Facile synthesis and proposed mechanism of α,ω-oxetanyl-telechelic poly(3-nitratomethyl-3-methyl oxetane) by nitrato displacement method in basic media.

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Abstract

The synthesis of a novel, heterocyclic-telechelic polymer, α,ω-oxetanyl-telechelic poly(3-nitratomethyl-3-methyl oxetane), is described. Infra-red spectroscopy (IR), gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) spectroscopy have been used to confirm the successful synthesis, demonstrating the presence of the telechelic-oxetanyl moieties. Synthesis of the terminal functionalities has been achieved *via* displacement of nitrato groups, in a manner similar to that employed with other leaving groups such as azido, bromo and nitro, initiated by nucleophiles. In the present case, displacement occurs on the ends of a nitrato-functionalised polymer driven by the formation of sodium nitrate, which is supported by the polar aprotic solvent, *N,N*-dimethyl formamide. The formation of an alkoxide at the polymer chain ends is favoured and allows internal back-biting to the nearest carbon bearing the nitrato group, intrinsically in an S_N1 reaction, leading to α,ω-oxetanyl functionalisation. The telechelic-oxetanyl moieties have the potential to be cross-linked by chemical (e.g. acidic), or radiative (e.g. U.V.) curing methods without the use of high temperatures, usually below 100 ^oC. This type of material was designed for future use as a contraband simulant, whereby it would form the predominant constituent of elastomeric composites comprising rubbery polymer with small quantities of solids, typically crystals of contraband substances, such as explosives or narcotics. This method also provides an alternative approach to ring-closure and synthesis of heterocycles.

Introduction

According to IUPAC definition, telechelic polymers are "pre-polymers capable of participating into further polymerization or other reactions with their reactive end functional groups."[1] These polymers are often low molecular weight, less than about 5000 number average molar mass. This is to allow the polymer to be liquid and so easier to mix with the solid filler prior to cross-linking into a network, which is often elastomeric. Energetic material composites may be made in this way by using the polymer as the binder and adding a solid oxidiser, in the case of a propellant composite, or an explosive solid, in the case of a polymer bonded explosive (PBX) composite. The binders may be energetic[2-4], if they are functionalised with energy-rich groups e.g. nitro, azido, nitrato etc. or inert e.g. hydroxyl-terminated polybutadiene (HTPB) or polyisobutylene.

Hydroxyl-terminated polymers are usually cured with isocyanates[5] to form networks. However, isocyanates are toxic and alternative more versatile curing strategies are in demand, especially if these can be made more environmentally friendly or recyclable, which would render them more cost effective. PolyNIMMO [poly(3-nitratomethyl-3-methyloxetane)] is an energetic nitrated oxetane polymer consisting of nitrate ester functional groups and ether links[6] (shown in Scheme 1) and it can be used in a wide range of applications, including use as an energetic binder in low vulnerability gun propellants, high impulse rocket propellants, elastomer modified double-base propellants and high energy PBXs.[7]

A number of oxetane based energetic materials have been developed and investigated[8-10] but polyNIMMO is one which has promising properties for use as a propellant binder when crosslinked with isocyanate cure systems. This polymeric support could act as a replacement for the non-energetic polymer, hydroxyl-terminated polybutadiene (HTPB), which is used extensively in composite propellant systems around the world.[11] Telechelic-polyoxetanes bearing hydroxyl functional groups and epoxy functionalised polymers have been previously reported.[12] Recently, a series of oxetane-terminated epoxy-functional telechelic oligomers have been synthesized and revealed that they can be used to control the final mechanical properties of the networks.[13]

We report here the synthesis of a novel, heterocyclic-telechelic polymer, α,ω-oxetanyl-telechelic poly(3-nitratomethyl-3-methyl oxetane) and the proposed mechanism. This novel approach will generate a range of contraband (especially explosive) simulant materials for the calibration or testing of high-level security instruments and also, this method is expected to be useful for the synthesis of heterocyclic rings, particularly 4-membered oxetane (or thietane) substances.

Experimental

Materials. PolyNIMMO (batch PP820, to specification NGS695, was manufactured ca 1997 and supplied by Chemring Energetics, Ardeer, formerly Nobel Explosive Co.) was used as received.

Tetrahydrofuran (BDH, analar grade), potassium ethoxide (Aldrich), dichloromethane (DCM, Fisher, anhydrous), ethanol (Aldrich reagent grade), sodium hydrogen carbonate (Aldrich) were all used as received. De-ionised water was used for the dissolution of $NaHCO_3$ (Aldrich) and other processes as required e.g. separating the aqueous layer used to wash out the bases from the DCM layer. Sodium metal cuboid pieces in oil (Aldrich) were washed with petroleum ether (Aldrich) in a petri dish under an inert nitrogen atmosphere and then cut into thin slices before addition to the reaction flask.

Procedure. All syntheses were carried out using oven dried glassware at 120°C and cooled under an inert dry nitrogen atmosphere. The general method of synthesis involved the use of both base and polymer dissolved in various solvents such as THF, DCM or ethanol.

Preparation of sample HDPN02CR02 (**4**) Run 1: The polyNIMMO batch PP820 (1.3642g, assumed molecular weight of 3000, hence 1.3642/3000 mol corresponded to 9.095×10^{-4} moles of hydroxyl groups, assuming a hydroxy-telechelic difunctional starting polymer) was weighed into a 2-necked round bottom flask. This polyNIMMO was dissolved in 20cm^3 of DCM and allowed to stir. The flask, fitted with a condenser and an oil bubbler to maintain an N_2 atmosphere, was immersed in a water bath. An excess (relative to the number of moles of hydroxide present) of potassium ethoxide (0.1087g, 1.292×10^{-3}mol) was added to the solution of polyNIMMO, followed by 1cm^3 of ethanol. The mixture was then stirred overnight at room temperature and a yellow colour, assumed to be due to KNO_3 or NO_x, was observed. The reaction mixture was washed with deionised water and neutralised with dilute HCl (Aldrich) monitored by using litmus paper. After separation of the aqueous and organic phases by a separating funnel, the lower organic layer was collected and the DCM was removed by vacuum distillation to leave 0.84g of the final polymer.

Preparation of sample HDPN05CR01 (**4**) Run 2: The same method was used as for HDPN02CR02, except that 6.09g of polyNIMMO were added and a lower molecular weight of 2000 was assumed. This was to make sure that there was enough base added to generate the alkoxide from as many chain-ends as possible. Hence, the number of moles of polyNIMMO was calculated to be 3.045×10^{-3}. This polymer was dissolved in 25 cm^3 of DCM and potassium ethoxide (2.05g, 2.436×10^{-2} mol) was added. A slurry of potassium ethoxide formed, then 5cm^3 of absolute ethanol was added to dissolve it. At this time the temperature of the oil bath was raised to 42°C for 5 minutes then allowed to cool to room temperature. The mixture was stirred overnight and a yellow-orange colour was observed. The reaction mixture was washed with water, DCM and neutralised with dilute HCl. The final yield of polymer was 5.75g.

Preparation of sample HDPN06CR01 (**4**) by Route 1 in Scheme 1, Run 3: The following method is the one which produced oxetanyl-telechelic polyNIMMO and involved the use of sodium (Na) metal in the presence of dimethyl formamide (DMF). PolyNIMMO (6.3g, assumed molecular weight 2000) was added to a flask with 10cm^3 of THF as solvent. Then thin scalpel-cut slices of Na metal (1.30g, 5.65×10^{-2}mol) were washed with petroleum ether and added to the flask under a flow of N_2. This heterogeneous mixture was stirred for 1.5 days, then 10cm^3 of DMF was added using a syringe. The temperature of the oil bath was raised to 40°C for 2 hours (for Na metal to dissolve). The bath temperature was then raised to 90°C and the solution was allowed to reflux for 2 hours. After cooling to room temperature, a yellow-slurry was observed. DCM (200cm^3) was added to dissolve the polymer into an organic layer which was immiscible with water. THF and DMF were then extracted by shaking with water in a separating funnel. The layers were separated and the DCM was removed *in vacuo* to yield 6g of the final polymer.

