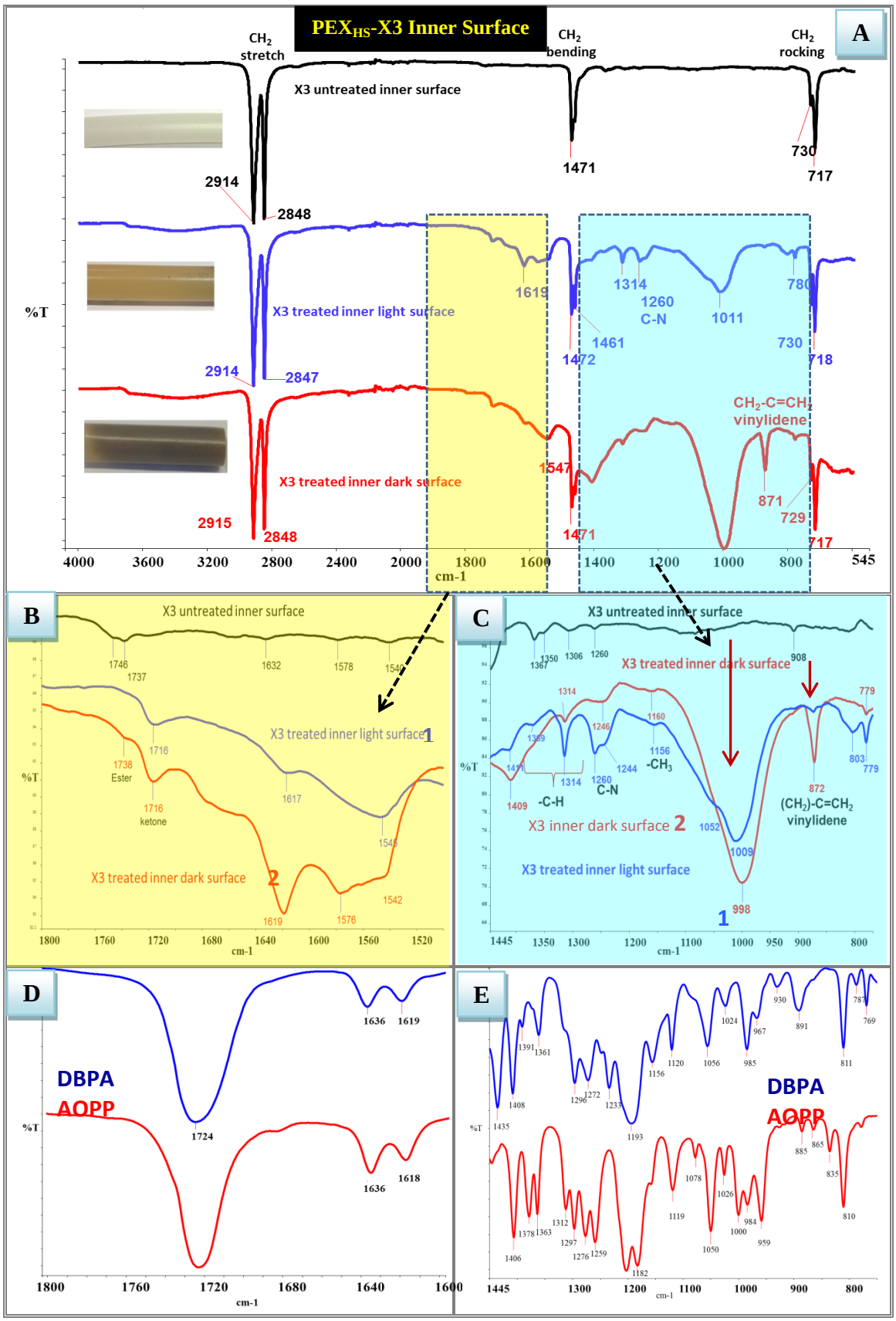


Figure 4. 19: FTIR-ATR spectra of inner surfaces of untreated hydrostatically failed PEX_{HS}-X3 pipe the ATR was taken from surfaces taken from section 1 &2 after 2023hr of hydrostatic test, See **Figure 4.23** for visual appearance**.** In D and E the FTIR spectra of the neat antioxidants is also shown.

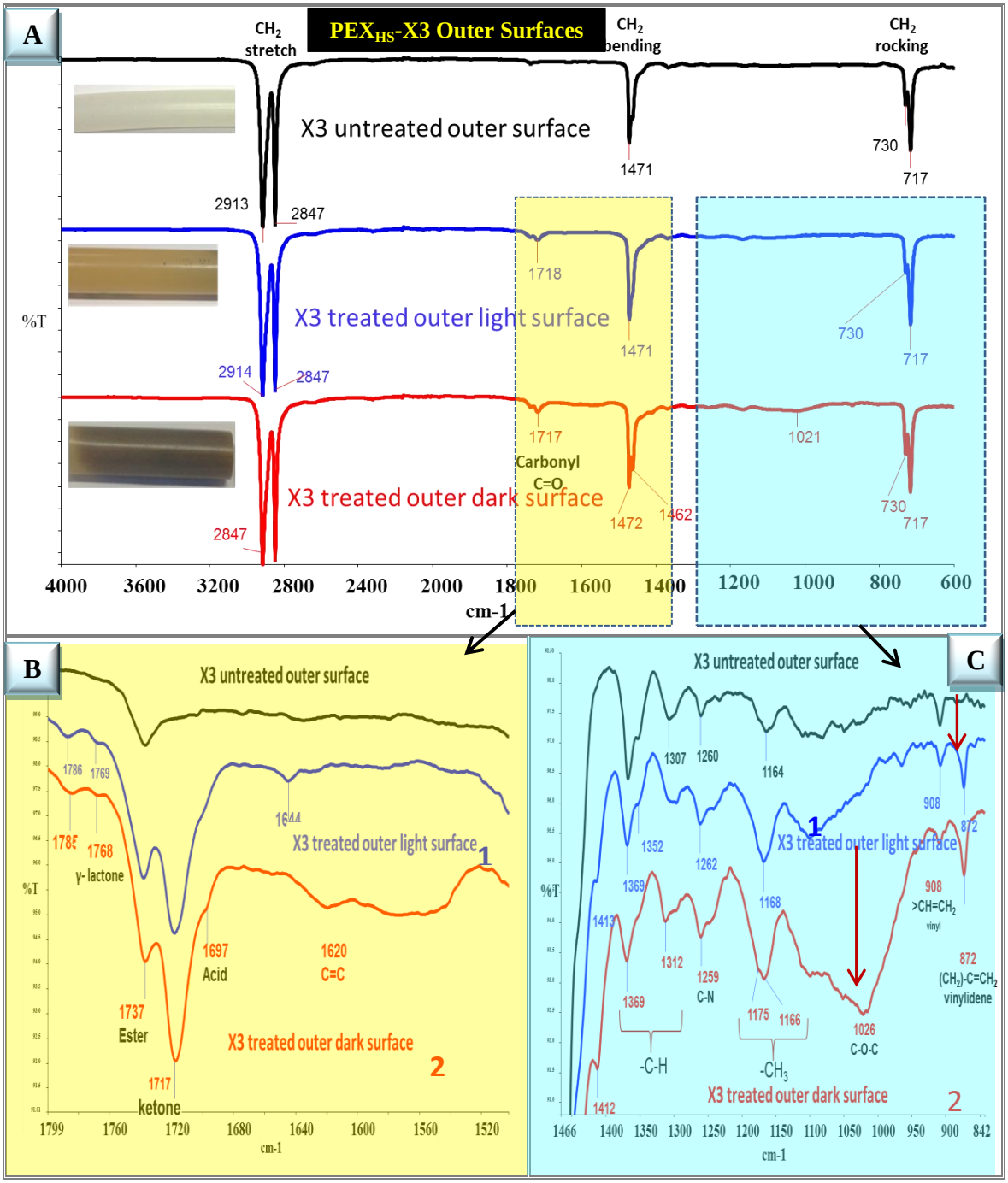


Figure 4. 20: FTIR-ATR spectra of **outer surfaces** of **PEX$_{HS}$-X3** pipe, both the untreated and the hydrostatically failed surfaces taken from sections 1 &2 (after 2023h) of hydrostatic test, See **Figure 4.23** for visual appearance.

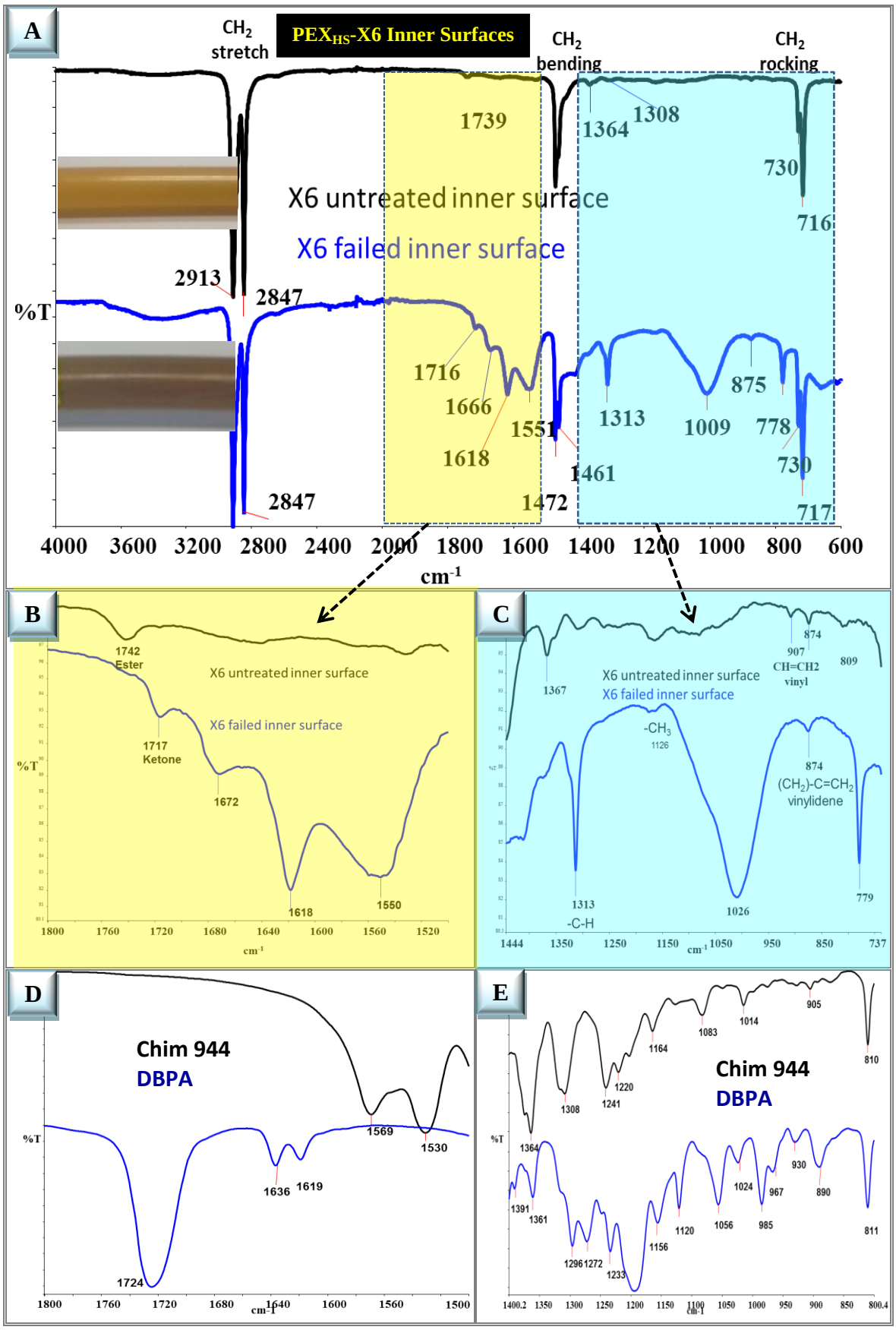


Figure 4. 21:FTIR-ATR spectra of inner surfaces of untreated and hydrostatically failed (4028hr) **PEX$_{HS}$-X6** pipe, , See **Figure 4.23** for visual appearance.

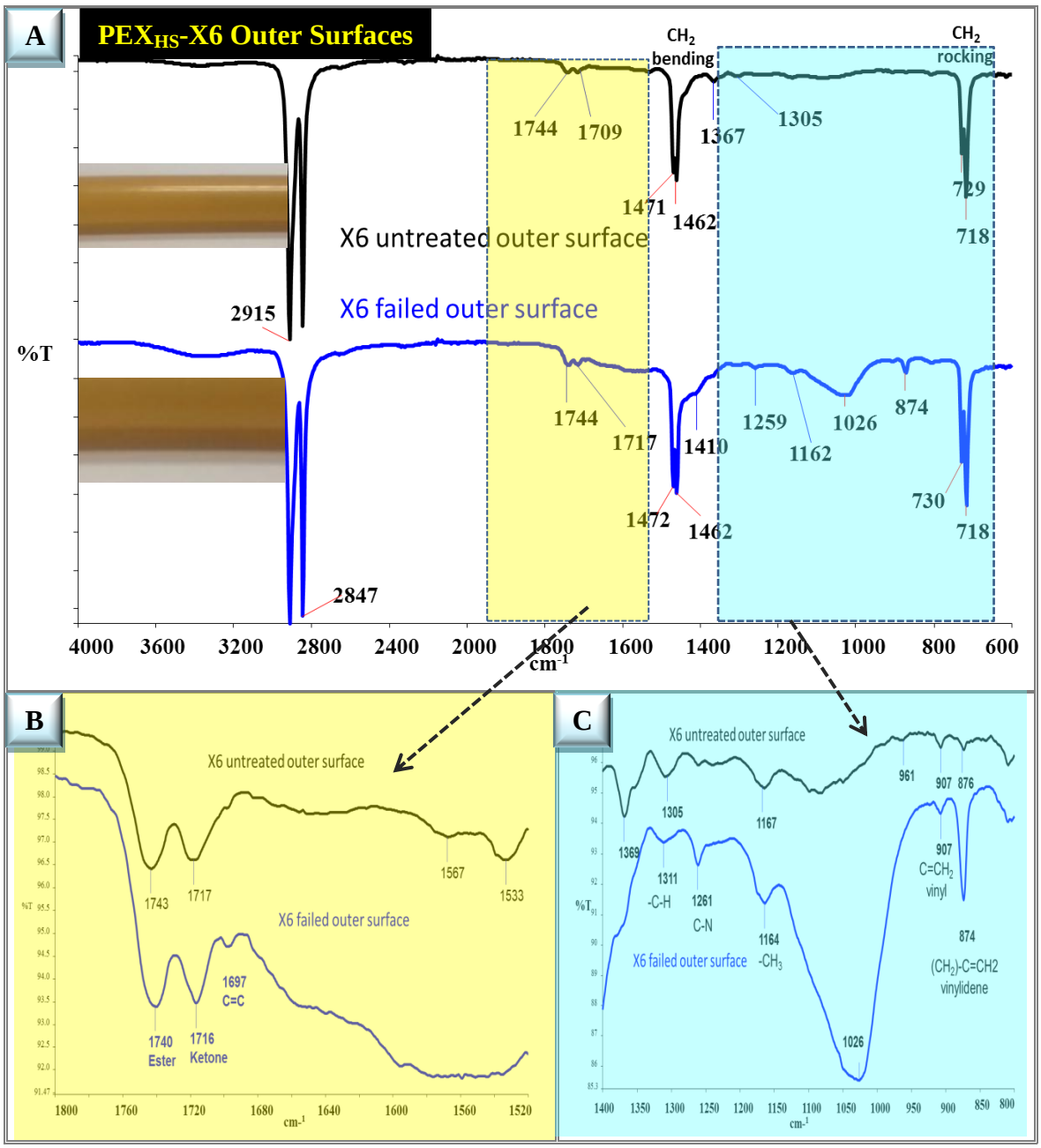


Figure 4. 22: FTIR-ATR spectra of outer surfaces of untreated and hydrostatically failed (4028hr) **PEX$_{HS}$-X6** pipe , See **Figure 4.23** for visual appearance.

