" THE MELTING OF CRYSTALLINE POLYMERS. "

by

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SUMMARY.

It has been shown that the thermograms of many 66 nylon samples contain two melting endotherms. White, originally reported this phenomenom for drawn fibres. It has now been observed with precipitated and annealed 66 nylon and with other suitably annealed crystalline polymers.

The new endotherm always appeared at a lower temperature than the original single melting endotherm of the untreated polymer. On annealing, the development of the new endotherm was usually dependent on both the time and temperature of annealing.

With 66 nylon, as the annealing time at a given temperature increased, the area of the new endotherm increased at the expense of the final melting endotherm. Simultaneously, the melting temperature of the new endotherm increased slightly. Prolonged annealing at 242°C. resulted in a single melting endotherm at a temperature lower than that of the unannealed polymer. Subsequent quantitative annealing experiments confirmed these observations.

The crystallization of molten 66 nylon at 242°C. produced polymer with two melting endotherms. These were shown to have resulted from an annealing process, rather than the primary crystallization.

Further experiments on annealed 66 nylon, including quantitative and X-ray diffraction measurements showed that changes in the polymer occurred during annealing. These however could not be attributed to changes in the molecular weight distribution or in the visual morphology of the polymer, during the annealing process.

Slow, rather than fast precipitation of 66 nylon favoured the formation of polymer with two melting endotherms. Other properties were also shown to depend on the precipitation method used.

The apparatus used, together with the experimental techniques and methods of sample preparation, are described.

The results obtained and the possible causes of the double melting endotherms are discussed in relation to the current concepts of polymer morphology.

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1. INTRODUCTION. THE PROBLEM.

In 1955, White (1) published his observations on the melting of crystalline polymer fibres, notably 66 nylon, using the technique of differential thermal analysis (D.T.A.). He reported a single broad melting endotherm at 240°-265°C. for undrawn 66 nylon fibre. When a drawn fibre was melted, two melting endotherms at 240°-257°C. and 259°-265°C. were observed. The relative sizes of the two endotherms were dependent on the degree of drawing of the fibre.

When the drawn fibre was heated to the temperature between the two endotherms and allowed to cool, there was no sign of fusion having occurred. However, the X-ray diffraction pattern, the optical birefringence and the melting curve all resembled those characteristic of the undrawn fibre. White suggested that the lower temperature endotherm resulted from the drawing process, and was caused by the disorientation of ordered crystalline regions produced by this process. The second endotherm was caused by the final fusion of these crystalline regions.

There was other evidence (2) that certain non oriented 66 nylon samples also showed two melting endotherms. The problem therefore was twofold; firstly, was this behaviour a property of only highly oriented polymers, and did it occur in other polymers apart from 66 nylon. Secondly, to discover the variation in structure responsible for the differences in the melting behaviour.

The published literature was searched for information possibly relevant to the basic problem, and this can be considered in several sections. Firstly, what was the present concept of polymer structure, and how did it develop?. Secondly, what was the relationship between a polymer's melting point and its actual structure?. Thirdly, what information about polymers and polymer structure has been obtained by examining polymers using differential thermal analysis?. Finally, have the polyamide polymers, any properties which could possibly influence the observed results?.

2. POLYMER MORPHOLOGY, MELTING, AND THE DIFFERENTIAL THERMAL ANALYSIS OF POLYMERS.

2:1 DEVELOPMENT OF THE CONCEPTS OF CRYSTALLINE POLYMER STRUCTURE.(3-7,14)

In the late nineteenth century, as methods of determing molecular weights became more sophisticated, it was evident that materials, such as cellulose, had very high molecular weights. X-ray diffraction studies suggested the presence of small discrete crystalline units which were called "micelles". They were often given cyclic structures, incorporating several monomer units to explain empirical formulae. The micelles were thought to be held together by partial valence forces, thus forming a "colloidal-like", association compound.

In 1920, Staudinger, as a result of his studies on the viscosities of polymer solutions, proposed an alternative theory. He suggested that polymers consisted of long chains of atoms held together by normal covalent bonds. He thought that low molecular weight polymers could form individual crystallites, whereas the higher molecular weight polymers formed continuous imperfect crystals.

The conflict between these two approaches was resolved by the development of the "fringed micelle" theory in the early 1930's. The basic postulate of this theory was that the structure of the polymer consisted of a long molecule passing continuously through both crystalline and non crystalline regions. A more detailed account of this theory and its wide interpretation has been given by Hearle. (3)

The fringed micelle theory, especially the crystalline/amorphous concept, satisfactorily explained many observed polymer properties. X-ray crystallography further confirmed the idea of the presence of crystalline regions within a polymer. The "unit cell" dimensions, and the packing and configuration of the individual polymer molecules within this unit cell were calculated for many polymers, using X-ray data.(4,6) However, later work has shown that the fringed micelle theory was not a complete picture of polymer structure.