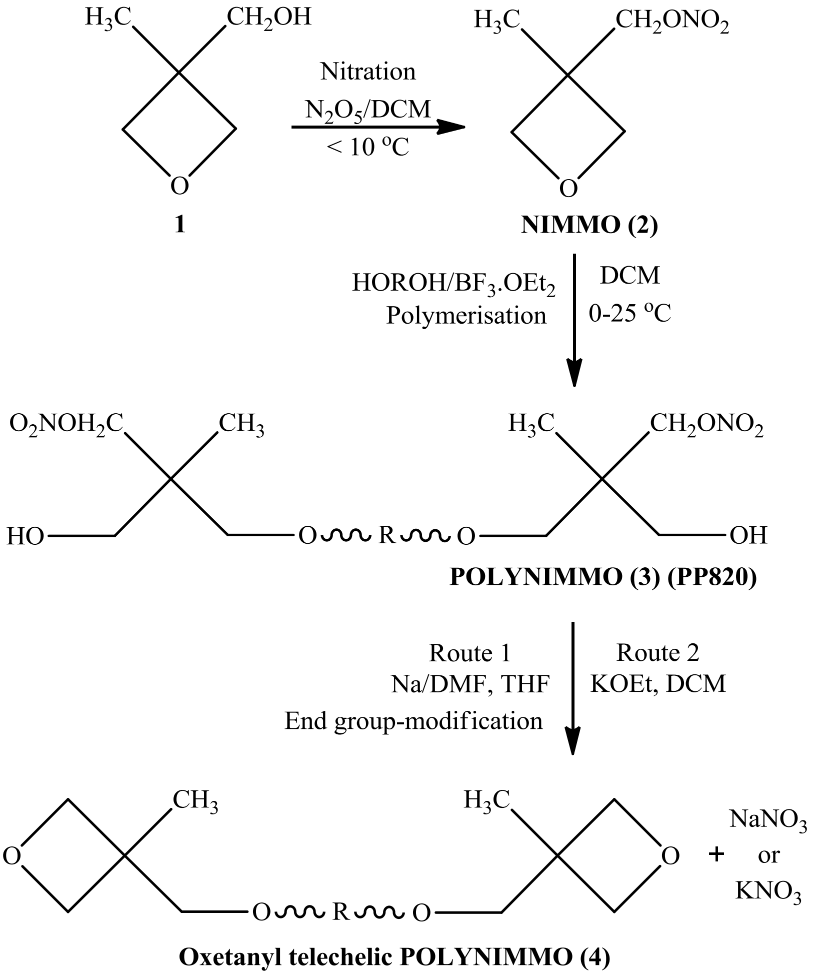
Characterisation.

NMR. The NMR analysis was carried out by Qinetiq, Fort Halstead using the following methods:-
Instrument: a Bruker Avance 400 spectrometer fitted with a 5mm QNP probe or a 10mm VSP probe. For ^{1}H and 2D NMR measurements 0.30±0.03g of sample were dissolved in deuterated chloroform ($CDCl_3$, 1.1±0.2g) containing 0.1% tetramethylsilane (TMS).
The samples were characterised using ^{1}H and ^{13}C, Distortionless Enhancement by Polarization Transfer (DEPT), proton-proton correlation (COSY), proton-carbon correlation (HMQC) and long-range ^{1}H – ^{13}C correlation (HMBC) NMR experiments.
For quantitative ^{13}C NMR measurements, 0.08g of chromium (lll) acetylacetonate was dissolved in 5g of deuterated $CDCl_3$ along with 2.3±0.3g of polyNIMMO. Where applicable, samples were filtered through a 0.45 PTFE syringe filter into 10mm NMR tubes. Over 100,000 $\pi/2$ pulses were collected with a repetition time of 2.5 seconds using the IGATE pulse sequence.

Confirmation of hydroxyl assignment was achieved by derivitisation with hexafluoroacetone (HFA). The reactive gas was bubbled through the polyNIMMO solution at room temperature for 30 minutes. The sample was allowed to react for 30 minutes before NMR measurements were made.
Sample HDPN06CR01 was subjected to extra purification as it contained a fine white powder that was insoluble in chloroform and was difficult to filter out. The residual solid caused the NMR signals from the sample to be broad. The sample was dried *under vacuum* at 60°C overnight, dissolved in chloroform, filtered through glass wool and then 1" 0.45 PTFE inline syringe filters. The sample was dried first in air, then *under vacuum* overnight. Sample dissolution yielded a clear solution.

Results and Discussion

Methods of synthesis for polyNIMMO and it’s molar mass control have been reported by Desai *et al.*[2,14]. Scheme 1 shows the proposed 2 modification routes for polyNIMMO to generate oxetanyl end-groups [An alternative K_2CO_3 method was not attempted during the current work due to a shortage of the starting material, polyNIMMO (PP820)]. Prior to modification the substrate was characterised to establish its base structure and molecular weight. Data for the unmodified material are shown in Figure 1 (FT-IR), Figures 3 and 4 (NMR) and Figure 7 (GPC). In Figure 7, the ‘Pmmo’ label refers to polyNIMMO PP820.



Scheme 1: Synthesis of oxetanyl-telechelic polymer from 3-nitratomethyl-3-methyl-oxetane (NIMMO) showing the proposed routes.

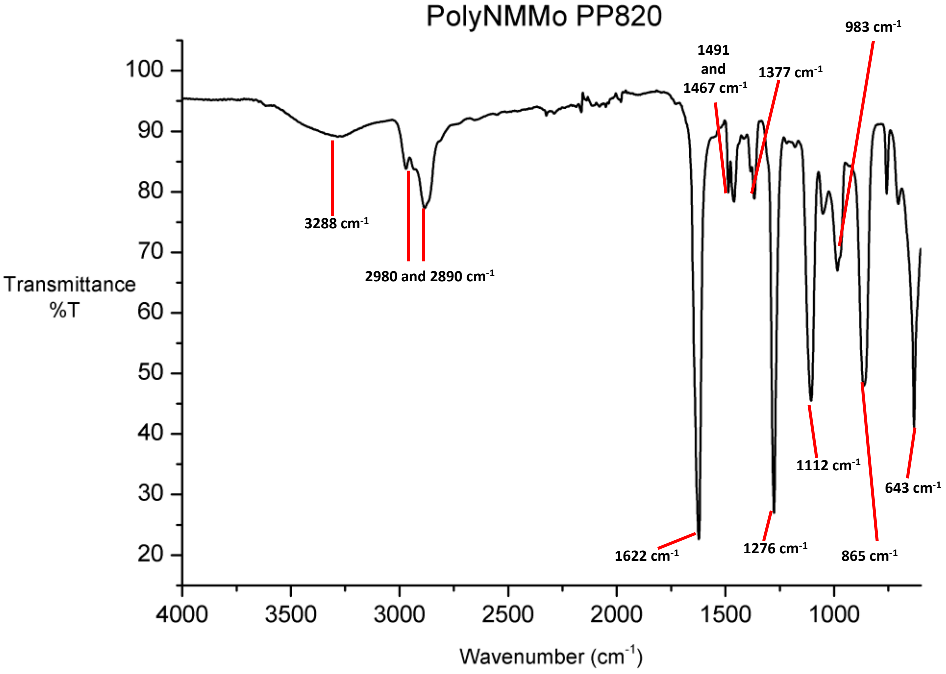


Figure 1: FT-IR Spectrum of unmodified PolyNIMMO sample PP820.

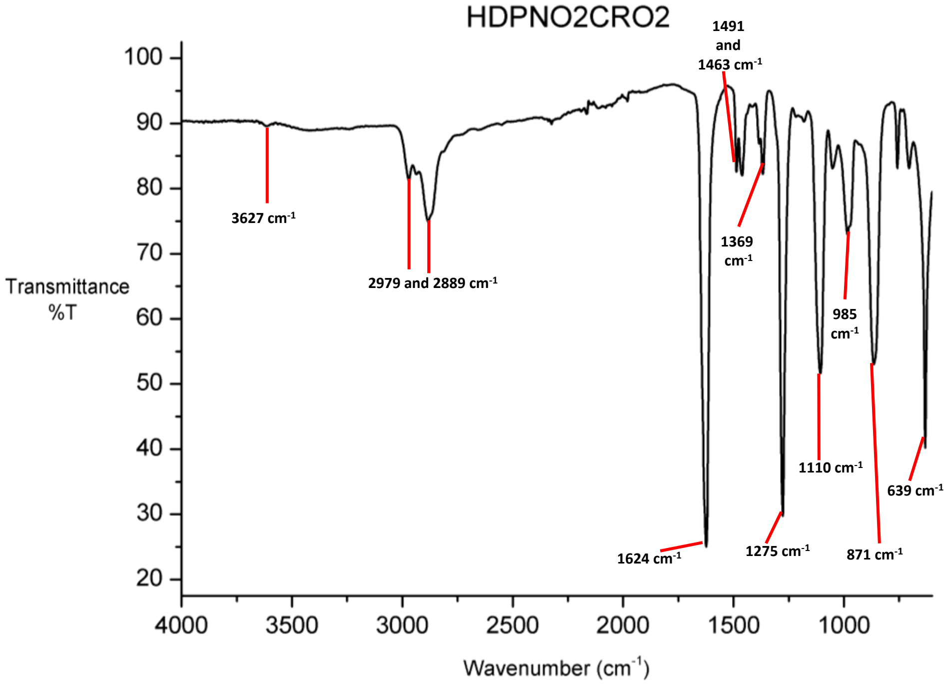


Figure 2: FT-IR Spectrum of potentially modified PolyNIMMO.