.

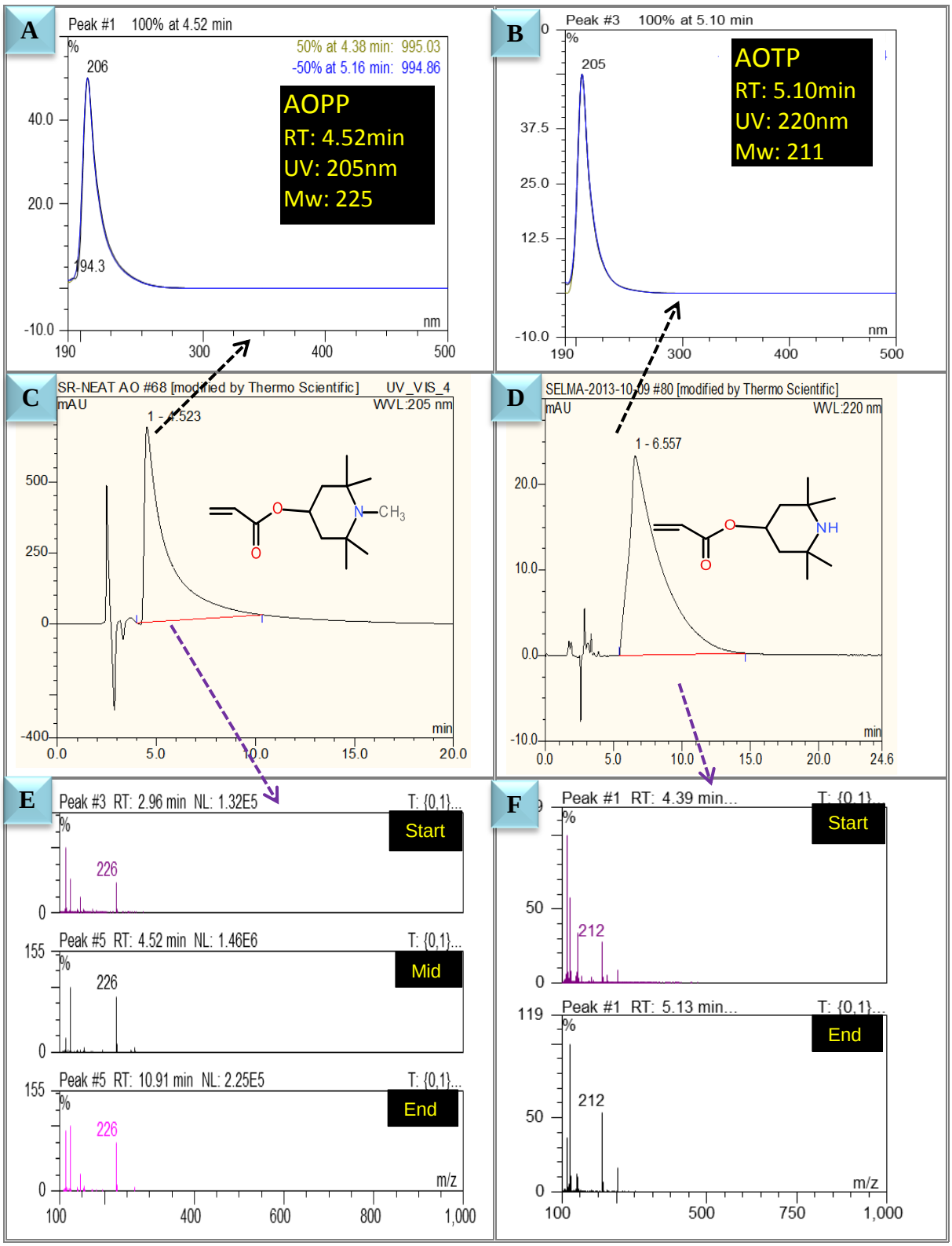


Figure 4. 23: HPLC-UV and mass spectra of **neat AOPP and AOTP** , **A & B** are UV spectra, **C & D** are the LC chromatograms and **E & F** are the Mass spectra of AOPP and AOTP respectively. *(mobile phase of 90% ACN:5% THF:5%MEOH, 20°C oven temperature, flow rate 1ml/min, APCI positive ion mode, Probe temperature:600°C)*

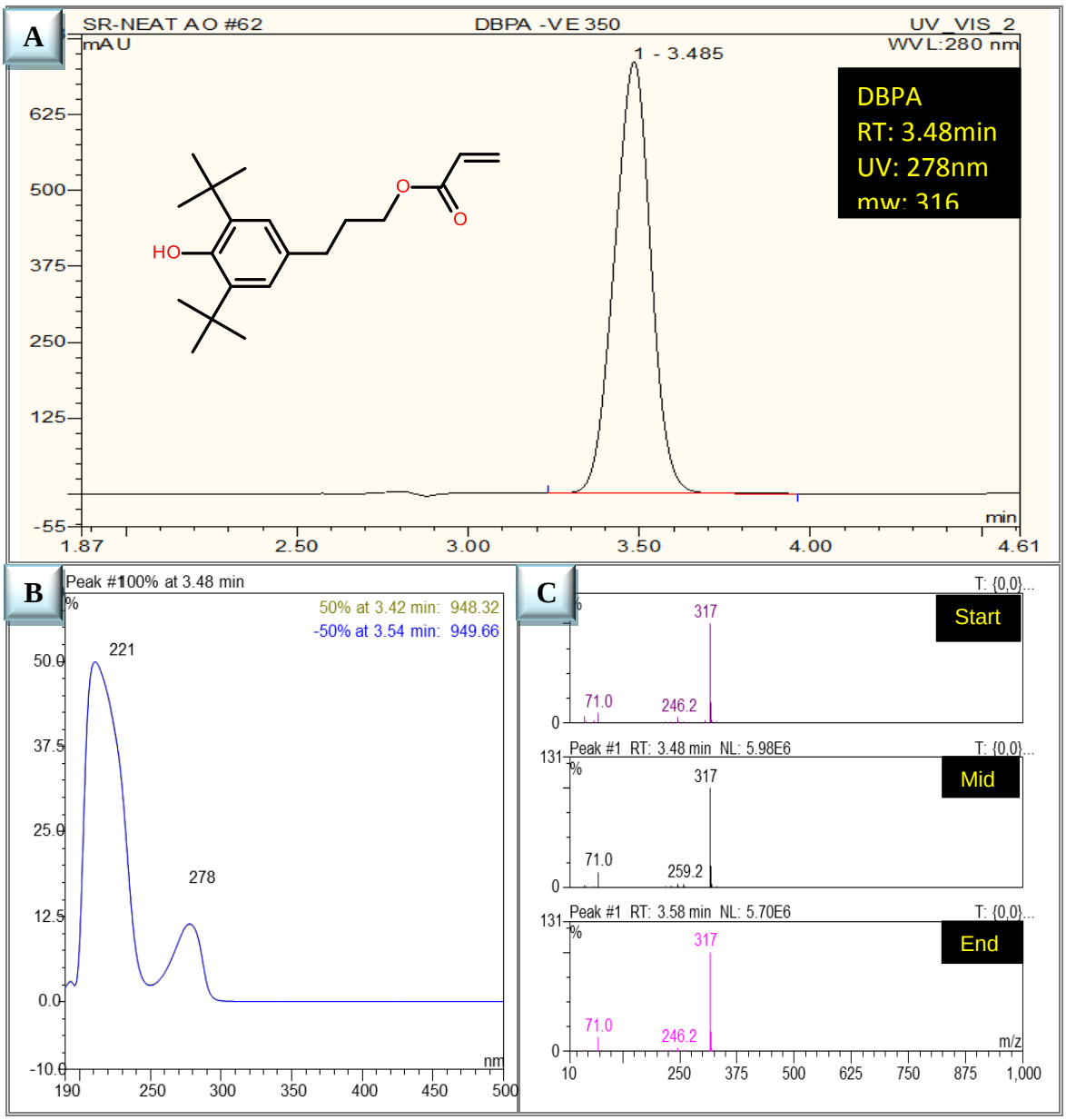


Figure 4. 24: HPLC (A), UV (B) and (C) mass spectra of **neat DBPA** *(mobile phase of 90% ACN:5% THF:5%MEOH, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C)*

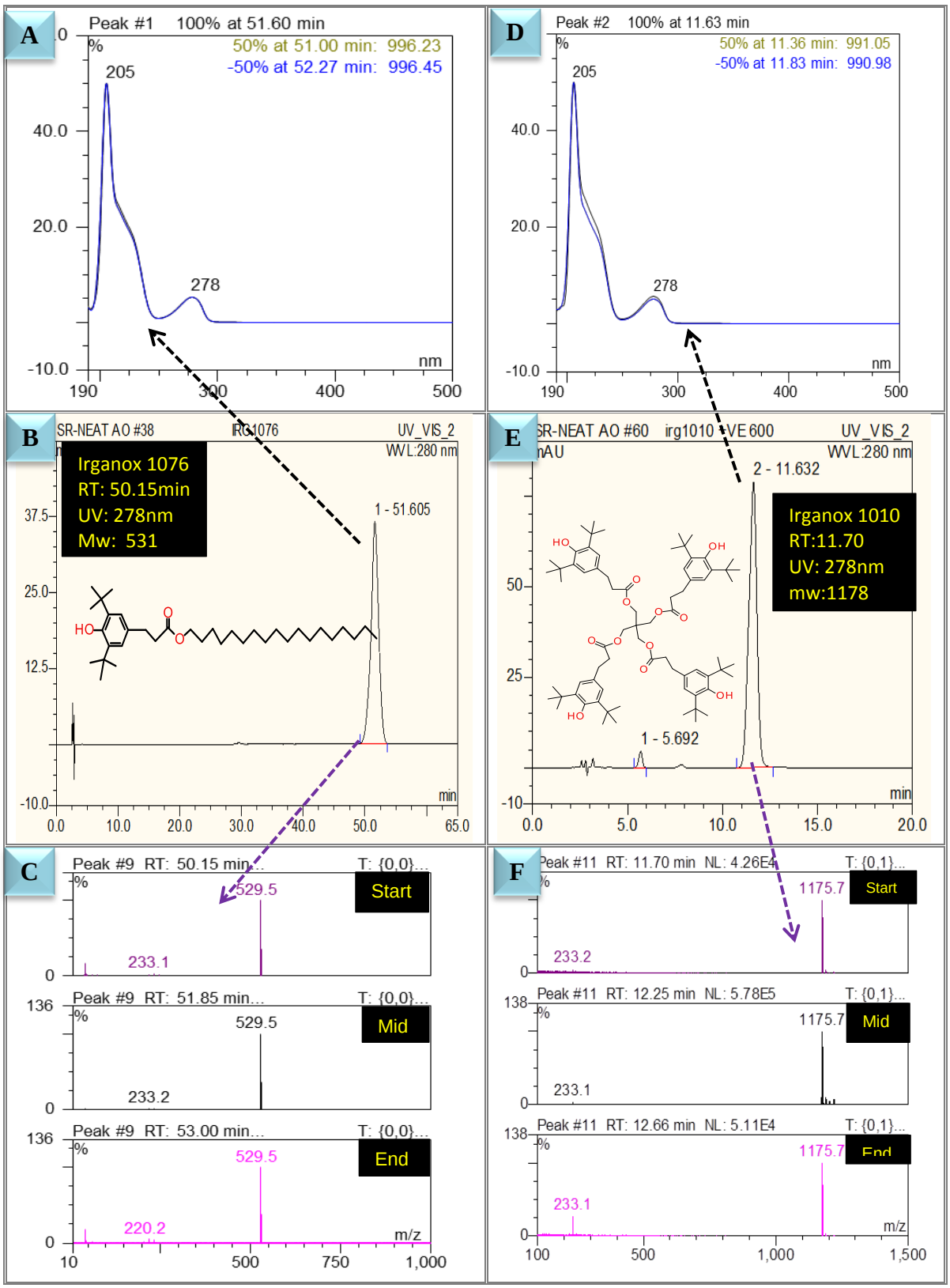
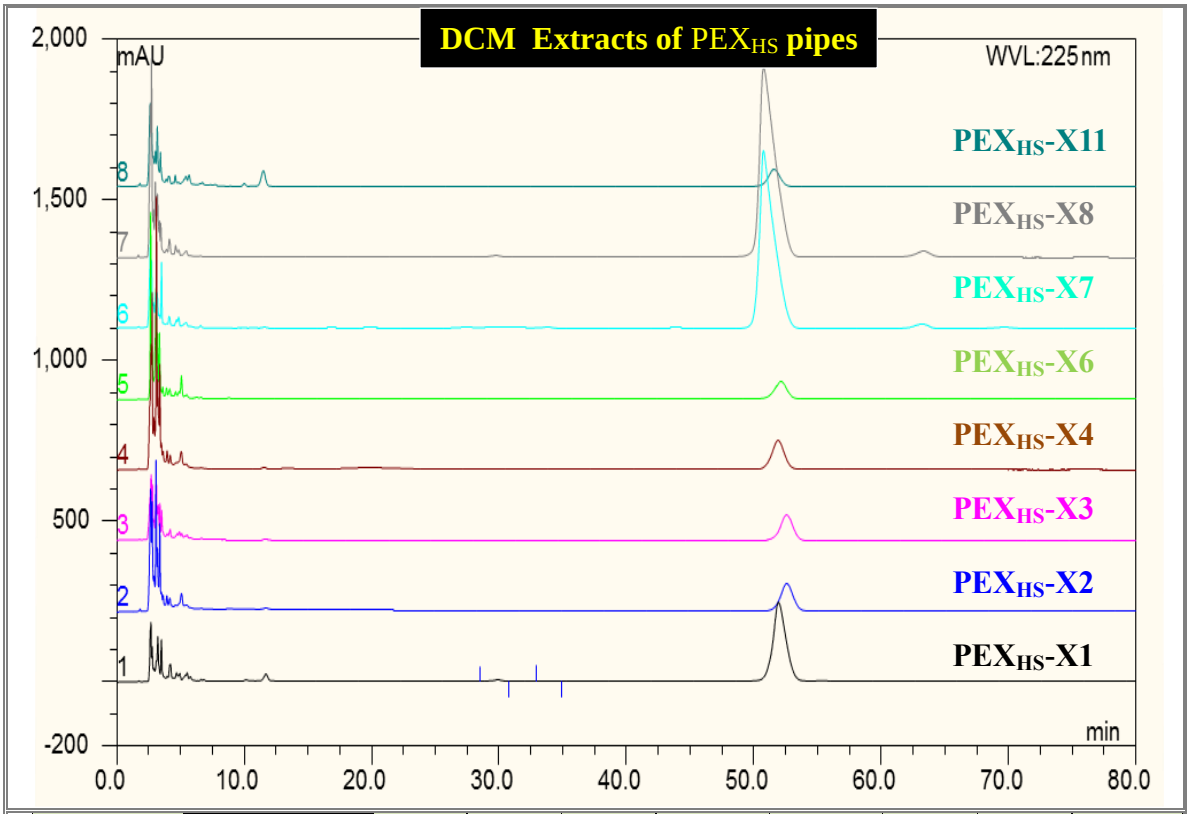