In 1945, the first spherulites were observed in synthetic polymers. They were recognised by their characteristic appearance in a polarising microscope. They consist of radiating crystalline fibrillar structures of a larger magnitude than envisaged by the fringed micelle theory. The axis of the spherulitic fibrils has been shown to correspond to a particular crystallographic axis. The characteristic extinction patterns that have been observed, have been explained on the basis of the periodic twisting of the radiating fibrils. The orientation of the molecular chains has been shown by micro X-ray diffraction to be either normal or slightly inclined to the fibrillar axis and the orientation is said to be "tangential" to the radiating fibrils. Electron microscopy of spherulites has shown the presence of intertwining fibrillar structures, and in some instances, the formation of ribbon like lamellae. More detailed accounts of the ideas of spherulitic structure are given by Keller; Keith and Geil. (4-6)

In 1957, the first polymer single crystals were prepared by crystallization from a dilute solution. (4-6) Before this, it was thought that polymers could not form single crystals, because of the chain entanglements envisaged by the fringed micelle theory. Since then, single crystals of many polymers have been prepared, (6) those of poly(ethylene) having been studied most intensely.

Poly(ethylene) single crystals have been observed in various crystal habits, usually as lamellae about 100Å thick. The orientation of the polymer molecules in the crystals has been determined by electron diffraction. The molecules are aligned perpendicularly to the lamella crystals. The length of a polymer molecule was expected to be five or ten times greater than the thickness of a single crystal. Hence the molecules could not be perpendicular to the lamellae and remain straight. It was proposed that the individual polymer molecules must be sharply folded at regular intervals. The length of the fold determined the crystal thickness. It has been shown that the fold length was dependent on the crystallization temperature and could be increased by annealing the single crystals at temperatures slightly below their melting point.

In both the melt, and in solution, polymer molecules are known to have irregular and random configurations. Yet on crystallization, these long chain molecules form spherulites in the melt, and single crystals in solution. Various theories have been postulated to explain this phenomenon.

Keith and Padden (9-10) have proposed a theory of spherulite growth, similar to that for metals, which accounts for the amorphous phase, which has been shown to exist from low angle X-ray scattering studies. They suggest that the impurities were rejected from the growing crystalline front and that protrusions were sent out into the melt, searching for more crystallizable material. This gave rise to the characteristic branched fibrillar spherulitic structure, with the impure material concentrated in between the crystalline fibrils. This impure material was then thought to account for the observed amorphous content of the polymer.

Two main theories have been postulated for the growth of single crystals. The kinetic or nucleation determined growth theory of Lauritzen and Hoffman, (11) suggests that in dilute solution, nuclei may form by inter-molecular crystallization - ie. chain folding, whereas in concentrated systems, there would be a greater chance of molecules combining to form spherulitic type bundles.

The alternative theory of Frank (12) and Peterlin and Fisher (13) is based on the thermodynamic considerations of states of lowest free energy. They suggest that a crystal, containing folded chains, has a lower free energy than one where the chains are straight, and that the minimum free energy state occurs for fold lengths similar to those actually observed. A more detailed comparison of the two theories is given by Geil. (6)

The relationship between single crystals and spherulites has not been definitely established. Structures, called hederites, showing some properties of both simultaneously, have been observed. Electron microscopy of the surface of spherulitic bulk polymer has shown definite "lamella-like" structures. In certain orientations, single crystals resemble the fibrous bundles from which spherulites can develop.

The structure of oriented polymers, such as drawn fibres has not been definitely established. (4,6) The large periodicities along the fibre axis and the existence of fine fibrils within the fibre have always been interpreted on the basis of the fringed micelle theory, or some variation of it. (3,4,6)

In a drawn fibre, the molecules are thought to be in an extended chain configuration and highly aligned in the draw direction. It has been shown that in the drawing process, folded chain lamellae unfold to produce the micro fibrillar structure characteristic of both synthetic and natural fibres. (4,6) In some instances it appears that the remnants of undeformed lamellae can be incorporated in the fibre. (6,8,14)

Peterlin, (14) has suggested, since some of the chain folds which form the surface of the polymer crystal may not immediately re-enter the crystal, this could explain some of the observed crystal defects. In melt crystallized material, there will be the likelihood of far more chains not re-entering lamellae. These can then be incorporated into more than one lamellae, forming tie molecules which prevent the intervening material from crystallizing and so produce an amorphous region. This is similar to the fringed micelle theory, the improvement being that the chain folds are proposed as being responsible for the discontinuity between crystalline and amorphous regions in the polymer.