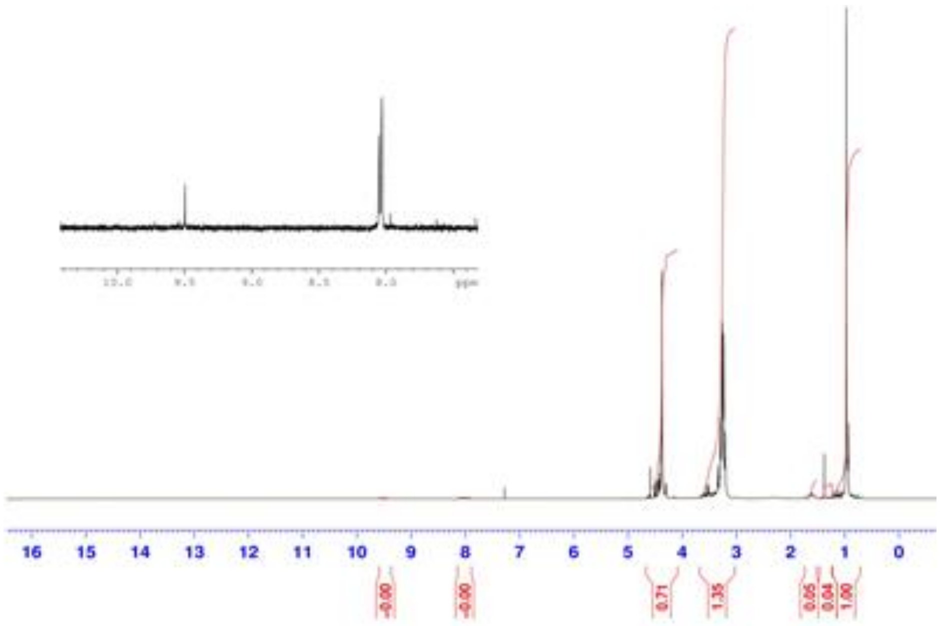


Figure 3: ^{1}H NMR spectrum of PolyNIMMO sample PP820 (in $CDCl_3$).

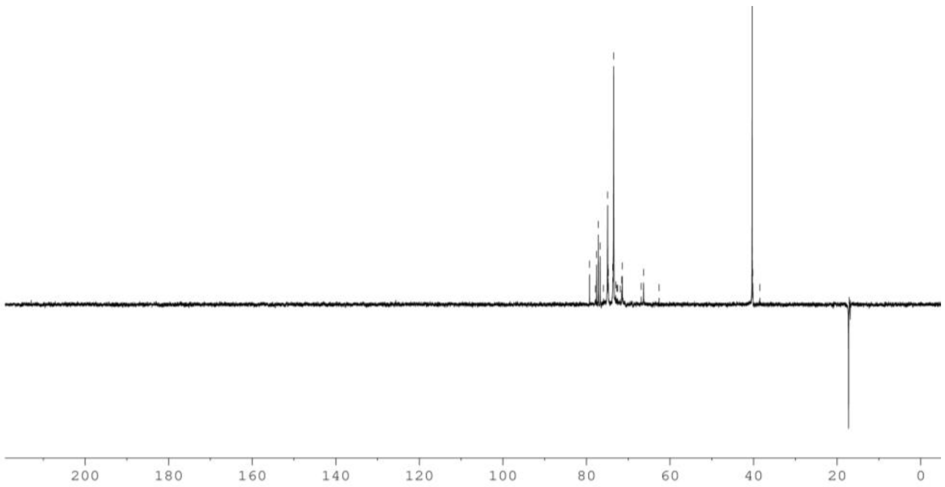


Figure 4: ^{13}C PENDANT NMR spectrum of PolyNIMMO sample PP820 (in $CDCl_3$) (***Note:*** *CH_3 and CH carbons phased downwards, CH_2 and quaternary carbons phased upwards*).

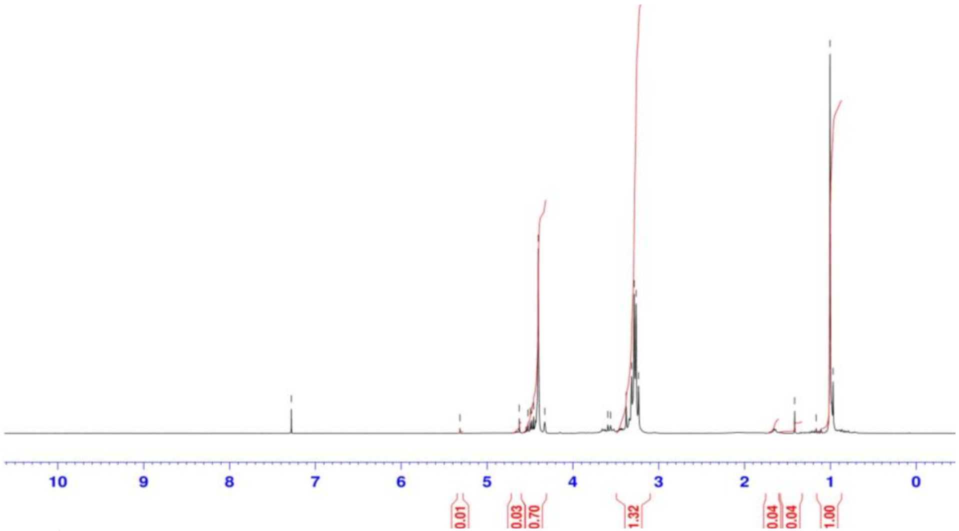


Figure 5: ^{1}H NMR spectrum of PolyNIMMO sample HDPN02CR02 (in $CDCl_3$).

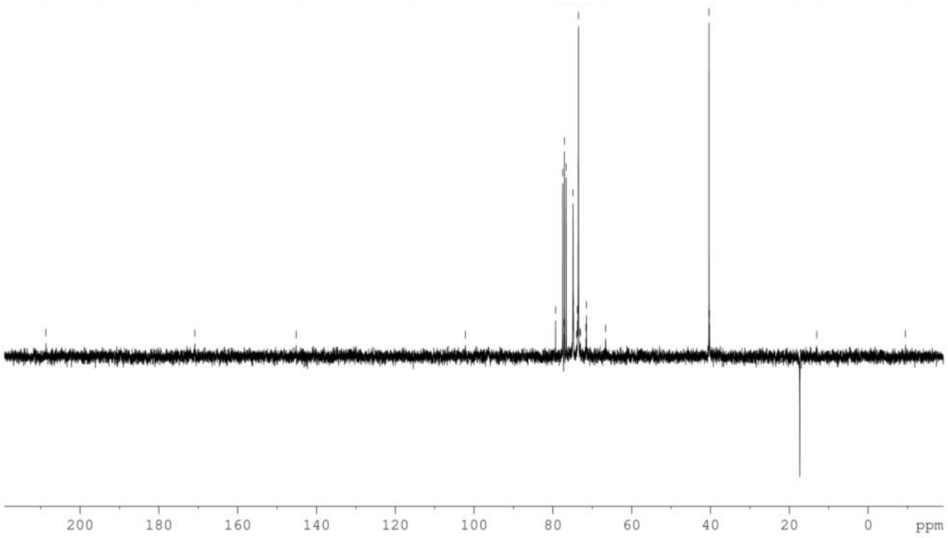


Figure 6: ^{13}C PENDANT NMR spectrum of PolyNIMMO sample HDPN02CR02 (in $CDCl_3$).