Figure 4. 25: HPLC-UV, mass spectral LC-chromatogram of **neat Irganox 1076 and Irganox 1010**.**A & D** are UV, **B & E** are the LC chromatograms and **C& F** are the Mass spectra of Irganox 1076 and Irganox 1010 respectively *(mobile phase of 90% ACN:5% THF:5%MEOH, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C).*

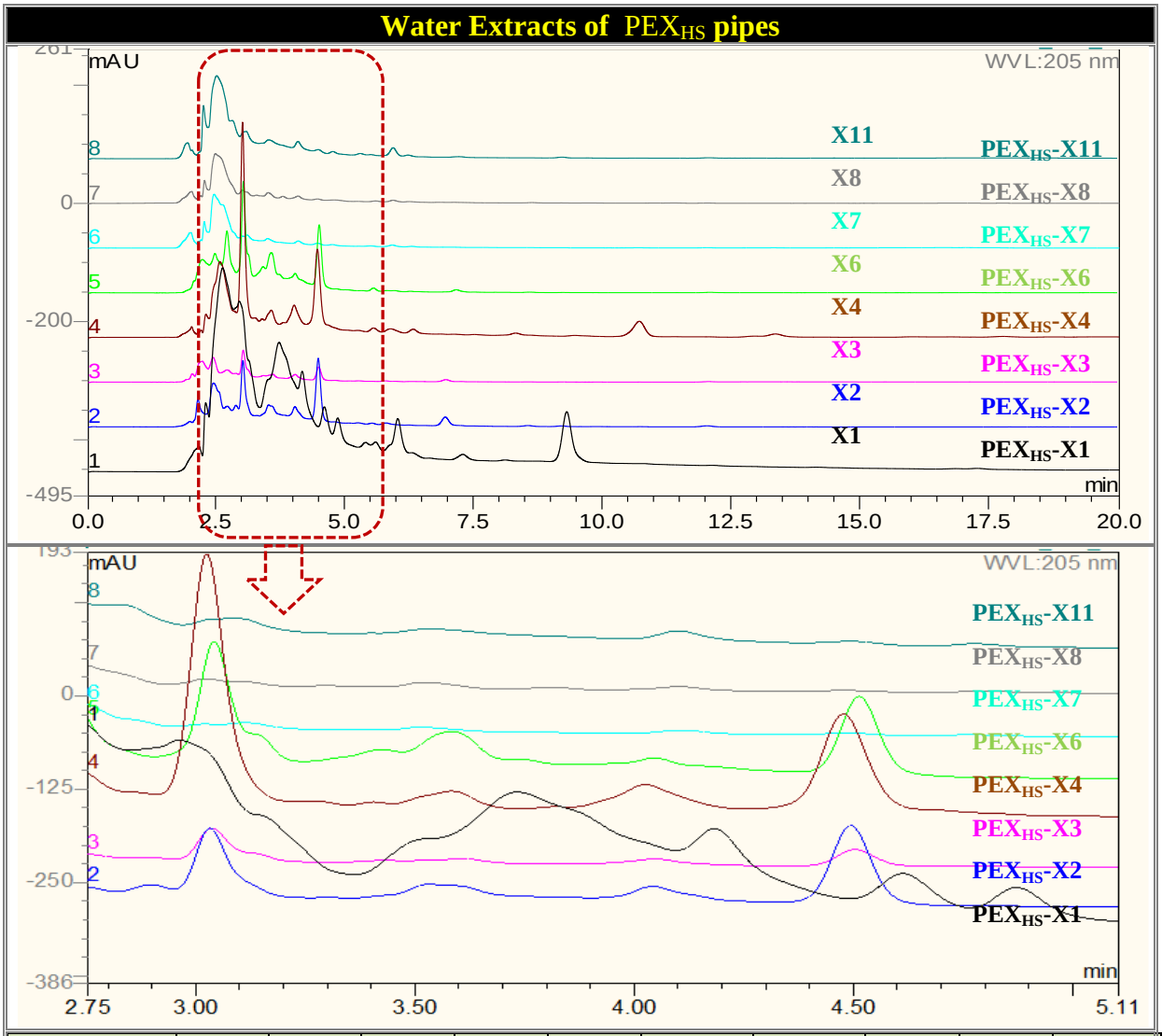


RT(min)	3.08			3.38	3.95	5.05	11.47	29.91	34.11	50.77	63.31
UV λmax (nm)	278			277	276	278	278	278	278	278	312
Mass (m/z)	317	263	233	305	333	623	1175	473	545	529	527

For LC:
Zorbax-RX-C18, Isocratic
Mobile phase: 90%ACN, 5% THF, 5% MEOH
Column oven temperature: 20°C
Flow rate: 1ml/min
Injection volume: 20µl

MS: Positive ion mode for Nitrogen compound with Probe temprature:600°C
MS: Negative ion mode for Oxygen compound with Probe temparure : 350°C, 600°C

Figure 4. 26: HPLC-chromatogram of **PEX_{HS}-pipes** ASE-DCM extracts (X1-X11 Pipes (**see Table 4.6** for formulations & **Scheme 4.8, sample A**



UV-RT(min)	3.03	3.41	3.59	4.49	5.84	5.88	6.04	9.32	10.73	17.5
UV max (nm)	**276**	**237**	**281**	**278**	**305**	**316**	**247**	**270**	**278**	**307**
Mass (m/z)	**231**	**261**	**247**	**263**	No MS signal	NO MS signal	408	299	317	No Ms signal

For LC:
Zorbax-RX-C18, Isocratic
Mobile phase: 80%ACN, 20%water
Column oven temperature: 20°C
Flow rate: 1ml/min
Injection volume: 20µl

MS: Positive ion mode for Nitrogen compound with Probe temprature:600°C
MS: Negative ion mode for Oxygen compound with Probe temparure : 350°C, 600°C

Figure 4. 27: HPLC-UV and MS, full chromatograms of water extracts ($W_{2\text{-}4}$). MS, full chromatograms of water extracts ($W_{2\text{-}4}$).

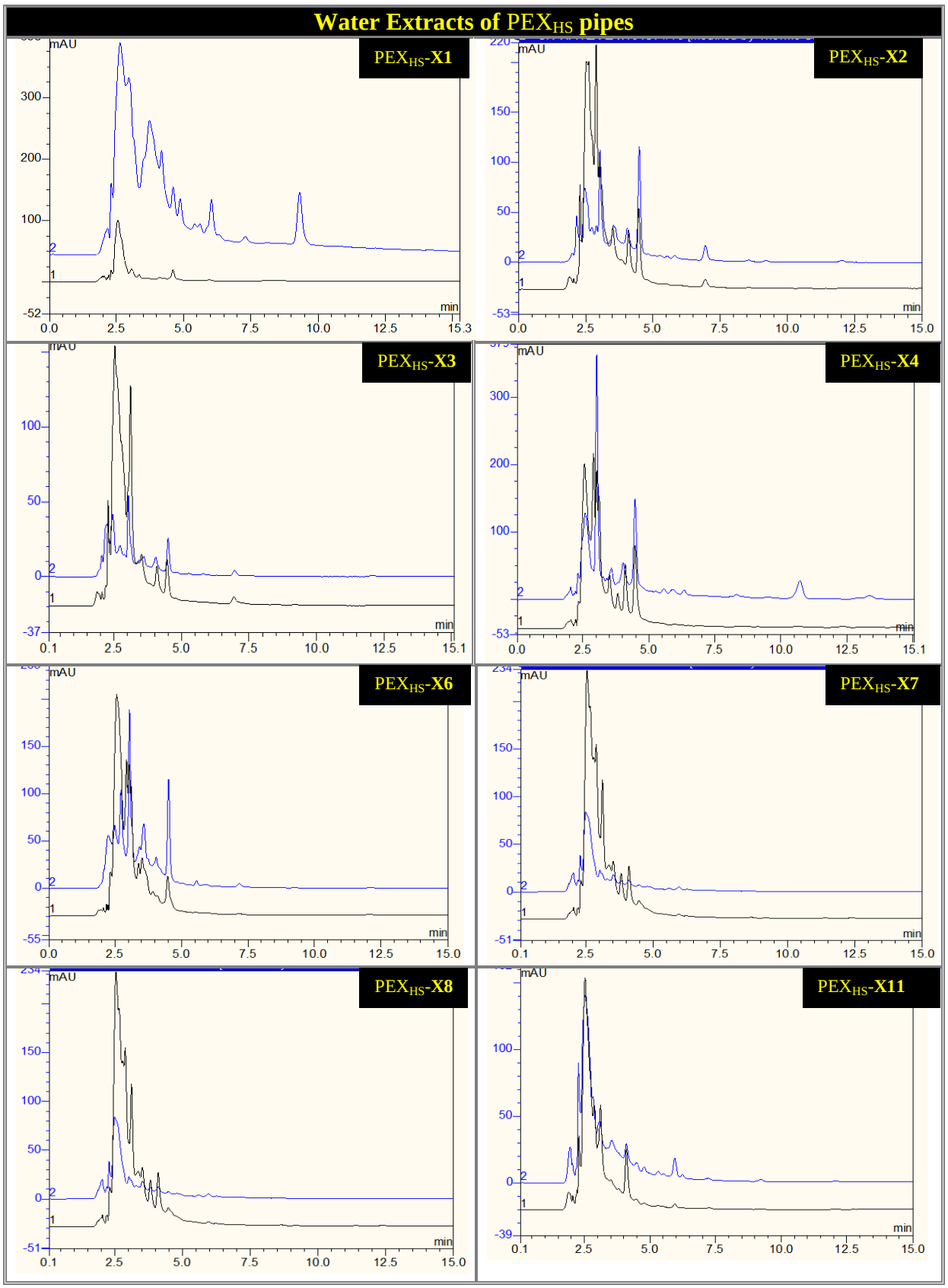
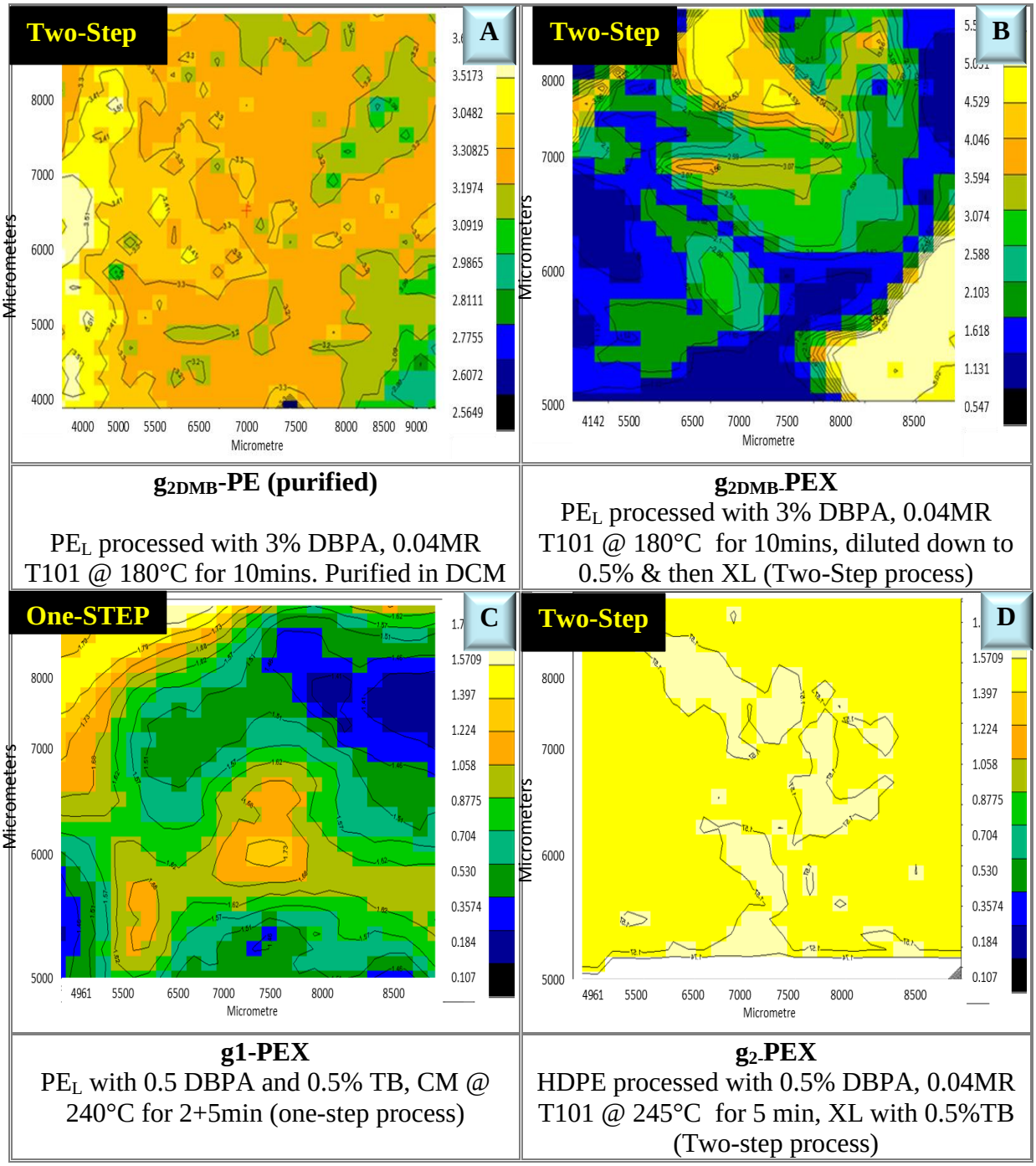


Figure 4. 28: Comparison of water chromatograms of extract in the region of 0-15minutes **W_1(black) and W_{2-4} (blue) for Pipes PEX_{HS}-X1-X11** *(Mobile phase of 80% ACN:20% water, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C)*



g_{2DMB}-PE (purified)

PE_L processed with 3% DBPA, 0.04MR T101 @ 180°C for 10mins. Purified in DCM

g_{2DMB}-PEX

PE_L processed with 3% DBPA, 0.04MR T101 @ 180°C for 10mins, diluted down to 0.5% & then XL (Two-Step process)

g1-PEX

PE_L with 0.5 DBPA and 0.5% TB, CM @ 240°C for 2+5min (one-step process)

g_2-PEX

HDPE processed with 0.5% DBPA, 0.04MR T101 @ 245°C for 5 min, XL with 0.5%TB (Two-step process)

Figure 4. 29: The distribution of g-AO in sample produced by Two-step and one-step process analysed by FTIR-microscopy