He has further proposed that on orientation, the tie molecules in the amorphous regions become highly strained and aligned compared to their more normal relaxed state in the bulk polymer. Now, they can be regarded as being in a "psuedo-crystalline" state and so increase the overall crystalline content of the polymer. The decrease in properties, such as dyeability, diffusion and permeability observed in drawn polymer fibres and films, can then be explained on the basis of this increase in crystallinity resulting from the orientation of the tie molecules in the amorphous regions caused by the drawing process.

2:2 THE EFFECTS OF STRUCTURE AND ANNEALING ON POLYMER MELTING POINTS.

Melting of a substance occurs when the thermal vibrations reach such an amplitude that the structure disintegrates. Small or imperfect crystals will require less thermal energy to disintegrate than larger or more perfect crystals and so will melt at a lower temperature. Since polymeric materials are thought to consist of crystalline regions of widely varying sizes and degrees of perfection, their normal characteristically broad melting ranges could be expected on the basis of the above hypothesis, although it is not the only criterion.

This can be illustrated by considering the melting points of linear and branched poly(ethylenes) determined under identical conditions. (15) The branched polymer melts at a lower temperature, over a somewhat wider range than the linear one. It was suggested that this was due to the decrease in crystalline perfection, as a result of the branches disrupting the uniform packing of the linear polymer chain.

Thermodynamically, the melting point is defined by the relationship;

$$T_M = \Delta H_f / \Delta S_f \qquad \text{------Eqn.2:1}$$

where ΔH_f and ΔS_f are the differences in enthalpy and entropy, between the liquid and crystal at the melting temperature T_m respectively. In polymers with strong intermolecular attractions, such as the hydrogen bonding in polyamides, ΔH_f is increased, and higher melting points result. (16) ΔH_f can be measured by calorimetry (17) or by quantitative differential thermal analysis (see 2:3) or differential scanning calorimetry (18) although a knowledge of the degree of crystallinity is required with these methods. An alternative method of determining ΔH_f is by calculation, using Flory's equation, (30) based on the depression of the melting point caused by the addition of a diluent.

In high molecular weight polymers, the entropy of fusion becomes significant. On melting, a crystalline polymer not only gains entropy from the destruction of its crystalline lattice, but also because of the greater freedom of molecular motion of individual segments of the polymer chain, possible in the liquid state. Hence the value of ΔS_f will now depend on the energy differences between different rotational isomers in the molten state. (19) For example, in poly(ethylene), the energy differences between different rotational isomers in the melt is low, and hence the distribution between the two forms will be almost equivalent. In poly(tetrafluoroethylene), the energy difference between the isomers is much higher and the lower energy form predominates even in the melt. (20) Thus poly(ethylene) gains more entropy on melting than poly(tetrafluoroethylene) does, and so will have a lower melting point, as predicted by equation 2.1.

The actual shape of the molecules also helps to determine the melting point, (21). Steric hindrance to free rotation will tend to increase ΔS_f. For example, compare the melting points of poly(ethylene), 137°C. and the more sterically hindered isotactic poly(propylene), 176°C. (22,23) If the shape of the molecules is such, that they can move without destroying the crystalline lattice, the entropy of the crystalline state will be increased and ΔS_f decreased. Hence, according to equation 2:1, the melting point will increase. (24) This onset of molecular motion sometimes known as "pre-melting" can be detected by nuclear magnetic resonance (N.M.R.) studies, (25-28) and has been observed for poly(tetrafluoroethylene),(24) and to a lesser extent in poly(ethylene) (25,27,28), poly(propylene) (24) and polyamides (26,29,8). In 66 and 610 nylons, at about 160°C. the crystal lattice structure changes to the higher entropy psuedo-hexagonal structure, from the lower entropy triclinic structure, as a result of the onset of the molecular motion of the paraffinic segments of the chains. (8)

Flory (30) has shown that the melting point of a polymer will increase with increasing molecular weight. He assumed that the free ends of the polymer chains will act as a diluent in the polymer, thus depressing its melting point. As the molecular weight increases, the number of free chain ends decreases, and so does the diluent effect, hence the melting point rises. Once a certain molecular weight has been reached, the effect of the small number of free chain ends becomes insignificant and the melting point remains effectively constant. Isotactic poly(propylene) is an example of this type of behaviour. (31) Samples, having a number average molecular weight of 900, melt at 90°C., of 2,000, at 114°C. and 30,000 at 176°C. Above 30,000, the melting point is constant, independent of the molecular weight.