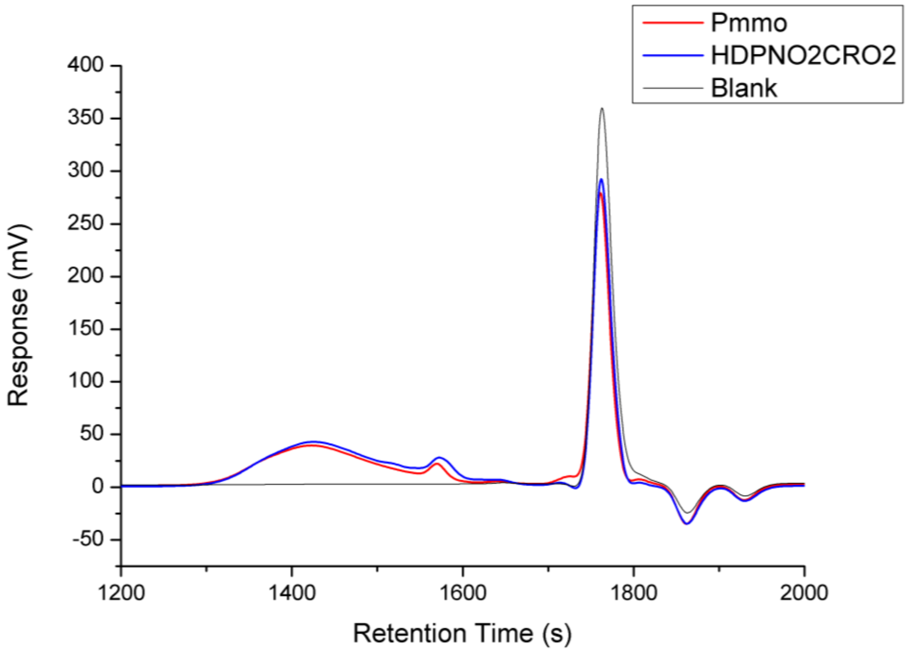


Figure 7: Gel Permeation Chromatograms (GPC) showing that no chain scission arose due to attempted modification of PolyNIMMO by the KOEt route.

The NIMMO monomer is typically polymerised in the presence of a diol by boron trifluoride etherate, to yield telechelic PolyNIMMO. Batch PP820 used here was made by the general process described in the literature[14].

The nitrato displacement reactions attempted used Na/THF and KOEt/EtOH. The FT-IR results (Figures 1 and 2) suggest that the KOEt route has removed the terminal hydroxyl groups, as bands around 3000-3800 cm^{-1} were not detected in the product. A pale yellow solution was observed in the flask to make sample HDPN02CR02 after stirring overnight and before any further washing. This implied that some nitrate esters may have been removed.

However, the NMR results (Figures 3 and 5) imply that the polymer has not been modified, because the –OH peaks observed in the starting material remain. Nevertheless, these may be due to the presence of residual moisture or ethanol.

Due to the ambiguity of these results, additional samples were prepared using the same methods (run 2) and studied in detail using NMR spectroscopy. The data obtained were then compared with those from historic samples of polyNIMMO, previously analysed by Qinetiq. The spectra acquired by Qinetiq are shown in Figures 8 to 15 and are consistent with those obtained elsewhere by the universities of Aston, Leeds and Hertfordshire[17] (see SI).

Starting Material PolyNIMMO PP820:

The 1D NMR spectra (Figures 8 to 10) of polyNIMMO PP820 exhibit spectra typical of previous materials prepared by ICI Explosives. The sample contains polymer functionalised with primary hydroxyl and butanol species, monomer (^{1}H: 4.61, 4.52, 4.47, 1.40 ppm; ^{13}C: 79.3, 77.7, 38.5, 20.9 ppm), and cyclic tetrameric oligomer (^{1}H: 4.32, 3.3, 0.96 ppm; ^{13}C: 76.0, 71.3, 41.1, 16.9 ppm) in addition to hydroxyl end-groups. A small amount of the polymer is also terminated with ethyl species originating from breakdown of the boron trifluoride diethyl etherate synthesis catalyst. Table 1 summarises the main assignments for polyNIMMO. The ^{13}C assignments are also given in Figure 10.

The -OH value (Table 2) ís typical of other polyNIMMO samples produced at Nobel Explosives Company/Chemring Energetics (PP660 to PP1010) whose hydroxyl values varied from 29.3 to 45. The original specification for PP820 was 40.9 -OH value and 0.45% monomer, and these figures compare reasonably well with those determined here. As well as the normal hydroxyl peak signals, there are small peaks at 65.2, 65.0, 64.7 and 63.8 ppm in the ^{13}C spectrum. These are thought to be associated with hydroxyl peaks along the polymer backbone, either due to nitrate ester degradation or backbone oxidation. Although the assignments are not fully understood, they are included in calculations of the polyNIMMO hydroxyl content.
There are small peaks (^{1}H at 8.07 and 8.05 ppm in Figure 11 and ^{13}C at 161.6 and 160.9 ppm, not shown here) which are associated with breakdown of the polymer to formate/formic acid species. Additionally, in Figure 11 there is a minor peak at 9.52 ppm in the proton spectrum associated with an aldehyde breakdown product of polyNIMMO.

Fragment	Proton/ppm	Carbon-13/ppm
-CH$_2$-C(CH$_3$,CH$_2$ONO$_2$)-**CH$_2$**O-	3.27	75.5
-CH$_2$-C(**CH$_3$**,CH$_2$ONO$_2$)-CH$_2$O-	1.00	17.2
-CH$_2$-C(CH$_3$,**CH$_2$**ONO$_2$)-CH$_2$O-	4.40	75.0
-CH$_2$-**C**(CH$_3$,CH$_2$ONO$_2$)-CH$_2$O-	-	40.4
PN-O-**CH$_2$**CH$_2$CH$_2$CH$_2$OH	3.45	71.3
PN-O-CH$_2$**CH$_2$**CH$_2$CH$_2$OH	1.63	26.2
PN-O-CH$_2$CH$_2$**CH$_2$**CH$_2$OH	1.63	29.8
PN-O-CH$_2$CH$_2$CH$_2$**CH$_2$**OH	3.63	62.6
PN-O-CH$_2$**CH$_2$CH$_2$**CH$_2$O-PN	1.58	26.2
PN-O-CH$_2$-C(CH$_3$,CH$_2$ONO$_2$)**CH$_2$**-OH	3.55	66.2
PN-O**CH$_2$**CH$_3$	1.16	69.9
PN-OCH$_2$**CH$_3$**	3.44	15.0

Table 1: Assignments of polyNIMMO chain.

Name	OH milli-equivalent	OH value	monomer content %	oligomer content
polyNIMMO pp820	0.78	43.6	3.3	5.0

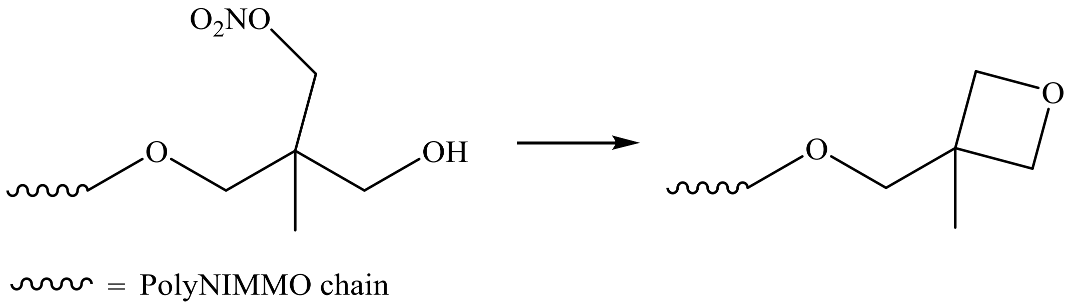
Table 2: Hydroxyl, oligomer and monomer content of polyNIMMO PP820.

PolyNIMMO HDPN05CRO1:
The 1D proton and ^{13}C NMR spectra (Figures 12 and 13) of sample HDPNO5CRO1 are very similar to the starting material PP820. Comparison of the proton spectra of

the PP820 with HDPNO5CRO1 (in SI Figures 23 to 24) suggests that there has been little change in the polymer backbone. The concentration of the monomer has decreased: this may be due to ring opening during the derivitisation process or evaporation during workup. A minor amount of dichloromethane is present.