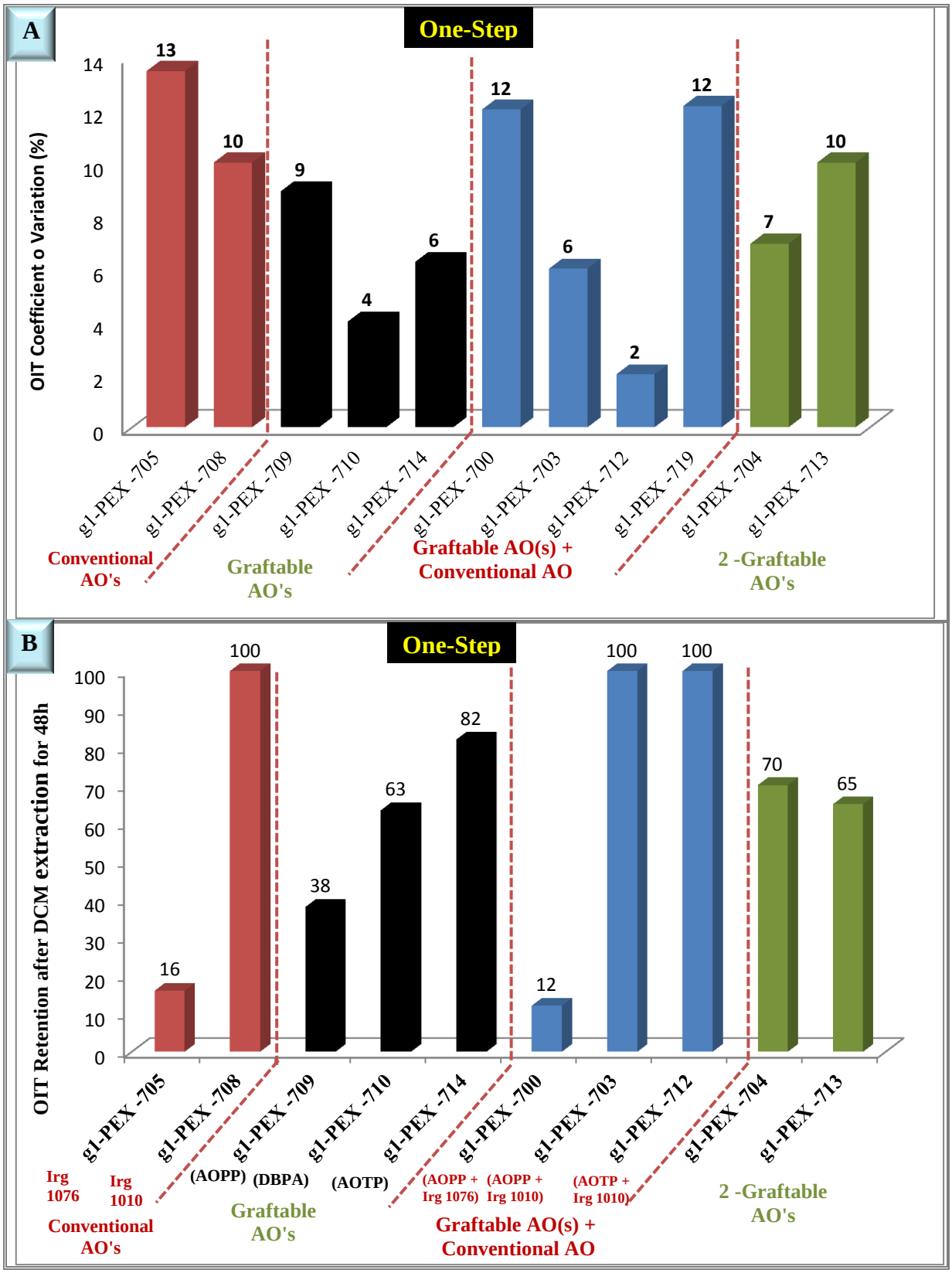


Figure 4. 30: %OIT coefficient of variation of untreated samples(A), OIT retention based after DCM extraction of one-step samples(B), see Table 4.4 for sample composition, See Scheme 4.2 D.

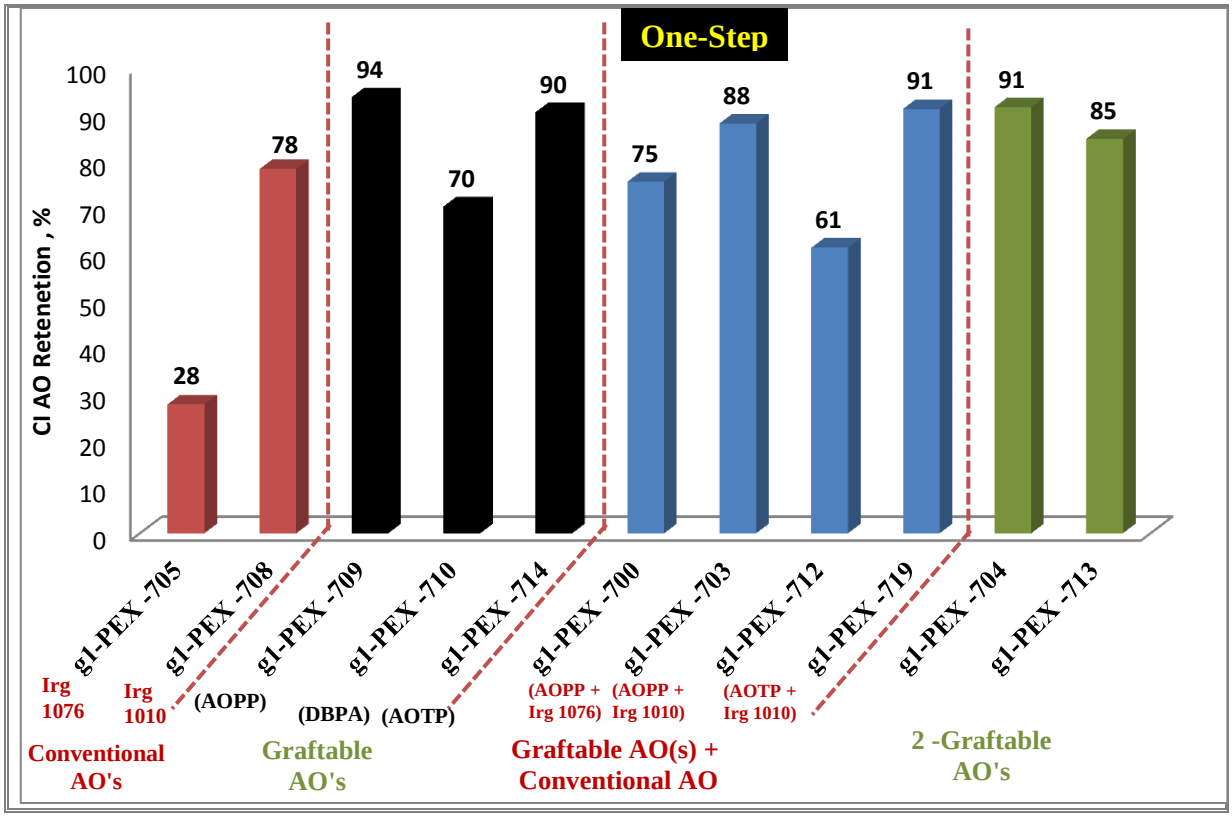


Figure 4. 31: % AO retention based on carbonyl index (CI) after DCM extraction of one-step samples; see Table 4.2 for sample composition, also see Scheme 4.2 B .

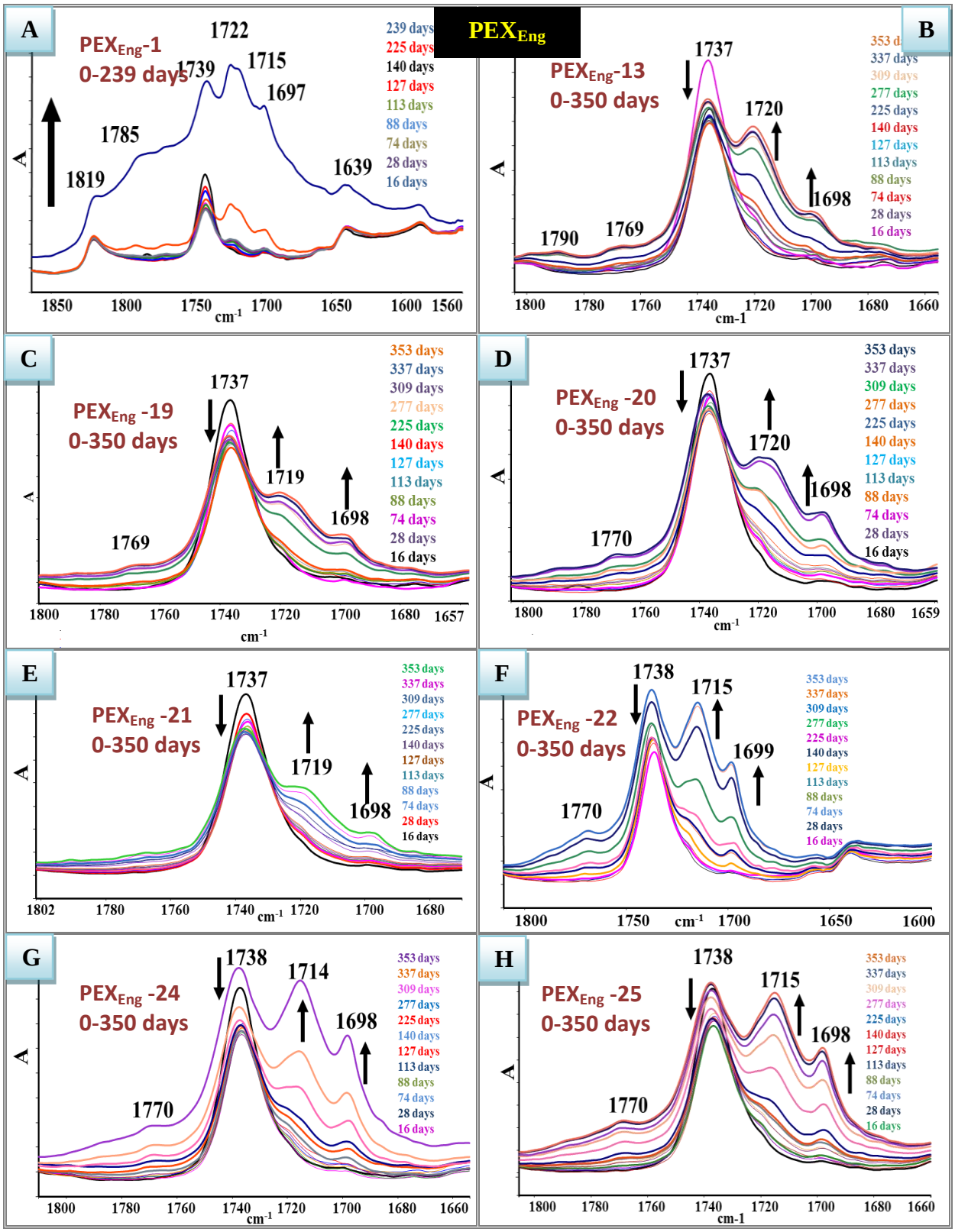


Figure 4. 32 : FTIR results of PEX_{Eng} pipe samples aged in Wallace oven at 125°C, see Table 4.5, see Scheme 4.4 (changes in carbonyl region with aging time: 1769-1785cm^{-1} γ-Lactone, 1739-1737cm^{-1} Ester, 1730cm^{-1} Aldehyde, 1718cm^{-1} Ketone, 1701cm-1 Carboxylic acid, 1698cm^{-1} unsaturated ketone)