The rate of crystallization from the melt will affect the subsequent melting point of a polymer. Rapid crystallization rates will produce relatively small crystals, whereas slower crystallization rates produce larger more perfect crystals that melt at a higher temperature. Reding (32) has demonstrated the effect of increasing the crystallite size on the melting point of poly(ethylene). The optical melting point increased from 105°C. for a crystallite 160Å long, to 132°C. for one 275Å in length.

The temperature of fusion and subsequent recrystallization can also affect a polymer's morphology and hence its melting point. Poly(propylene) has been crystallized in four distinct types of spherulite whose melting points are either 168°C. or 150°C. depending whether the crystal lattice is either a monoclinic or hexagonal modification. (33,34) 66 Nylon will also crystallize in at least three different spherulitic forms, whose melting points differ, depending on the fusion and crystallization conditions. (35,36)

Annealing of a crystalline polymer below its melting point will alter its structure and melting point, and comparisons can be drawn with the similar metallurgical process. Annealing will relieve stresses and strains set up during polymer processing, ie. a drawn fibre will shrink on annealing. (8) It will also improve the crystalline perfection of the polymer and so affect the melting point. The very slow heating rates used by Mandelkern and others (37,38) for poly(ethylene) can be regarded as a series of annealings at temperatures along the melting curve. At each temperature, the system was allowed to re-equilibrate, some partial melting and recrystallization being observed. The final melting point was relatively sharp and well defined.

More recently the annealing of polymer samples of a specific morphology, especially single crystals, and to a lesser extent spherulitic polymer, has been studied. (39) Single crystals or crystal mats of poly(ethylene) have been intensively studied. (40,41) Up to four fold increases in the long period, as determined by small angle X-ray diffraction, and hence also in the fold length and lamellae thickness, have been reported on the annealing of the poly(ethylene) single crystals. The increase in the long period is related to the temperature of annealing and a corresponding change in density has also been reported. (41) The increase in crystal lamellae thickness has been confirmed by electron microscopy. Simultaneously the surface area has been shown to decrease and voids develop in the crystals. (40) Nuclear magnetic resonance (N.M.R.) studies by Slichter and others (25,27,28) have shown that on annealing, the number of mobile segments in the chain and their relative freedom increases in poly(ethylene) single crystals. They have shown that there is a critical minimum temperature ($\simeq$110°C.) below which this mobility was undetectable, and this corresponded approximately to the lowest annealing temperature at which increases in the long period have been observed. (40)

Mandelkern and Allou (42) have suggested from their study of the fusion of poly(ethylene) single crystals that a partial melting and recrystallization process occurs on annealing similar to that proposed by Fisher and Schmidt (43) and Takayanagi and Nagatoshi. (44)

The mechanism, which causes the increase in fold length observed on the annealing of single crystals is not definitely known yet; Geil discusses some of the suggestions that have been made in his book.(39)

Similar observations have been made on the annealing of bulk, unoriented poly(ethylene). (41,45,46) Increases in the long period, dependent on the annealing temperature were reported. However the long period obtained by isothermal crystallization at a given temperature was always longer than that obtained by annealing at the same temperature. (45) This suggests that in bulk polymers the highest melting material will be obtained by isothermal crystallization at a high temperature rather than crystallization at a lower temperature followed by annealing, despite the fact that annealing increases the long period, which is related to the melting point. (32) No overall changes in spherulite size have been observed on annealing although the lamellae increase in thickness and voids may develop at the centre of the spherulite. (47) A change in density with the increase in fold length on annealing has been reported for poly(ethylene) (41,45) and poly(ethylene terephthalate).(48)

The annealing of other polymers has not been studied so extensively. Poly(oxymethylene) shows a similar increase in its long period with increasing annealing temperature. (39) The annealing of 66 nylon fibres has been reported in several papers. (8,49) As the annealing temperature increases, the crystallinity, the long period, and the number of mobile chain segments also increase; c.f. single crystals of poly(ethylene). (40,41,25,27,28,45,46)

2:3 DIFFERENTIAL THERMAL ANALYSIS AND POLYMERS.

Differential Thermal Analysis (D.T.A.) is a technique for studying thermal effects in materials when they are heated. These effects can be attributed to some physical or chemical change occurring in the sample on heating. The nature of the change controls the thermal effect; ie. melting is an endothermic process, whereas crystallization is exothermic.

Historically Le Chatelier (50) was the first to use such a technique. He used a single thermocouple to measure his sample temperature, which was then recorded as a function of time, and so obtained heating and cooling curves.

Modifications of Le Chatelier's method, using a differential thermocouple system (51) and a thermally inert reference material (52) gave the method increased sensitivity and formed the basis of the modern D.T.A. apparatus.