PolyNIMMO HDPN06CR01: successful modification of polymer end group.
The 1D proton and ^{13}C NMR spectra of hexafluoroacetone derivative are shown in Figures 14, 15; 2D NMR and other supporting spectra are illustrated in SI, Figures 25 to 32. As well as the typical polyNIMMO signals, DMF was also present in the spectra (^{1}H: 2.97, 2.87, 8.00 ppm; ^{13}C: 162.6, 36.6, 31.4 ppm).
A comparison of the HDPN06CR01 spectra with the starting material (see also in SI Figures 31 to 32) indicates that the polymer backbone has reacted. Relative to the quaternary carbon, the signals associated with the nitrate ester carbon have decreased. This suggests that the nitrate ester has been hydrolysed to a primary hydroxyl species as indicated by the broad peak at 67.5 ppm. DEPT measurement confirms that this peak is associated with a secondary carbon (primary hydroxyl species).
Confirmation of the hydroxyl assignment was made by derivitisation with hexafluoroacetone which readily reacts with alcohols at room temperature to form the hemiacetal species. The fluoride atoms cause the NMR signals of adjacent nuclei to shift by amounts which are dependent upon their relative distance away from the reactant group ($-CH_2OH$). In the case of sample HDPN06CR01, the $-C\mathbf{H}_2OH$ protons have shifted from 3.5 to 3.7 ppm whilst the $-(C\mathbf{H}_3)CCH_2OH$ methyl signal has moved from 0.95 to 0.88 ppm (SI, Figure 26). Similarly, in the ^{13}C NMR spectrum, the $-\mathbf{C}H_2OH$ carbon shifted from 67.5 to 66 ppm (SI, Figure 27). This shift is expected for the hydroxyl/hexafluoroacetone reaction. Hence, the experiment confirms the formation and assignment of the new polyNIMMO hydroxyl species.

The desired reaction is loss of the nitrate ester with the concurrent formation of the terminal oxetane ring as depicted below.



Scheme 2: Proposed formation of an oxetane ring by nucleophilic displacement of a nitrate ester group.

Initial inspection of the ^{13}C NMR spectrum might suggest that the hydrolysed polyNIMMO also contains residual monomer, as indicated by peaks at 80, 40, 21.2 ppm in the ^{13}C spectrum. However, the monomer nitrate ester methylene carbon, which is normally hidden under the chloroform signal, was not observable by DEPT measurements. Therefore such peaks are more likely to be associated with a 3-methyl substituted oxetane ring connected to the polyNIMMO chain. The new peaks were observed in the ^{13}C NMR spectrum at 80.2 ppm (oxetane methylene groups, ^{1}H 4.I7 and 4.36 ppm), 40.3 ppm (quaternary carbon) and 21.6 ppm (methylene group, ^{1}H 1.3 ppm). Long- and short-range proton-carbon-13 connectivity experiments (SI Figures

29 and 30) confirmed that the oxetane methylene peaks were within three bonds of the methyl, -CH_2O-PN carbon and quaternary carbon. Although the peaks are similar in position to 3-hydroxymethyl-3-methyloxetane (HMMO), there is no observable cross-peak with a –CH_2OH species. Therefore it is less likely that the oxetane peaks originate from hydrolysed NIMMO monomer.

Additionally, it was noted that the intensity of the polyNIMMO-CH_2OH peak was attenuated relative to the starting material (SI, Figures 31 and 32), suggesting that this species had been consumed during the oxetane formation reaction. It should be noted that the relative concentration of the oxetane seems to be greater than two times that of the polyNIMMO-CH_2OH. This suggests that the derivitisation process has caused the polyNIMMO to undergo chain scission and therefore has decreased the molecular weight. This should be confirmed by further GPC measurements.

The molar ratio of oxetane groups to polyNIMMO methyl was calculated to be 1:17.3 whilst the ratio of hydroxyl (assumed to be derived from nitrate ester degradation) was 3.6:17.3. This suggests that there are more hydroxyl end-groups than oxetane end-groups present in the final polymer. However, careful adjustment of the stoichiometry of sodium to polyNIMMO and of reaction times should improve this as both parameters should be reduced. Nevertheless, these experiments have shown that it is possible to displace nitrate ester groups within polyNIMMO by an internal alkoxide, leading to oxetanyl-telechelic polymers. As such polymers are designed to be liquid for easier processibility, lower molecular weights and some chain scission may be tolerable. This sort of material should be easier to cross-link into elastomers than conventional hydroxyl terminated polymers, perhaps using radiative but more likely by chemical (acid catalysed) curing techniques.

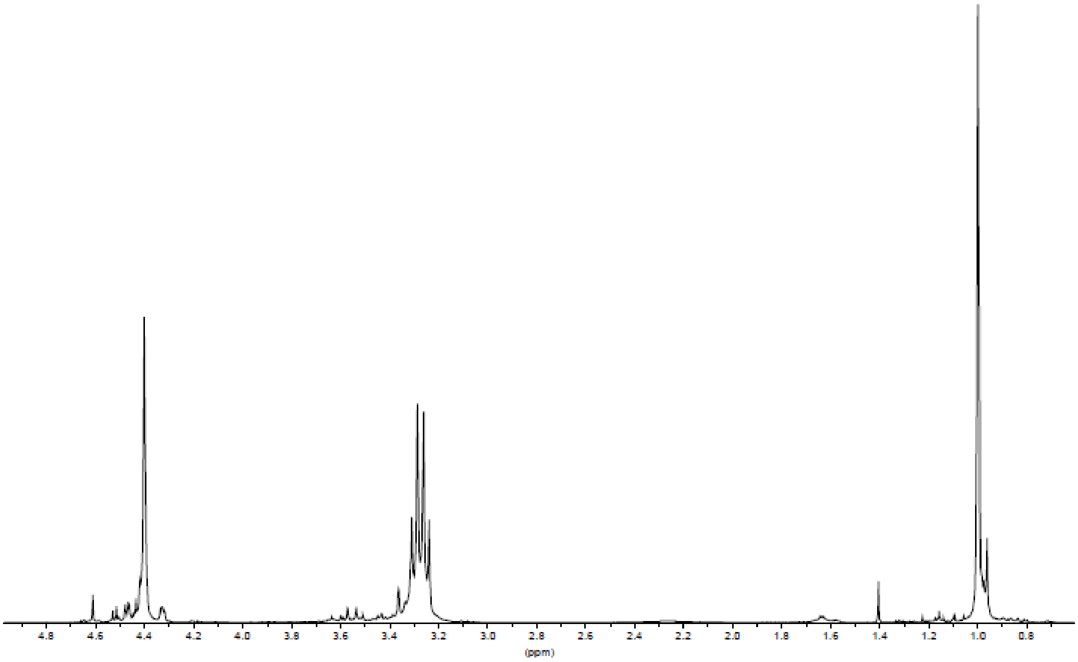


Figure 8: ^{1}H NMR spectrum of PolyNIMMO sample PP820 (in $CDCl_3$).