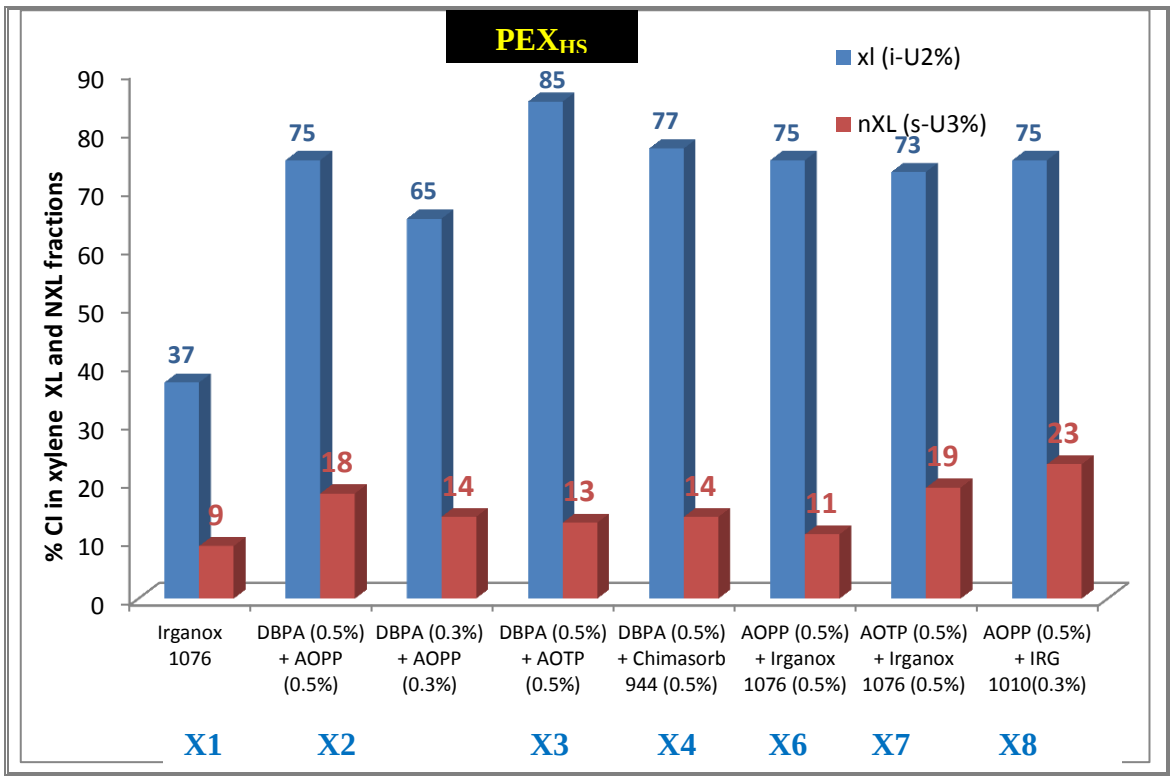
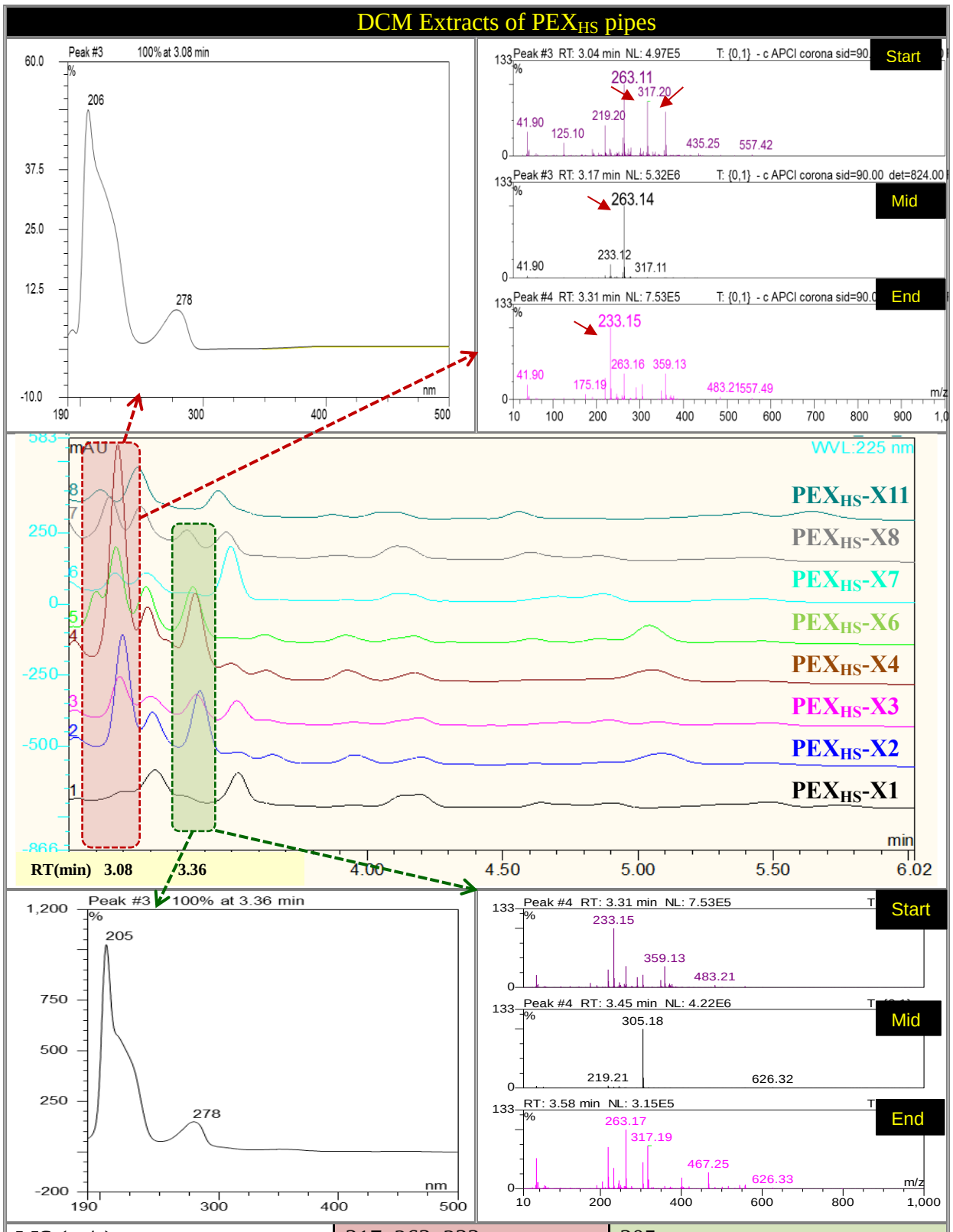
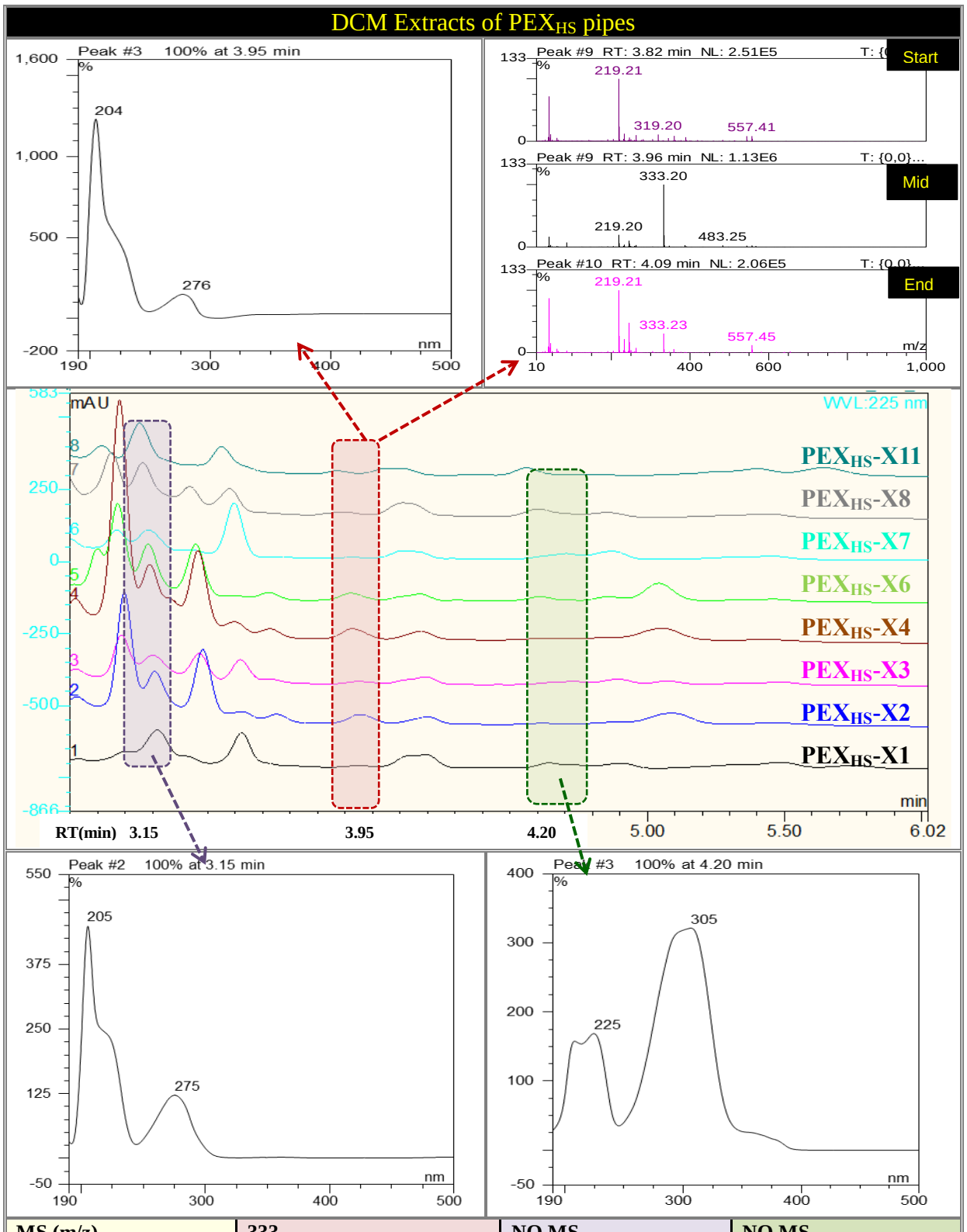


Figure 4. 33 : % Retention of Antioxidant based on carbonyl index of crosslinked and non-crosslinked films of **PEX_{HS} pipes** after xylene extraction see **Scheme 4.7.**



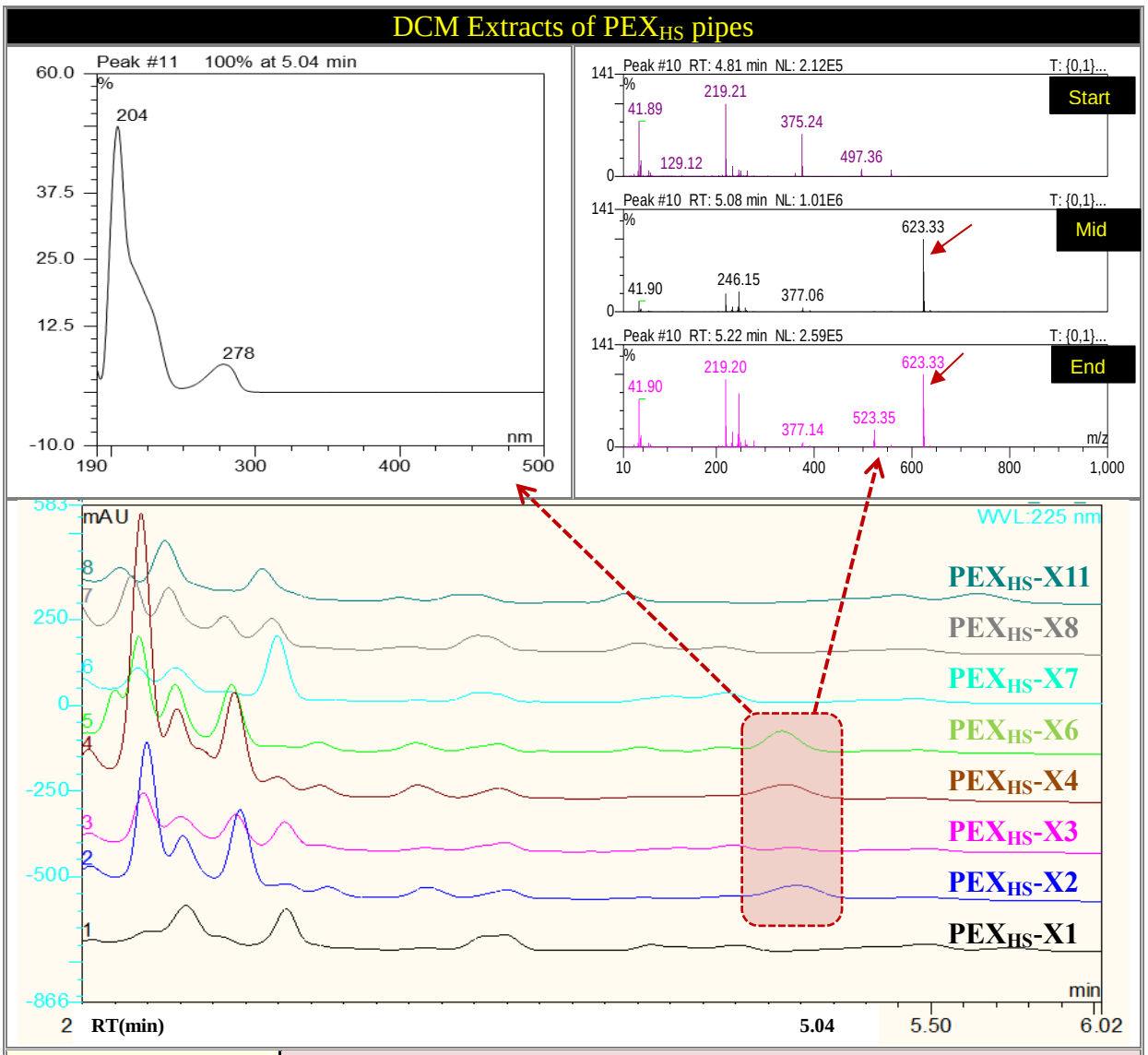
MS (m/z)	317, 263, 233	305
UV (nm)	278	278
RT (min)	3.08	3.36

Figure 4. 34: HPLC-chromatograms of extracts of PEX_{HS}-pipes X1-X11 (**see Table 4.6** for formulations) after ASE-DCM extraction, see **Scheme 4.8**. (The 3 Mass spectra plots for each peak denote the m/z at the start, middle and end of the peaks).



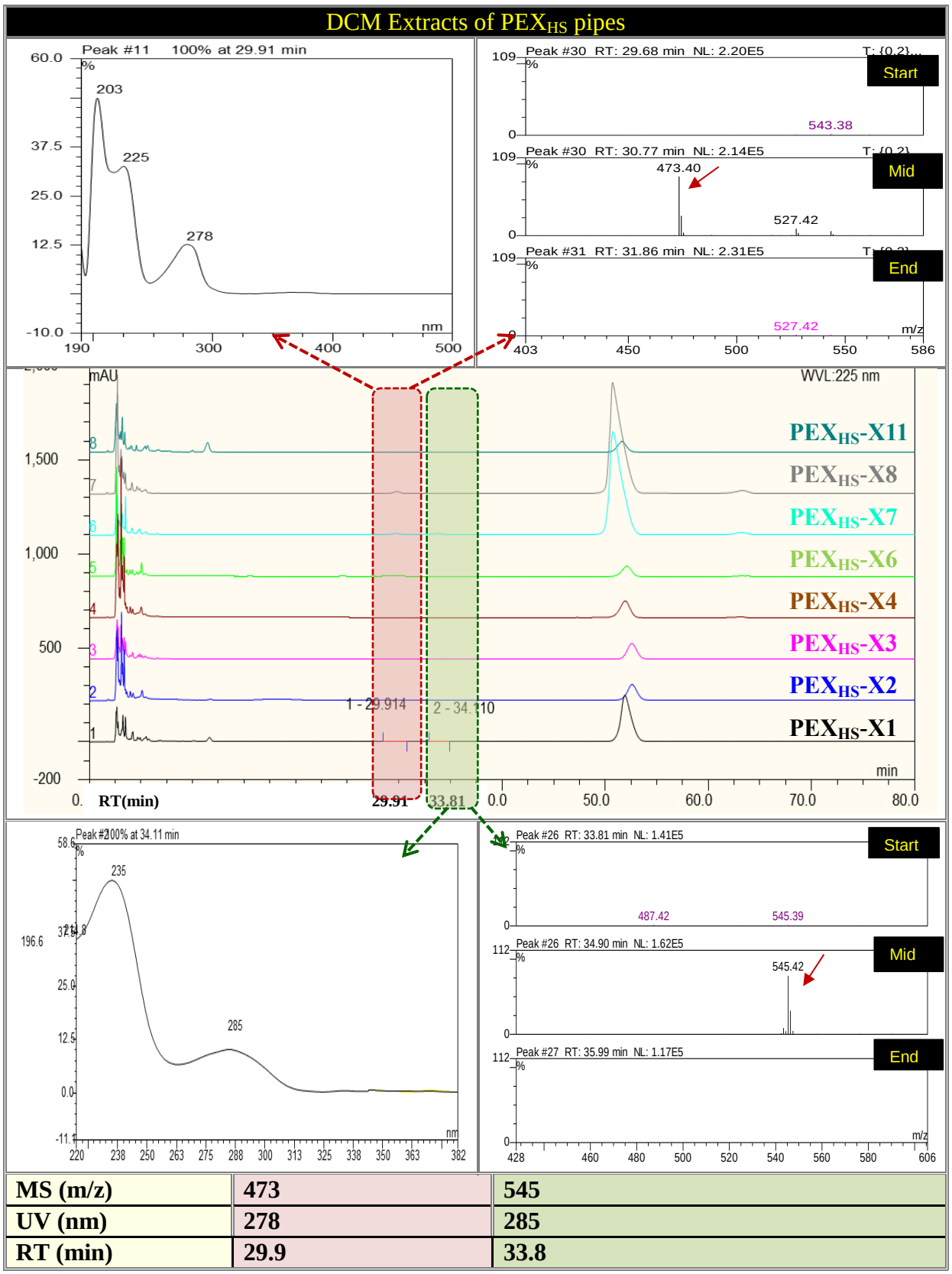
MS (m/z)	**333**	**NO MS**	**NO MS**
UV (nm)	**276**	**275**	**305**
RT (min)	**3.95**	**3.15**	**4.20**

Figure 4. 35: HPLC-chromatograms of extracts of PEX_{HS}-pipes X1-X11 (**see Table 4.6** for formulations) after ASE-DCM extraction, see **Scheme 4.8**. (The 3 Mass spectra plots for each peak denotes the m/z at the start, middle and end of the peaks).