In D.T.A. the sample temperature is continuously compared with that of a thermally inert reference material. This differential temperature (ΔT) is then recorded as a function of temperature, or alternatively, time, providing the temperature change with time is sufficiently constant.

Experimentally, in D.T.A., both sample and reference materials are heated at a uniform rate in an identical environment with matched thermocouples to detect any thermal changes. The system is therefore in a state of thermal equilibrium until some thermal effect occurs. This will alter the temperature of the sample, destroy the thermal equilibrium temporarily and a differential temperature signal will be created. After suitable amplification, this ΔT signal is recorded as a function of the sample temperature as a "thermogram".

The technique was initially used by ceramists and mineralogists, but in the last decade, it has been more widely applied, particularly to the fields of inorganic, organic and polymer chemistry. All types of apparatus have been designed and evaluated for a variety of applications, and the factors which could affect the results, both on a theorectical, or practical basis have been discussed. For more detailed information, the reviews of Murphy (53-58) and the books by Smothers and Chiang, (59) Garn, (60) Redfern (105) and Wendlandt (61) should be consulted.

Recently more specific articles and reviews have appeared on the use of D.T.A. to study polymers and fibres. (62-68) Poly(ethylene) has been subjected to the greatest study. The results include; the melting of high and low density and branched homopolymer; (69-71,85) various copolymers and polymer blends; (71-76) heats of fusion and crystallization; (69,84) the melting of single crystals; (42,77) the melting of polymer crystallized under both high (78-80) and normal pressures; (81) the effects of the previous thermal history on the melting thermogram; (70,82) and the formation of multiple melting peaks in homopolymer. (83) In addition two melting peaks have been observed for nitric acid treated drawn polymer. (86) Oxidation, thermal degradation, and the effects of high energy radiation have been reviewed by Ke. (63)

Poly(propylene) has been studied similarly. Results have been published for studies on the homopolymer, (69) which in certain instances shows multiple fusion peaks, (67,87-90,97) and as a copolymer (72,76) or a fibre. (67,90) The effects of heterogeneous nucleation on the crystallization process (91) and also a new method of studying the isothermal crystallization (92) together with values of the heats of fusion and crystallization have been reported. (69,84,87) The effects of molecular weight on the glass transition temperature and the effects of high energy radiation, oxidative and thermal degradation have been reviewed by Ke. (63)

Other polyolefins that have been studied include poly (4- methyl pentene-1); (63) poly(methylenes); (72) poly(butene-1) (93,94) which shows multiple melting peaks, attributable to the melting of different crystalline forms, and isotatic poly(propylene oxide). (95)

Polyamides have been studied by Ke and Sisko (96) who have reported thermograms for homopolymers showing glass transition temperatures, They have also reported thermograms of copolyamides; heats of fusion of 66 and 610 nylon and a double melting peak for a drawn 66 nylon fibre similar to the first described by White.(1) Inoue, (84) also studied the crystallization of 66, 6, and 11 nylon. He reported heats of fusion and crystallization for these polymers and described a double crystallization peak. Thermograms of 66 nylon fibres,similar to that of White's (1) have been described (66) and also of 66, and 6 nylon with only a single melting peak. (66,67) Some Japanese workers have recently described the effects of drawing and thermal history on 6 nylon. (97,98) They have shown that annealing the polymer below its melting point, resulted in double melting endotherms. The relative sizes of these peaks were dependent on the temperature and time of thermal treatment. They have also analysed copolymers of 6 and 66 nylon using D.T.A. techniques. (99)

Linear polyesters, particularly poly(ethylene terephthalate) have been studied. Investigations on the melting behaviour and the effect of copolymerisation have been reported. (100-102) Thermograms of the melting of fibres have been described and recent work has shown the formation of multiple melting peaks after the drawing and annealing of the polymer, (97,103,104) similar to those described for 6-nylon. (97,98)

For thermograms of other polymers, and the use of D.T.A. to study thermally stable polymers, glass transitions and other applications, see references (53) to (68).

2:3:1 QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS.

The area under a particular exothermic or endothermic peak in a D.T.A. thermogram is a function of the heat change involved in the actual reaction causing the peak. Hence D.T.A. can be used for the semiquantitative and in some instances, the quantitative determination of heats of reactions.

Theoretically, all that is necessary is the calibration of the apparatus under specified operating conditions, with materials of similar thermal conductivities, specific heats, and known heats of fusion. The area of the peak is then measured by some suitable means, and then related to the quantity of heat involved in the reaction. A known quantity of the material whose heat of fusion is required, is then run in the apparatus under identical conditions and the peak area measured. Then by simple comparison with the data from the standard material, the unknown heat of fusion can be determined.