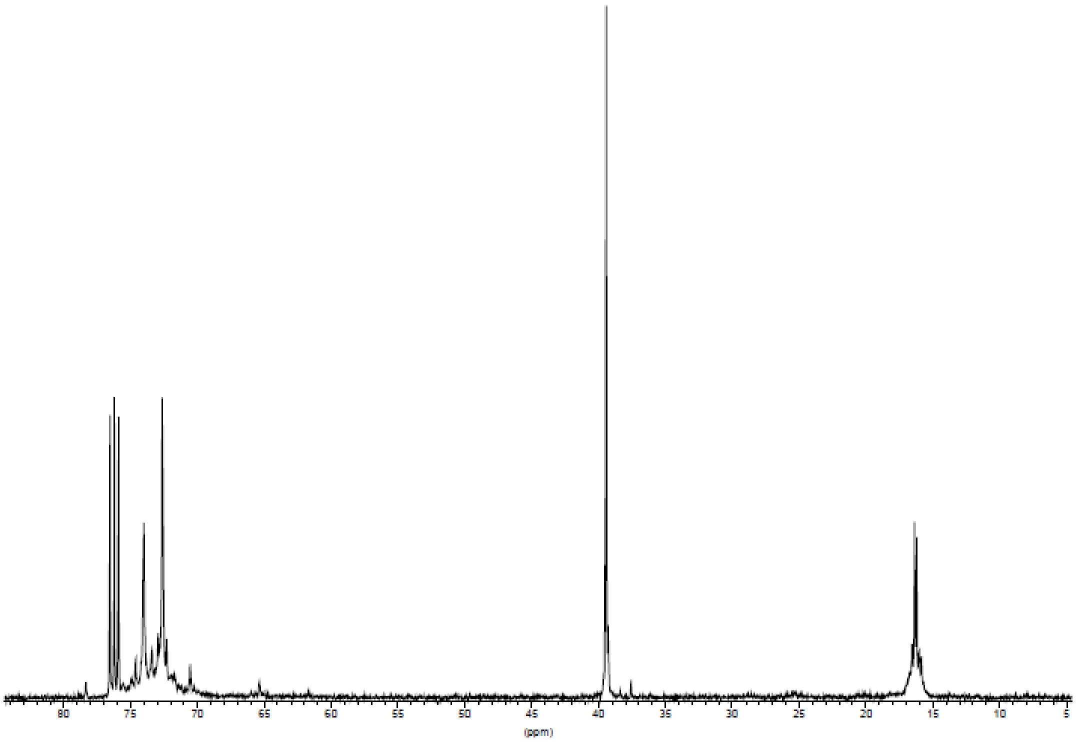


Figure 9: ^{13}C NMR spectrum of PolyNIMMO sample PP820 (in $CDCl_3$).

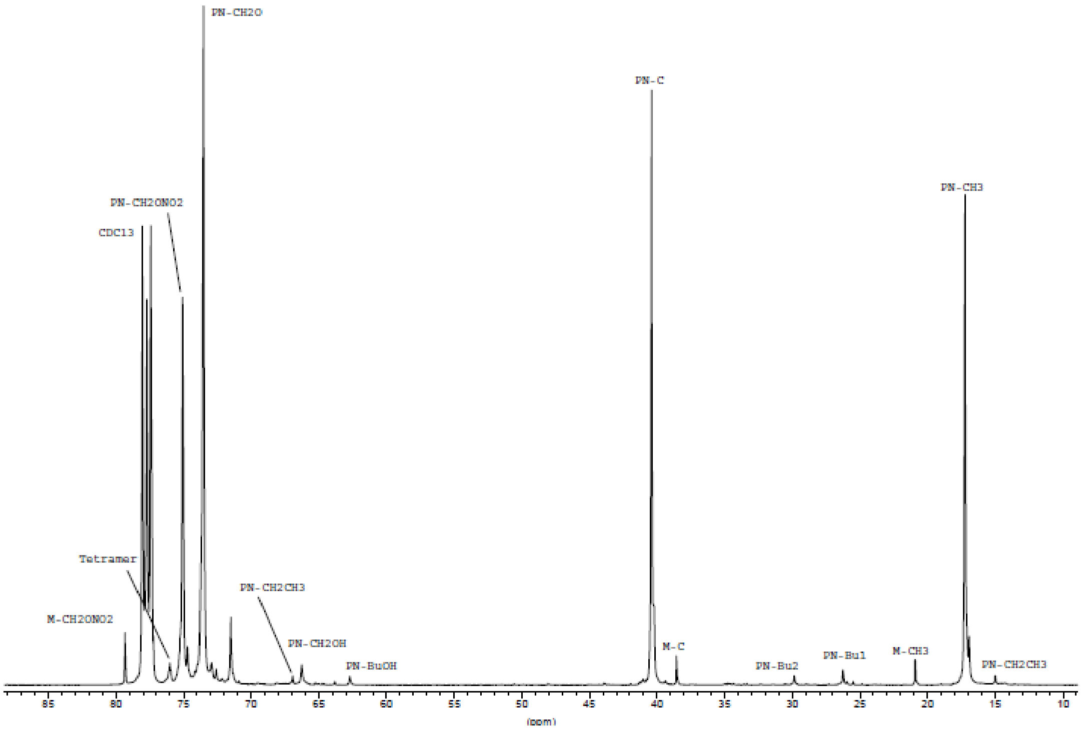


Figure 10: ^{13}C NMR spectrum of PolyNIMMO sample PP820 (in $CDCl_3$).

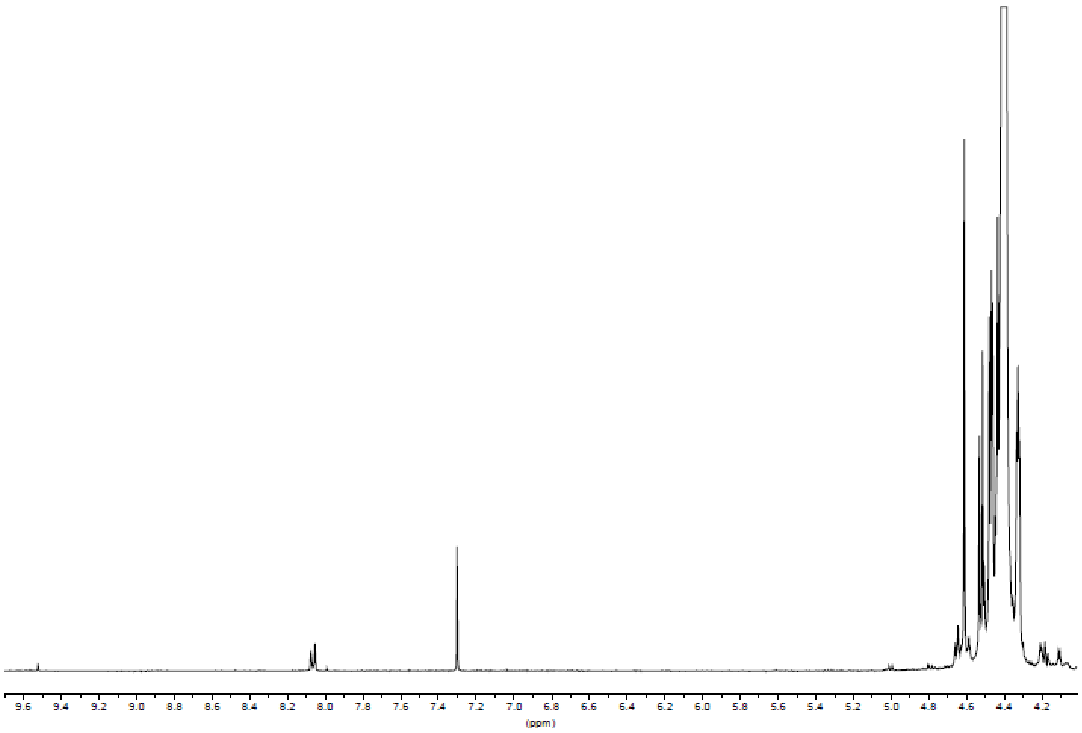


Figure 11: Breakdown product signals of PolyNIMMO PP820.

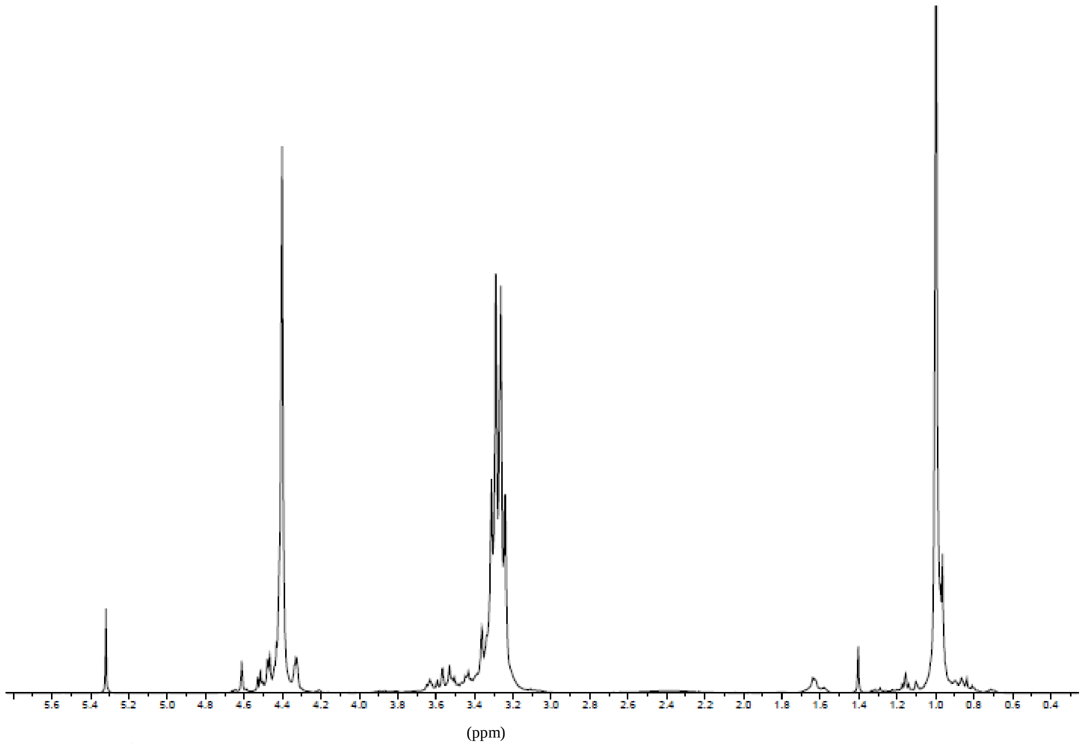


Figure 12: ^{1}H NMR spectrum of PolyNIMMO sample HDPN05CR01 (in $CDCl_3$).