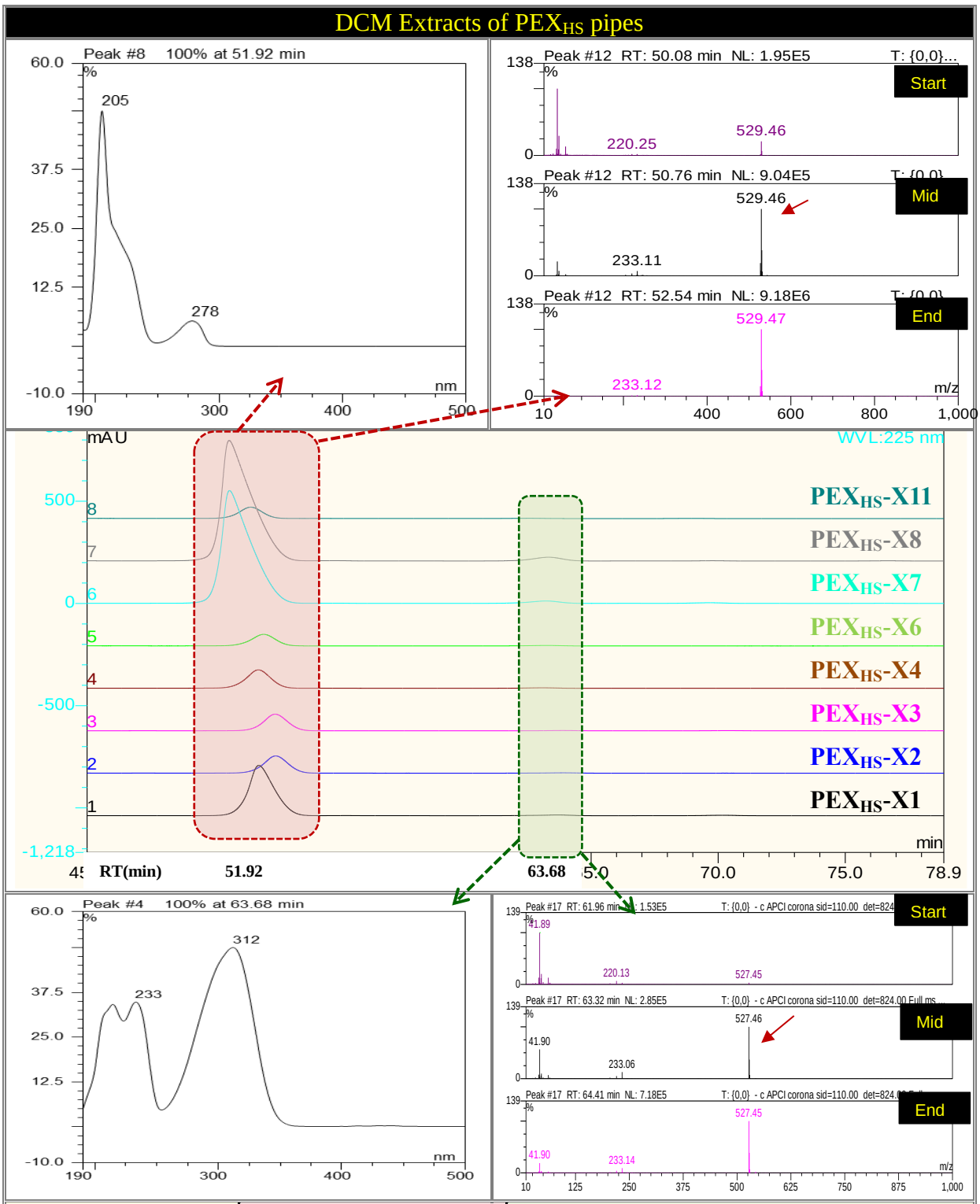
MS (m/z)	**333**
UV (nm)	**276**
RT(min)	**5.04**

Figure 4. 36: HPLC-chromatograms of extracts of PEX_{HS}-pipes X1-X11 (**see Table 4.6** for formulations) after ASE-DCM extraction, see **Scheme 4.8**. *(Mobile phase of 90% ACN:5% THF:5%MEOH, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C)* .



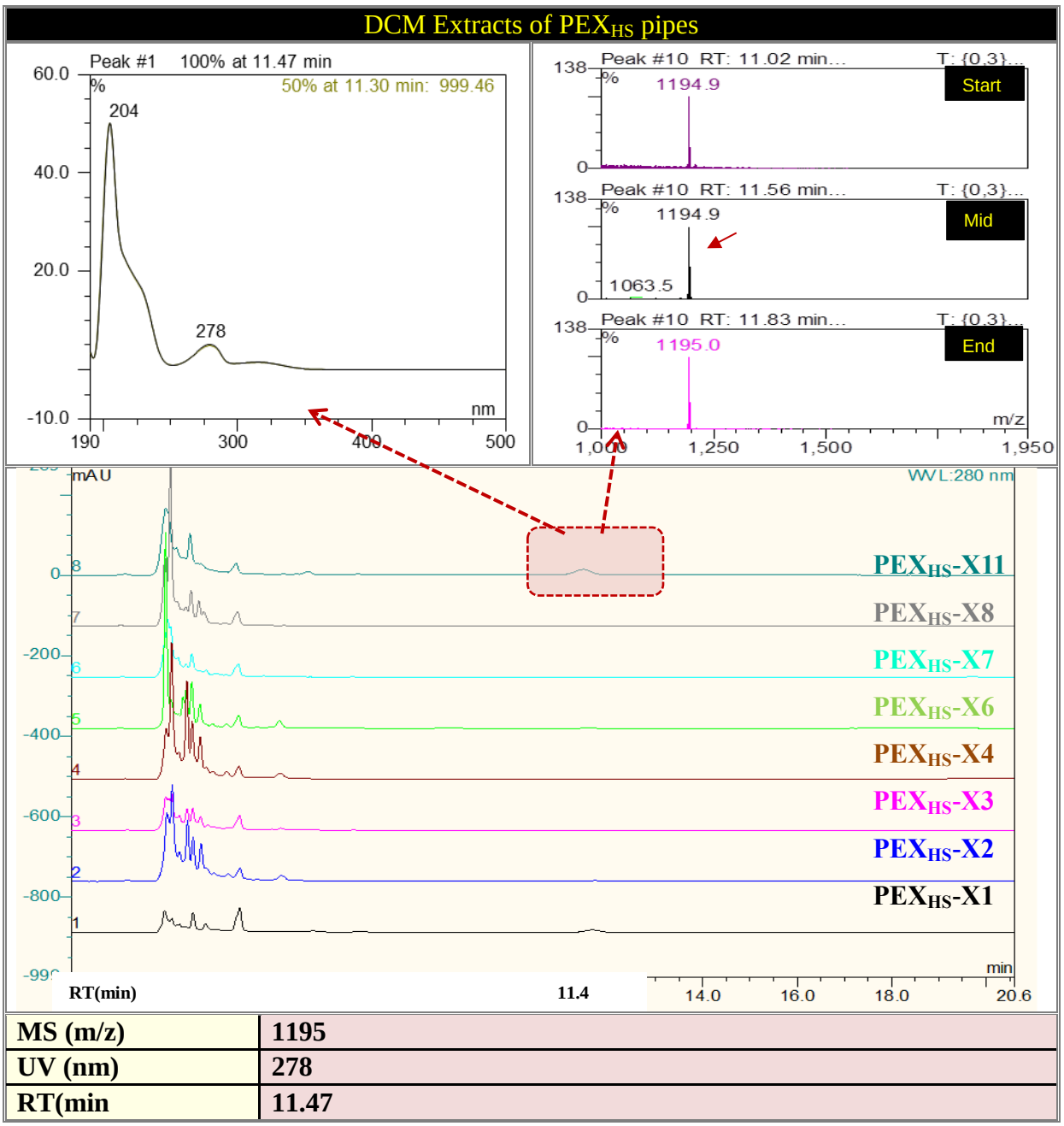
MS (m/z)	**473**	**545**
UV (nm)	**278**	**285**
RT (min)	**29.9**	**33.8**

Figure 4. 37: HPLC-chromatograms of extracts of PEX_{HS}-pipes X1-X11 (**see Table 4.6** for formulations) after ASE-DCM extraction, see **Scheme 4.8**. *(Mobile phase of 90% ACN:5% THF:5%MEOH, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C)* .



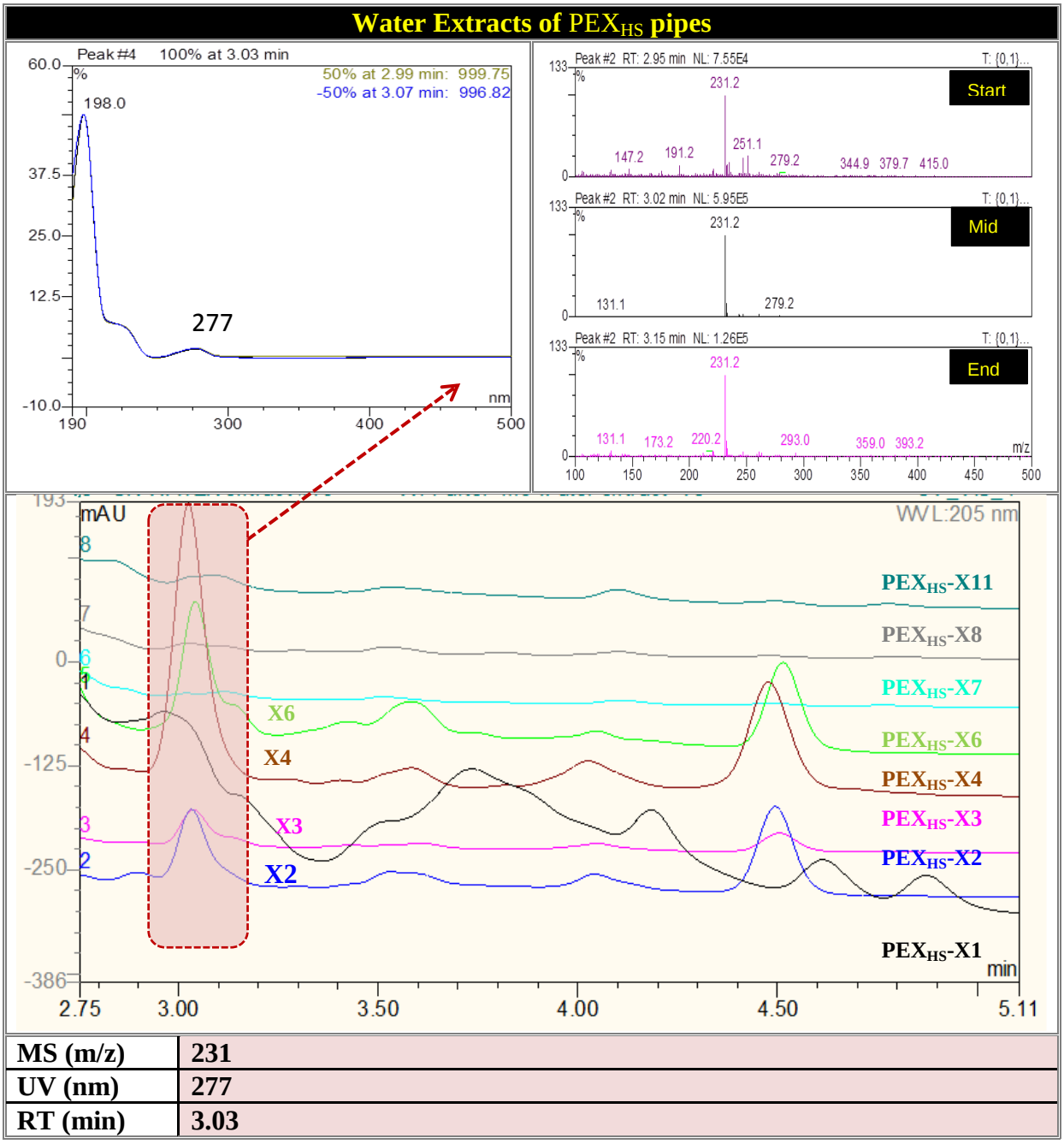
MS (m/z)	**529**	**527**
UV (nm)	**278**	**312**
RT(min	**51.92**	**63.68**

Figure 4. 38: HPLC-chromatograms of extracts of PEX_{HS}-pipes X1-X11 (**see Table 4.6** for formulations) after ASE-DCM extraction, see **Scheme 4.8**. *(Mobile phase of 90% ACN:5% THF:5%MEOH, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C)* .



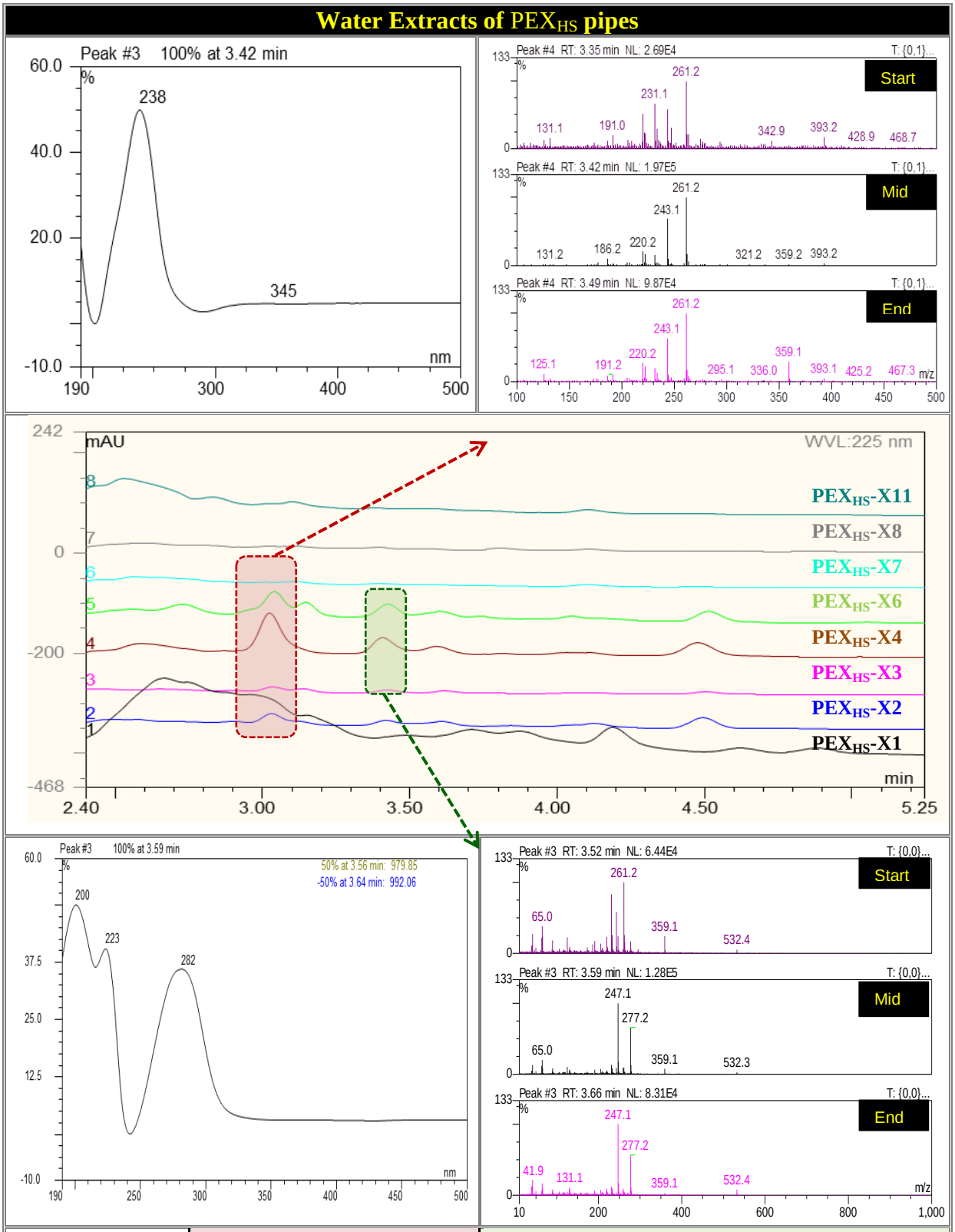
MS (m/z)	**1195**
UV (nm)	**278**
RT(min	**11.47**