The above method has formed the basis of most quantitative studies. Until recently, the majority of the studies have been carried out on minerals, clays and inorganic materials, (53-61) but apparatus more suited to polymeric applications has been described in the last few years. (106-113)

Calibration standards such as benzoic acid, (84) dotriacontane, (69,110) inorganic salts (115) and pure metals (110,113,114) have been used for polymer studies. The inorganic salts and pure metals have rather different thermal conductivities and melting points, to be strictly applied to polymeric systems. The thermogram of dotriacontane shows two melting endotherms, the lower temperature one being attributed to the onset of chain rotation, (116) the higher to the solid to liquid melting transition. (117) The total area of both peaks must be measured, if it is used as a standard as Ke did (69) when he used it to give the true heat of fusion of fully crystallized poly(ethylene).

Several authors have attempted to relate mathematically peak areas to the actual heat change involved in a reaction.(60,61,118-120)

The basic equation required to describe the process is:-

$$\triangle H = P \int_{t_1}^{t_2} \triangle T \; dt. \qquad \text{-------Eqn. 2:2}$$

where $\triangle H$ is the heat involved in the reaction and P is a proportionality constant, usually evaluated experimentally, t_1 and t_2 represent the time at the start and finish of the reaction respectively. The constant P, involves terms for the heat transfer and the geometry of the sample and sample holder.

Boersma (120) designed a D.T.A. cell in which the temperature difference was measured from outside the sample and reference materials, contained in metal cups. The peak area then depends only on the heat of the reaction and the instrument calibration, and is independent of sample properties, such as volume and thermal conductivity. The peak area is then related to the heat of the reaction by:-

$$\int_{t_1}^{t_2} \triangle T dt. = mQ/G \qquad \text{-------Eqn.2:3}$$

where m, is the sample mass, Q, the heat of reaction per unit mass and G, the heat transfer coefficient between the sample cup and the rest of the apparatus.

The Du Pont Calorimeter Cell,(114) which is a "plug-in" module for the Du Pont 900 Thermal Analyser, was used for the quantitative work described in this thesis. It was first described by Sarashon (110) and its design was based on the suggestions proposed by Boersma. (120)

Quantitative data can be readily obtained by differential scanning calorimetry. (113,121) In this method, the quantity of electrical energy required to null a differential temperature signal during an exothermic or endothermic transition is measured directly. This energy can be directly related to the peak area, once a suitable calibration has been carried out. This apparatus has been used to determine kinetic parameters in decomposition reactions. (122)

Quantitative studies applied specifically to polymeric materials are at present relatively few. They have involved studies on the crystallinity and heats of fusion of poly(ethylene),(69,84,85,109) poly(propylene),(69,84,87,115,123) polyamides. (96) Heats of polymerisation and of the cross linking of epoxy resins have been determined. (109,124) Clampitt has determined the heats of polymerisation of several polyester resins. (125,126)

2:4 THE CRYSTAL STRUCTURES OF POLYAMIDES.

The crystal structure of 66 nylon (poly(hexamethylene adipamide)) was first elucidated by Bunn and Garner (129) using X-ray diffraction methods. They used an annealed drawn 66 nylon fibre, since it was assumed that the polymer molecules would be aligned along the fibre axis. Previous workers (127) had shown that the annealing of a drawn fibre improved its crystalline perfection and so gave a more distinct X-ray diffraction pattern. Bunn and Garner interpreted their X-ray diffraction results in the following manner.

The polymer molecules were in an almost planar, extended zig-zag chain conformation. They were all aligned in the same direction and parallel to each other and the fibre axis. The molecules were linked together to form a monomolecular sheet by hydrogen bonding between the C=O and NH groups. The maximum possible number of hydrogen bonds were formed, when each molecule was displaced vertically a distance equal to one repeat unit of the chain zig-zag relative to the previous molecule in the sheet. (See Diagram 1 page 16).

The packing together of these monomolecular sheets gave rise to a triclinic unit cell. The polymer molecules are arranged so that they form the four long edges of the triclinic cell. (Diagram 2 page 18). Two different polymorphic unit cells are possible. In the more common α form, each sheet was displaced vertically 3.55 Å from the proceeding one. In the β form alternate sheets were displaced by 3.55 Å. (See Diagram 3 page 20).