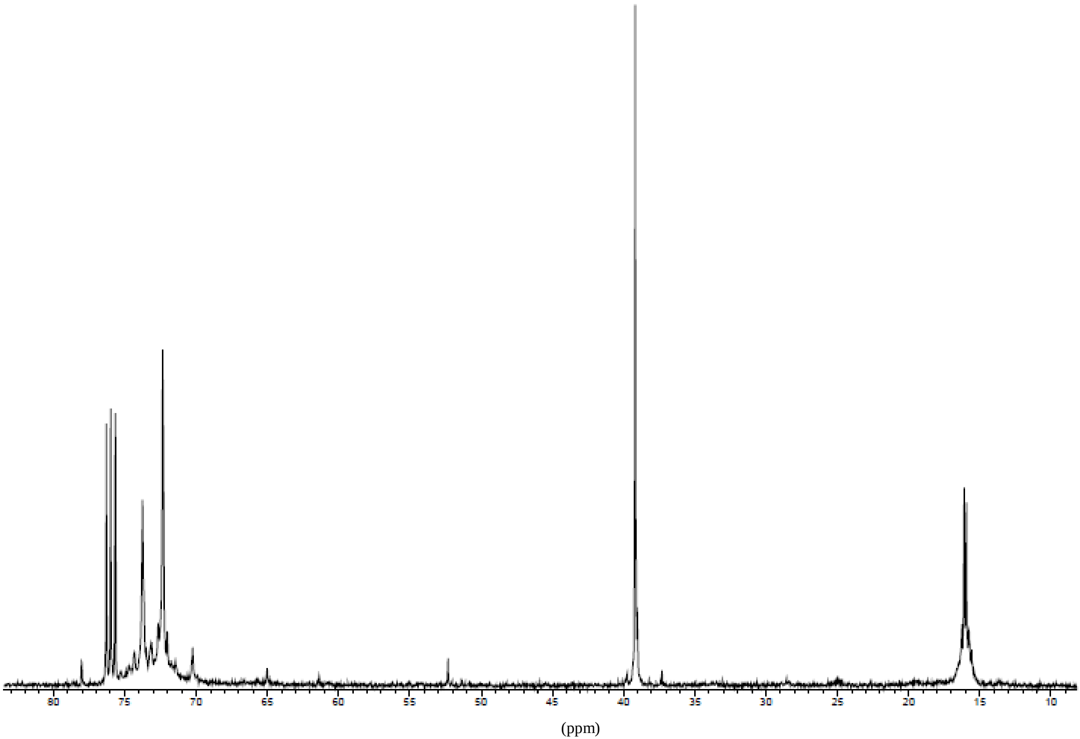


Figure 13: ^{13}C NMR spectrum of PolyNIMMO sample HDPN05CR01 (in $CDCl_3$).

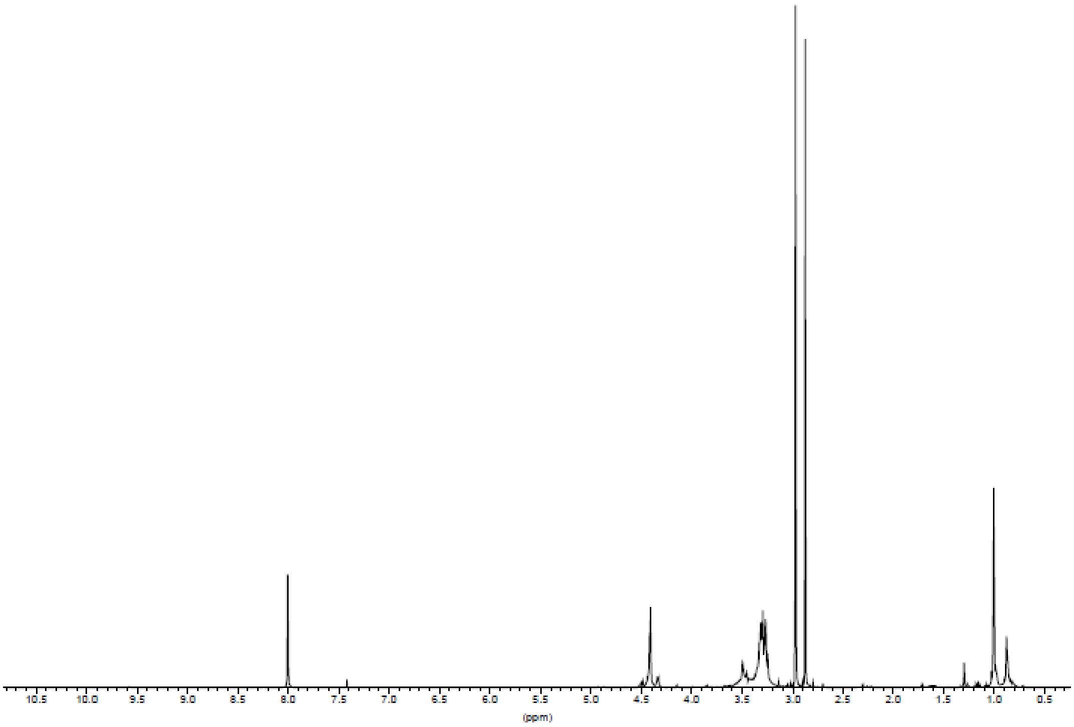


Figure 14: ^{1}H NMR spectrum of PolyNIMMO sample HDPN06CR01 (in $CDCl_3$).