Figure 4. 39: HPLC-chromatograms of extracts of PEX_{HS}-pipes X1-X11 (**see Table 4.6** for formulations) after ASE-DCM extraction, see **Scheme 4.8**. *(Mobile phase of 90% ACN:5% THF:5%MEOH, 20°C oven temperature, flow rate 1ml/min, APCI Positive ion mode, Probe temperature:600°C*



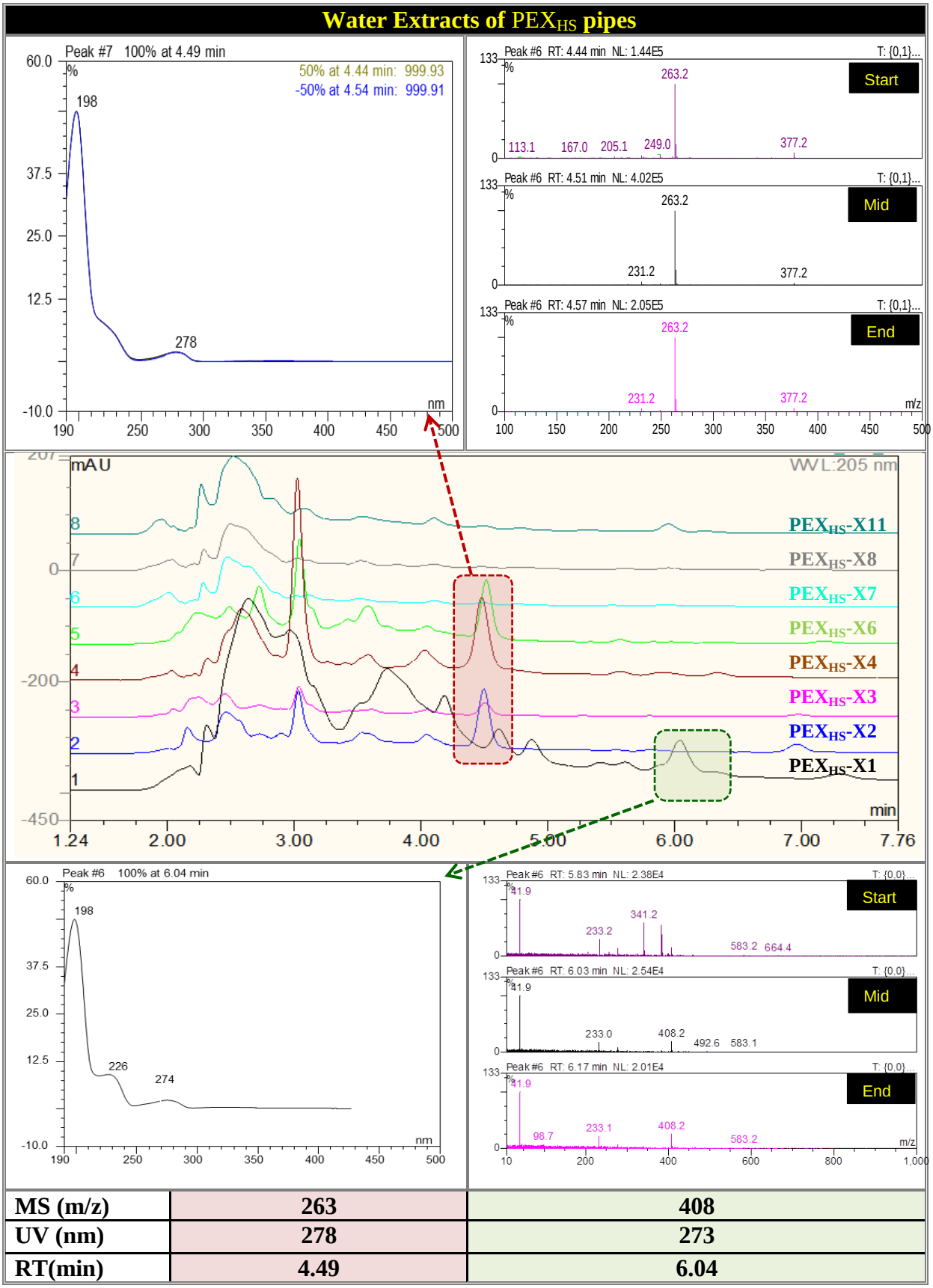
MS (m/z)	**231**
UV (nm)	**277**
RT (min)	**3.03**

Figure 4. 40: HPLC-UV and MS chromatogram of water extracts (W_{2-4}) of PEX_{HS} pipes. *(Mobile phase of 80% ACN:20% water, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C) .*



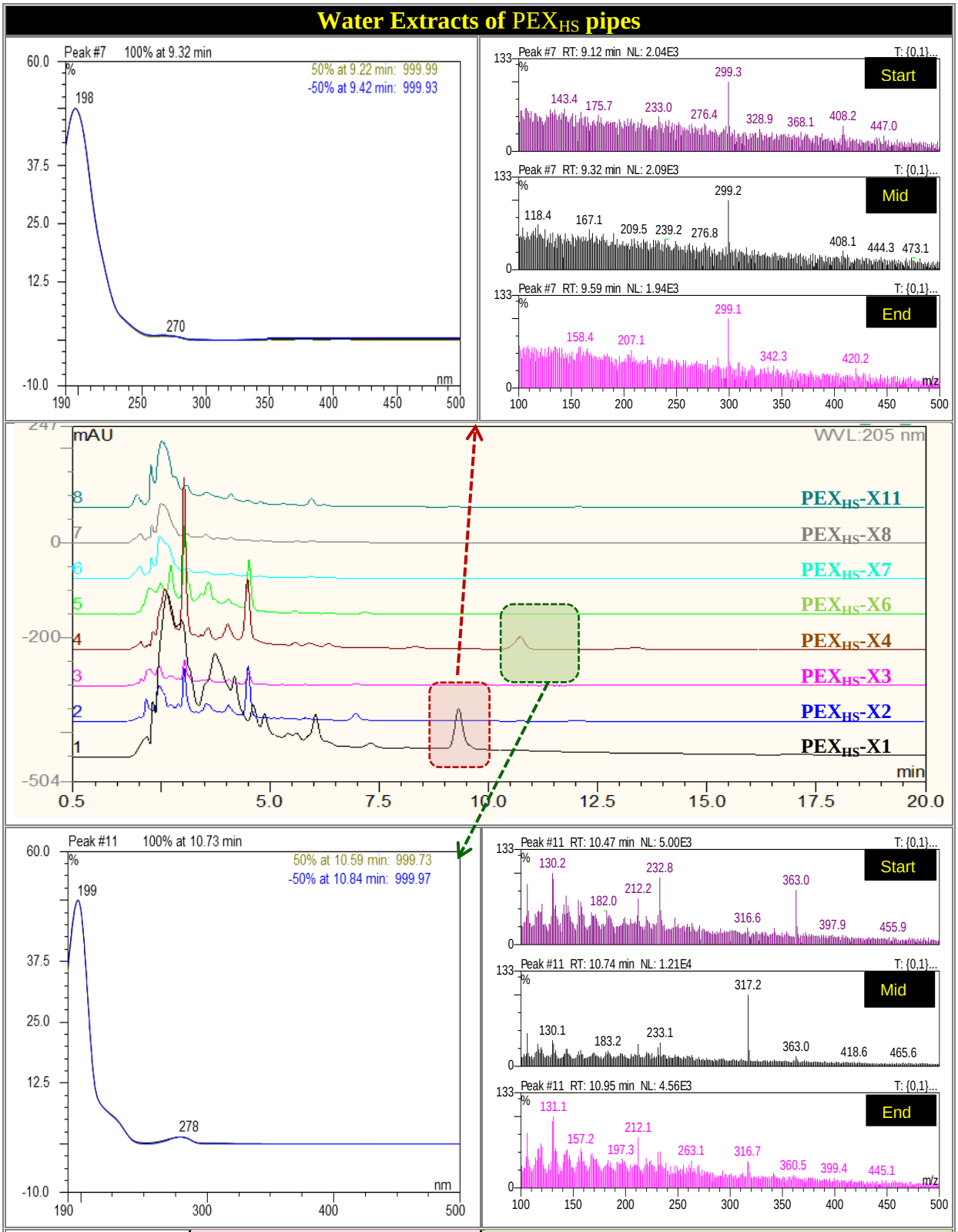
MS (m/z)	261	247
UV (nm)	238	282
RT(min)	3.42	3.59

Figure 4. 41: HPLC-UV and MS chromatogram of water extracts (W_{2-4}) PEX_{HS} pipes. *(Mobile phase of 80% ACN:20% water, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C) .*



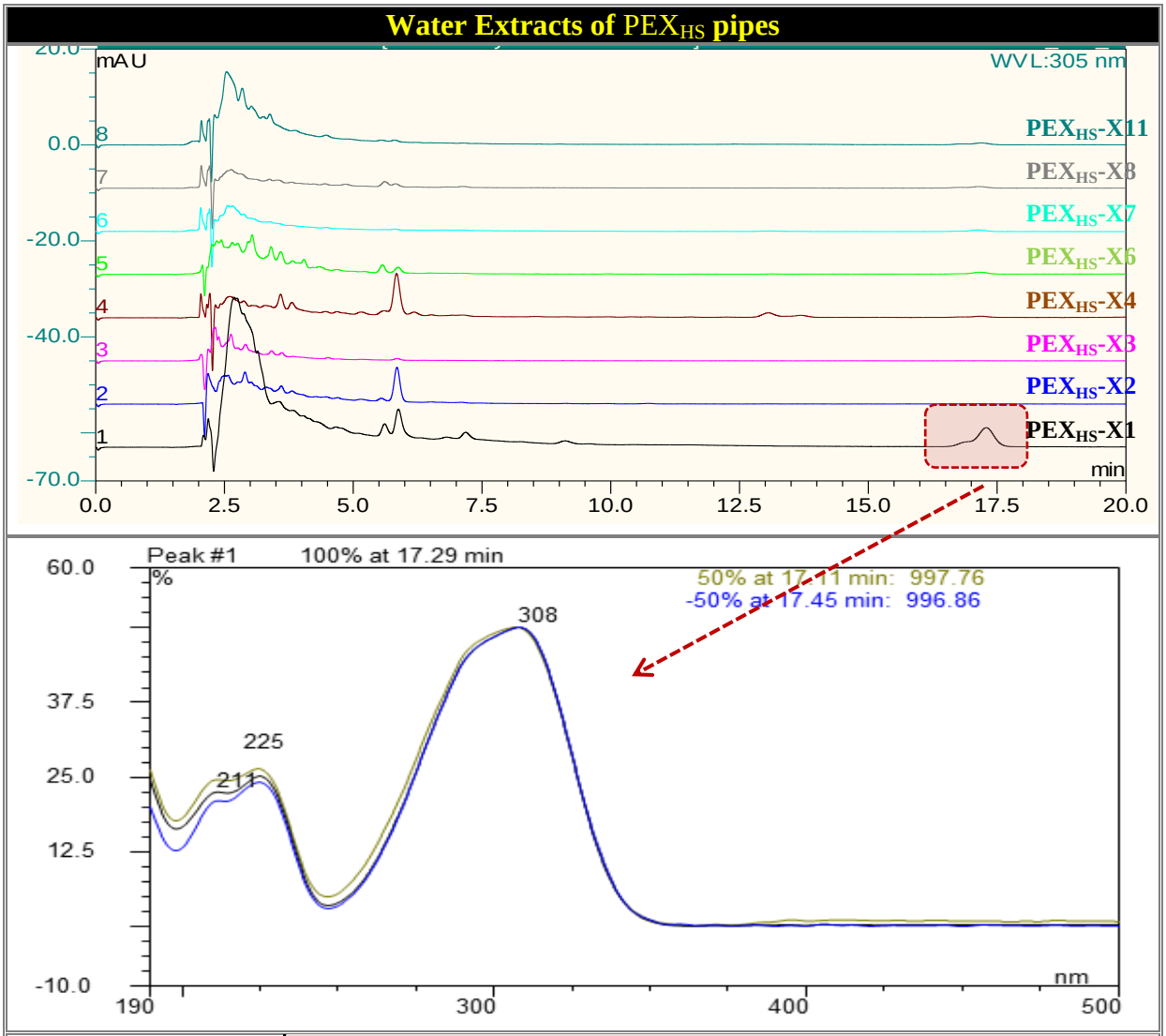
MS (m/z)	**263**	**408**
UV (nm)	**278**	**273**
RT(min)	**4.49**	**6.04**

Figure 4. 42: HPLC-UV and MS chromatogram of water extracts ($W_{2\text{-}4}$) PEX_{HS} pipes. *(Mobile phase of 80% ACN:20% water, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C) .*



MS (m/z)	**299**	**317**
UV (nm)	**270**	**278**
RT(min)	**9.32**	**10.73**

Figure 4. 43: HPLC-UV and MS chromatogram of water extracts ($W_{2\text{-}4}$) PEX_{HS} pipes. *(Mobile phase of 80% ACN:20% water, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C) .*



MS (m/z)	**NO MS signal**
UV (nm)	**308**
RT(min)	**17.29**

Figure 4. 44: HPLC-UV chromatogram of water extracts ($W_{2\text{-}4}$) PEX_{HS} pipes. *(Mobile phase of 80% ACN:20% water, 20°C oven temperature, flow rate 1ml/min, APCI negative ion mode, Probe temperature:350°C)* .