The unit cell constants for the α form are:-

a, 4.9 Å	$\alpha = 48\frac{1}{2}^{\circ}$
b, 5.4 Å	$\beta = 77^{\circ}$
c, 17.2 Å (fibre axis)	$\gamma = 63\frac{1}{2}^{\circ}$

and those for the form,

a, 4.9 Å	$\alpha = 90^{\circ}$
b, 8.0 Å	$\beta = 77^{\circ}$
c, 17.2 Å	$\gamma = 67^{\circ}$

The density of 100% crystalline 66 nylon was calculated by Bunn and Garner (129) to be 1.24 g. /ml., apparently independent of any particular polymorphic form.

The α form unit cell contains only one molecular repeat unit, whereas the β form contains two. As a result, the sheets are further apart in the β forms than in the α form. Normally both forms exist simultaneously in the same polymer, the α form being the most predominant. Intermediate forms also exist when small sections of one form follow the other at random. There is no evidence in the literature that the α and β forms of 66 nylon have different melting points.

No suggestions were put forward by the original workers (129) for bonding between the monomolecular sheets. All the possible hydrogen bonds were made in forming the sheets of molecules. Therefore, it

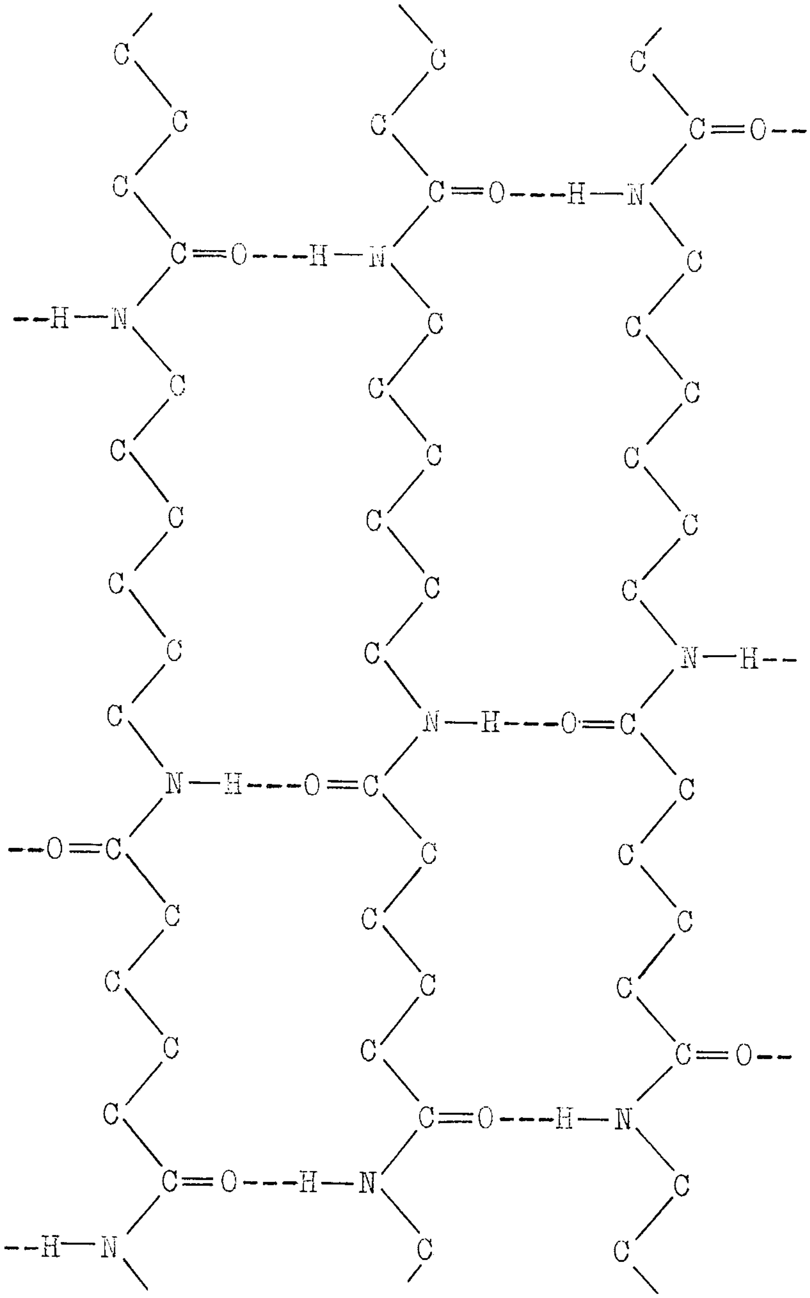


Diagram. 1. The Structure of 66 Nylon.

--- = Hydrogen Bond.

(After Bunn and Garner(129).)

might be expected that the sheets would readily slip over each other under an applied stress rather like graphite does. In practice, this does not occur, probably because of chain entanglements.