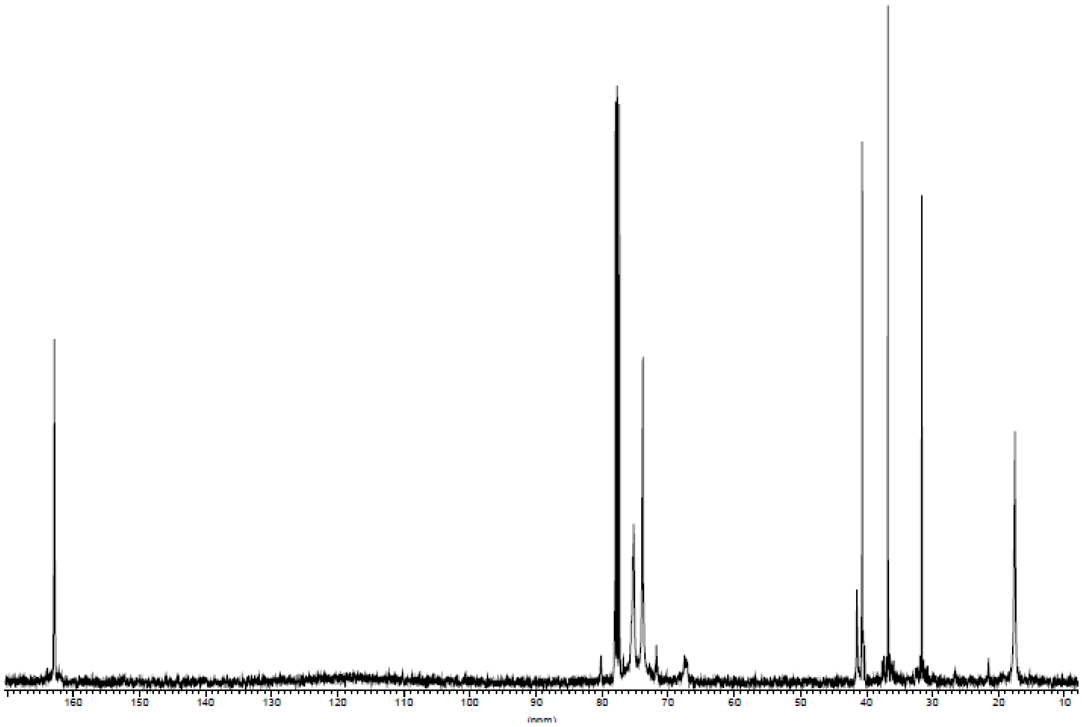
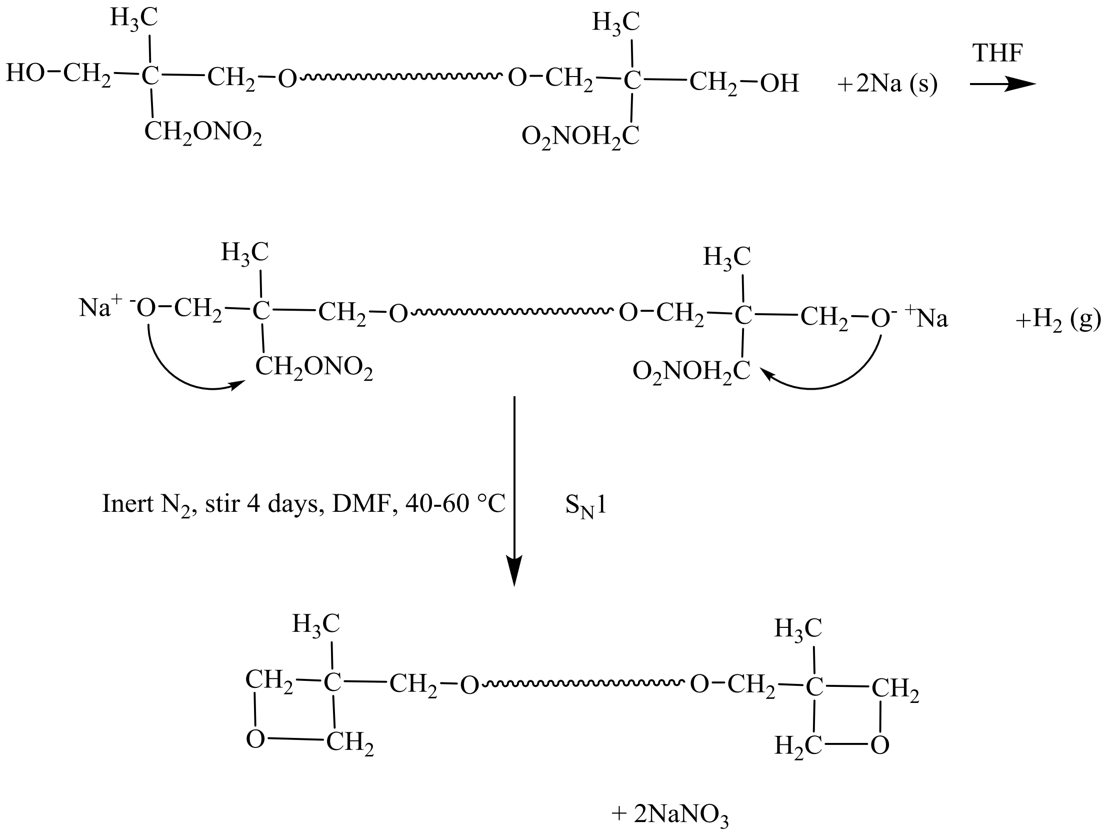


Figure 15: ^{13}C NMR spectrum of PolyNIMMO sample HDPN06CR01 (in $CDCl_3$).

The Gel permeation chromatography (GPC) results comparing the original PP820 material and the KOEt/EtOH treated sample HDPN02CR02 suggest that the polymer was not cleaved in this route. However, the Na/DMF route1 may have caused some chain scission. Scheme 3 below shows the proposed mechanism for nitrato displacement leading to the formation of oxetanyl-telechelic end-groups. The initial heterogeneous reaction between the sodium metal and the polyNIMMO hydroxyl end-groups is slow in a solvent, because dissolution reduces the concentration of -OH groups. Unfortunately, a solvent is required to reduce the viscosity of the polymer, otherwise the Na metal would be immobilised in the polymer away from unreacted hydroxyl groups. Heating the reaction for two hours, both, aids the formation of the alkoxide and increases the end-group dynamics to allow the neigbouring nitrato to be attacked in an internal S_N1 step by the alkoxide. The presence of DMF seems to be requisite in supporting the displacement, possibly by enabling dissolution of the $NaNO_3$. White *et al.*[15] have shown that polar aprotic solvents allow displacement of nitro groups in the synthesis of polyetherimides. Thiruvasagam and Venkatesan[16] have also shown this and in their work Dimethyl suphoxide (DMSO) and N-methyl pyrrolidinone (NMP) seem to be more effective at room temperature in supporting, in their case, the eliminated $NaNO_2$. These solvents may be considered instead of DMF in future studies.



Scheme 3: The proposed mechanism showing the formation of oxetanyl end-groups by an S_N1 step.

The HDPN06CR01 polymer prepared here appears to have the oxetane end-groups, as shown by the NMR spectra in Figures 14 and 15 (see also Figures 25 to 32 in SI). These end-groups should facilitate acid catalysed cross-linking reactions to form networks, in this case elastomeric networks due to the flexible backbone of polyNIMMO. Radiative cross-linking, especially with suitable photosensitizers may be possible and was the original concept behind the reported work here. This approach would allow explosive or oxidiser fillers to be surrounded by the elastomer then cured by relatively low-heat-generating radiative processes less likely to affect the fillers. In principle, highly filled polymer bonded composites should also be possible, although the thickness of the composite may be limited.

Further work

Subject to availability of polyNIMMO (which is currently unavailable commercially) attempts should be made to prepare more oxetanyl-telechelic material by this process (Na/THF) in order to determine if there is any chain scission of the backbone or production of extra cyclic species. The KOH/EtOH/(DMF) method should also be explored and may work if the $–OH^-$ or $-OEt^-$ group is effective in abstracting the proton from the polymer end to form the alkoxide. Due to the limited amount of polyNIMMO available these reactions were not assessed during the current study.

The curability of the oxetanyl material should also be evaluated to ascertain whether it may be cross-linked effectively using acidic or radiative catalysis, either with or without photosensitizers.

Other oxetanyl polymers may be attained by end-capping with a suitable monomer containing a good leaving group, analogous to NIMMO monomer and subsequent base enhanced elimination of the leaving group in the presence of an aprotic solvent. Other heterocycles may also be viable, perhaps by replacing the O atom with N, but in particular, S atoms to form thietanes, whose bioactivity could be of interest.

Conclusions

This work has shown that treatment of polyNIMMO with potassium ethoxide did not appear to significantly alter the structure of the polymer. Thus, aside from loss of monomer, the procedure to produce polyNIMMO HDPNO5CRO1 did not yield any observable products that differed chemically from the initial polyNIMMO substrate. However, the reaction process employed for sample PolyNIMMO HDPN06CR01 did modify the polymer chain. Thus, there is evidence that this reaction displaced the terminal nitrate ester functionality with ring closure to generate an oxetane and it is likely that the molecular weight of the main chain polymer decreased. Spectroscopic evidence indicates that the observed oxetane functionalities are likely to be chemically connected to the main polyNIMMO backbone at the chain ends.

This procedure constitutes a novel method for the *in situ* formation of oxetane rings, utilising base catalysed displacement of nitrato groups. The method may be equally applicable to the formation of cyclic structures at the chain-end of other polymers. The technique may also facilitate the generation of heterocyclic species within very different chemical structures of potential interest to unrelated applications for example in antibiotic molecules.

It is concluded that oxetanyl-telechelic polyNIMMO has been prepared, by using Na metal to instigate an S_N1 reaction. This product is likely to be amenable to acid or radiative catalysed cross-linking reactions. Such procedures should have the advantage of effecting a low heat generation cure, thereby reducing the degradation risk to any fillers, especially if energetic. Also, in contrast to urethane cures, this process will avoid the use of toxic isocyanates and should avoid bubble formation due to gas generation within networks.

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