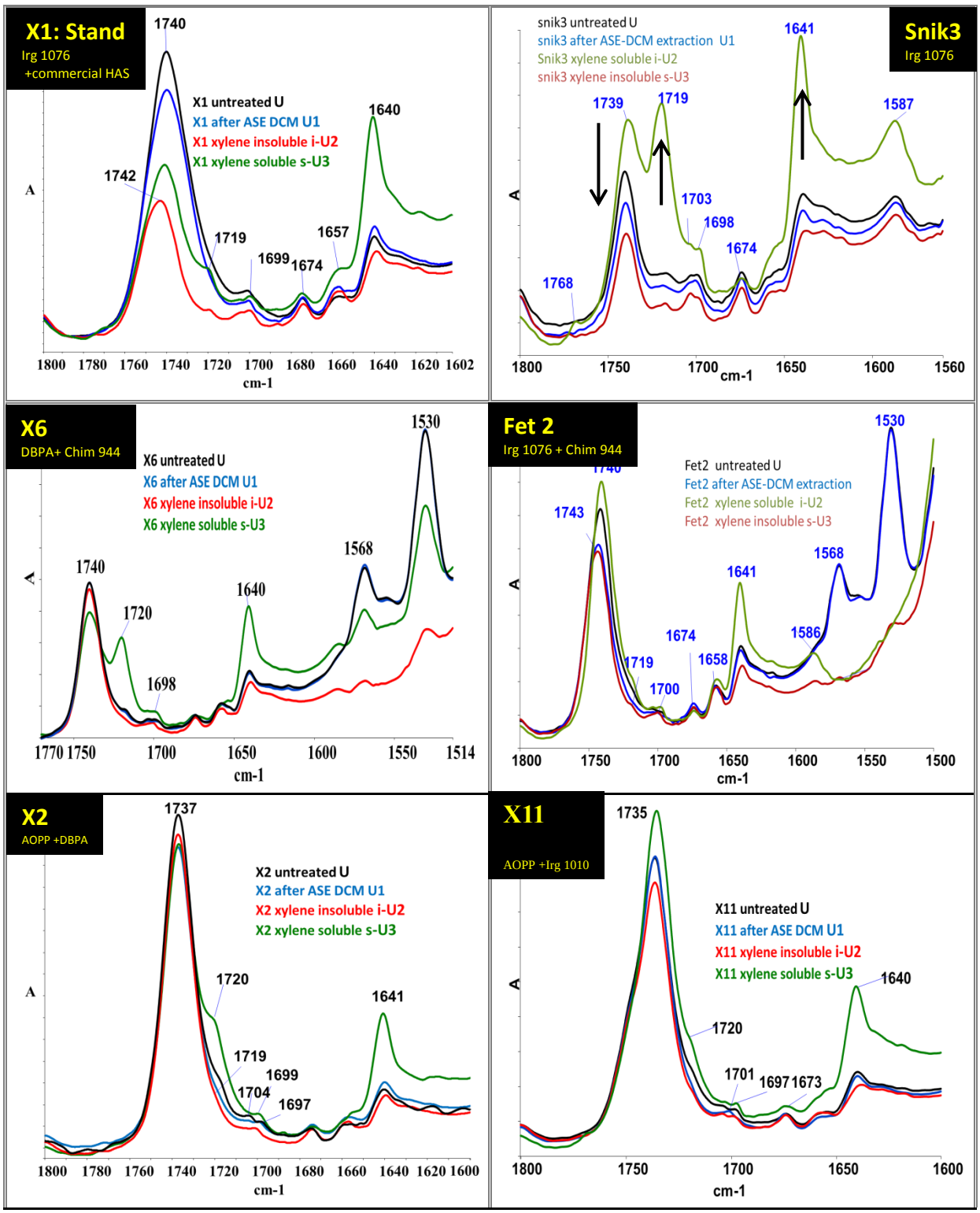


Figure 4. 45: FTIR of PEXHS-pipe films in the carbonyl region between 1800-1600cm-1 before (samples "U"), after ASE-DCM extraction system (samples "U1") and after xylene extraction in the sequential DCM-Xylene extraction (samples " i-U2"- is xylene insoluble and "s-U3" is xylene soluble fractions, **see Scheme 4.7, Route II and III)**

Chapter 5

Conclusions and Recommendations for future work

5.1 Conclusions

The main aim of this work was achieved in that, high level of grafting of synthesised reactive hindered amine and hindered phenol antioxidants took place, in peroxide crosslinked (PEX) lab-prepared HDPE samples, and in commercially manufactured peroxide crosslinked (PEXa) pipes used typically for potable water applications. Furthermore, the results also showed that the peroxide initiated crosslinking process did not interfere with the reactive (grafted) hindered phenol DBPA as evidenced by its much higher level of retention after solvent extraction compared to the corresponding non-graftable hindered phenol Irg 1076. Detailed conclusions of the work reported are outlined below.

5.1.1 The synthesised reactive hindered amine antioxidant AOPP was shown to melt graft onto HDPE in the presence of the organic peroxide T10, giving rise to a high level of grafting of up to 90%, **Figure 3.11**. An optimum grafting system was dependent on optimising the chemical composition and the processing conditions resulting in lower extent of interference of the expected side reactions. It was shown that the overall grafting level increased with increasing the peroxide concentration; but this has also contributed to an increase in the extent of homopolymerisation of AOPP and crosslinking of HDPE. Furthermore, increasing the processing temperature from 180-240°C, resulted in an increase in AOPP grafting from 60% to 80%, see **Figures 3.13,** and this was paralleled by lower extent of polymer crosslinking (lower gel content)**.** Optimised grafting conditions of AOPP on HDPE were found to be achieved at high processing temperature and low peroxide concentration (see optimum conditions below, **Figure 3.13**).

[AOPP] =3%: [T101]/ [AOPP] = 0.005MR: Temp 240°C, Rotor speed =65rpm).

5.1.2 The melt free radical grafting of the second reactive hindered amine, AOTP, on HDPE in the presence of T101 led to similar behaviour to that of AOPP. For example, an optimum melt grafting conditions for AOTP were found to be at [AOTP] 3%: [T101]/[AOTP]= 0.005MR; Temp 200°C, Rotor speed 65rpm resulting in 74% grafting, see **Figure 3.15.** This high level of grafting of AOTP contrasts results from previous literature work [122] of grafting AOTP on polypropylene (PP) where maximum level of grafting was shown to be less than 50%.

5.1.3 The melt free radical grafting of the bifunctional HAS, AATP, at processing temperature of 180°C in the presence of 0.005 T101, gave rise to a much higher extent of homopolymerisation which has resulted in phase separation of the HAS from the

polymer. Being a bifunctional HAS (with two reactive acryloyl functions), it can therefore be expected to be much more reactive than the monofuntional reactive HAS antioxidants (AOPP and AOTP), thus its much higher susceptibility to homopolymerisation leading to phase separation giving rise to the observed crumbling of the polymer, see **Figure 3.17**.

5.1.4 Antioxidant grafting and PE crosslinking was achieved by two different methods, a one-step and a two-step process. The two-step process (g_2-PEX), where an AO (hindered phenol DBPA) masterbatch (MB) was used, gave rise to high level of variation in the oxidative induction time (OIT) used as a guide for the thermal stability of the polymer (see **Table 4.3**). In addition to OIT measurements, FTIR-microscopy-mapping analysis of the DBPA antioxidant has clearly shown a fairly inhomogeneous antioxidant distribution (see **Figure 4.29 B**).This is suggested to be due to the poor granulation of the masterbatches and the homogenisation processes conducted at low temperature (140-150°C) in the first step. In contrast, in the two step grafting and homogenisation process where the antioxidant was directly grafted at the required low concentration of0.5% followed by the crosslinking step, an excellent distribution of the g-AO in the polymer was clearly seen from FTIR-microscopy imaging (**Figure 4.29 D)**.

5.1.5 Antioxidant grafting and crosslinking of the polymer in a one-step process (g_1-PEX) was successfully achieved. The overall antioxidant (DBPA) distribution in the one step samples (g_1-PEX crosslinked without prior homogenisation in the toque rheometer) was also better than that of samples produced via the two-step route, especially when a MB was used and diluted in the first-step (see **Figure 4.29 B &C**).

5.1.6 Stabilisation of PEXa samples with graftable AOPP was enhanced when used in combination with hindered phenol stabilisers. Combining AOPP or AOTP with the conventional hindered phenol Irg 1010 was shown to give the highest OIT retention after DCM extraction suggesting a higher polymer thermal stability, see **Figure 4.31**.

5.1.7 PEX_{Eng} pipes were successfully produced using commercial Engel process, the amount of AOs retained after the commercial pipe production method revealed that the grafted antioxidants e.g. g-Ph (DBPA) was retained to much higher extent than Irganox 1076 (retention of 85% vs 50%, respectively, see **Table 4.5**).

5.1.8 Peroxide crosslinked pipes obtained by the Engel process, PEX_{Eng} (in the presence of one of three peroxides **TB, T145, T101**) showed generally inhomogeneous distribution of the antioxidants due to the lack of mixing in the Engel extruder, **see Table 4.5.** FTIR analysis suggested that successful grafting of the reactive HAS with a graftable hindered phenol (DBPA) antioxidant was achieved with high AO retention after DCM extraction, **see Figure 4.6 B**. The overall thermoxidative stability of pipes was shown to be substantially enhanced when using combinations of g-HAS stabilisers with g-DBPA, **see Figure 4.4B**.

5.1.9 In the PEX_{Eng}-pipes, a higher OIT retention was observed when the formulations contained g-HAS with the g-hindered phenol (DBPA) compared with pipes containing the g- HAS and the conventional hindered phenol Irganox 1076, see **Figure 4.6A**. Furthermore, it was shown that PEX_{Eng}-pipes containing g-HAS with Irg 1076 extracted in oxygenated water gave generally much higher OIT values than when they were extracted in DCM **(Figure 4.5 and 4.6).** A significant decrease in OIT was observed for PEX_{Eng} samples containing two g-AO's after exhaustive extraction in oxygenated boiling water, **Figure 4.5**. It is suggested that under these conditions, the ester group associated with the grafted antioxidants was subjected to hydrolysis. Generally, DCM extraction (see **Figure 4.6**A) gave rise to higher OIT for pipes containing g-DBPA only (**PEX_{Eng} - 5,6 and16**) compared to pipes containing the Irganox 1076 **PEX_{Eng} 1,3 and 26** , PEX_{Eng}-pipes containing two g-AOs (g-hindered phenol and g-HAS), generally gave higher thermoxidative stability (OIT retention) compared to those containing a g-HAS with Irganox 1076 (**Figure 4.6B)**. It was also clear from carbonyl index measurements of the AOs (**Figure 4.6 B**) that DCM extracted PEX_{Eng} pipes containing g-HAS in combination with Irganox 1076 gave rise to a lower AO retention than when g-DBPA was used with the g-HAS (**Figure 4.6B)** due to the mobility and ease of extraction of Irganox 1076.

5.1.10 The overall antioxidant distribution in the PEX_{HS}-pipes containing all g-AOs was found to be homogenous in the radial direction of the pipes, but less homogeneous in the longitudinal direction of the pipes, **see Figures 4.7, 4.9 and 4.10**.

5.1.11 Sequential solvent (DCM followed by xylene) extraction of PEX_{HS} pipes containing Irganox 1076 and a commercial HAS (pipe X1) showed much lower AO's retention of 46% (see **Table 4.9**) compared to pipes produced in the same process but containing two graftable AOs. For example, PEX_{HS}-pipes containing g-DBPA with either g-

AOPP or g-AOTP, (pipes X2 and X4) gave rise to a much higher retention of the two g- AOs of 93 and 97% ,respectively. The retention of the g-DBPA itself was shown to be very high at 91%(**Table 4.9, E2)**, in pipe containing g-DBPA and chim944 (X6) where the AO measurements in this case was for the DBPA only as it was based on the carbonyl absorbance of DBPA (chim 944 does not absorb in the same region).

5.1.12 A **hydrostatic test** at 115°C and 2.5 MPa pressure for the PEX_{HS} pipes with water inside and air outside for the PEX_{HS}-pipes showed that both Pipes PEX_{HS}-X6 containing g-DBPA and Chim 944 and pipe PEX_{HS}-X3 containing low concentration of g-AOs (0.3% g-DBPA and 0.3% g-AOPP) had failed prematurely at 4228 and 2023 hrs respectively, see **Table 4.10**. Visual inspection of the failed pipes showed localized failure with inhomogeneous discoloration, particularly in the inner surfaces of pipe X3, with failure occurring selectively at the point of contact with the air–water interface, **Figure 4.18**. This is most likely due to formation of a combination of polymer oxidation, accumulation of transformation/oxidation products of the phenolic AO on the surface, as well as hydrolysis, leaching and loss of the AOs leading to a stage III pipe failure. Quinonoid- based products of DBPA must have been responsible for the brown discoloration of the pipes.

5.1.13 Since the PEX-pipes examined in this work were targeted for water applications, the fate of AOs in a water boiling test was examined using HPLC-MS analysis to identify products formed and extracted in water. PEX_{HS} pipes X2, X3, X4 and X6 which contained DBPA, showed more fragments present in their water extracts compared to pipes containing Irganox 1076 pipes X7, X8 and X11 (**Figure 4.40**). This suggests that Irganox 1076 is more stable in water under these conditions than DBPA, and further suggests, that the g-DBPA may have undergone hydrolysis at a faster rate than Irganox 1076 resulting in the breakdown of its ester bond which has led to its loss from the polymer during the water extraction process.

5.2 Recommendation for further work

5.2.1 The production of PEX_{HS} pipes using a continuous industrial process was done without optimisation of the chemical composition or the process conditions in the system. The formulations and the extrusion conditions require optimisation in order to achieve the highest possible extent of grafting of the reactive antioxidants and stabilising performance in the peroxide crosslinked HDPE pipes.

5.2.2 The aim of the work was to achieve high level of grafting of the reactive antioxidants in crosslinked polyethylene pipes in order to prevent their migration in solvents and in water. High extent of grafting, and therefore high level of retention of the reactive AOs in the polymer was indeed achieved (AO retention was determined after exhaustive Solvent extraction). However, the reactive (grafted) hindered phenol AO used (DBPA) was shown to hydrolyse in boiling water and was detected, along with some of its transformation products, in the water extract. The principle of grafting AOs in PEXa samples with high retention when in contact with solvent media has been illustrated, but in order to extend this principle when in contact with water (for water pipe applications) to prevent AO migration, a different design of the synthesised hindered phenol AOs (and the reactive HAS) would be required so that they would not include a hydrolysable group in the alkyl "tail" of the AO molecule.

5.2.3 Stabilisation of PEXa samples produced in a two-step laboratory process showed a poor distribution of the antioxidants (AO) in the polymer. It is essential to optimise the procedure of dilution of the graft antioxidant-master batches in order to achieve a better AO homogenisation in the final PEXa material produced by this approach.

5.2.4 The HPLC-MS method developed was found to be suitable for analysing pipe extracts containing the hindered phenol AOs but not suitable for analysing the hindered amines (HAS) and their transformation products. It would be important therefore to develop different HPLC-MS methods that can also identify products formed from HAS that may be extracted from the PEXa pipes.

5.2.5 The transformation products formed from the hindered phenol antioxidants used (DBPA, Irg 1076 and Irg 1010) which were extracted with DCM and with water from PEX_{HS} pipes were identified but not quantified (using analytical HPLC-MS). It is important to quantify the amount of the parent hindered phenols and that of their oxidative transformation products formed in the pipes. Further, the products were only identified by their mass and UV spectra and will benefit from further identification by

FTIR and NMR spectroscopy to ensure their accurate identity. Preparative HPLC should be used to isolate each of the products, followed by their characterisation using different spectroscopic techniques and quantification using appropriate calibration curves.

5.2.6 For better understanding of the hydrolysis of the antioxidants (DBPA, Irganox 1076, Irganox 1010, AOPP and AOTP) that took place during the boiling water experiment for the PEX_{HS}- pipes, reactions of the neat AOs with water at elevated temperatures need to be conducted and products analysed and identified using different chromatographic and spectroscopic methods.

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