The triclinic cell, exhibiting α/β polymorphism, is the generally accepted structure for 66 nylon. Keller and Maradudin (128) have since suggested that Bunn and Garner's (129) interpretation of α/β polymorphism was incorrect. They have suggested that the X-ray evidence for the β form was consistent with the presence of incompletely developed α crystals.

Recent work on the annealing of drawn 66 nylon fibres under zero tension, by Statton and Dismore, (8) has suggested that some of the molecules change from an extended to a folded configuration on annealing. This change occurs with no apparent accompanying change in the crystal orientation. It was therefore likely that the samples Bunn and Garner used also contained some chain folds, but these did not affect the overall structure with respect to the wide angle X-ray diffraction patterns. Bunn and Garner gave no details of the annealing proceedures used.

The other even-even polyamides such as 6-10 nylon have similar structures to that of 66 nylon. It is believed that the molecules align themselves to give the maximum possible hydrogen bonding between the polymer chains. At higher temperatures, ie. 160°C. and above, the triclinic structure reverts to a more symetrical structure in which the polymer chains assume hexagonal packing. (29)

The odd-odd polyamides have not been structurally investigated in great detail. It is almost impossible to theoretically derive structures for polyamides such as 59 nylon in which the amide groups are so arranged that complete hydrogen bonding was possible. It is only in the odd-odd polyamides which contain equal numbers of methylene groups in both the acid and amide units ie., 57 nylon, that a completely hydrogen bonded structure can be devised. The X-ray crystal structure of the odd-odd polyamides such as 7 9 nylon indicates a hexagonal packing even at room temperatures with the amide planes nearly normal to the chain axis, unlike the tilted amide axis of the even-even nylons. (29) (cf. diagram 1 for 66 nylon.)

The structures of most of the polyamides derived from the

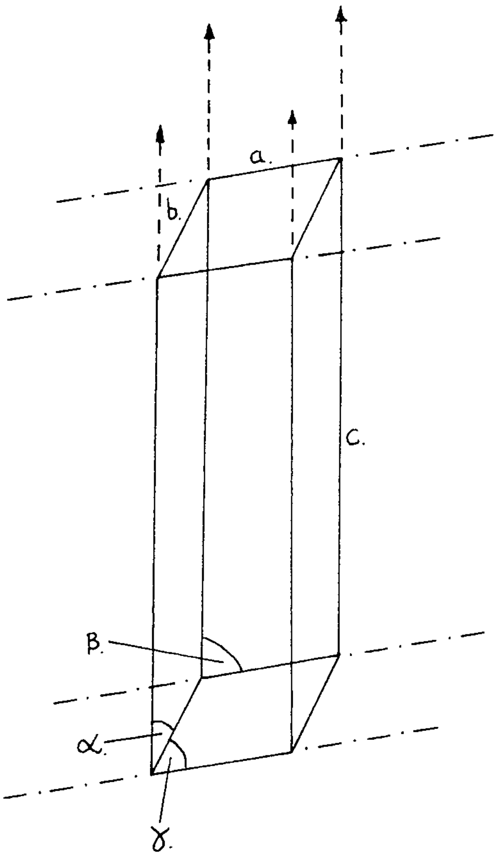


Diagram 2. The triclinic unit cell of 66 nylon.

a, b, c, = unit cell dimensions } see 2:4.
α, β, γ, = unit cell angles }

↑ = direction of molecules along the edges of the cell.

— · — · — represents the plane of the hydrogen bonds forming a mono molecular sheet.

α/ω amino acids, ie. 11 nylon have been described in the literature (13°). Of these, 6 nylon has been studied extensively. (6,131)

In 6 nylon, the molecules are also in an almost planar extended zig-zag chain conformation. Alternate molecules are inverted to form a monomolecular thick sheet. This arrangement enables the maximum number of hydrogen bonds to be made between the C=O and NH groups. Like 66 nylon, the arrangement of these monomolecular thick sheets gives rise to the unit cell. The most stable monoclinic α form is formed by the alternate displacement of neighbouring sheets identical to that for the β form of 66 nylon. (Diagram 3).

The molecular packing of the other forms of 6 nylon is not well defined. Several different structures have been proposed. (6) Holmes, Bunn and Smith (131) have suggested a β structure in which the hydrogen bonded sheets are not displaced relative to each other. Other forms have been proposed in which the molecules were not inverted relative to each other in the sheets. This results in the hydrogen bonds being tilted, rather than normal to the chain axis.

2:5 THE MORPHOLOGY OF SINGLE CRYSTALS AND SPHERULITES OF THE POLYAMIDES.

Single crystals have been described for various polyamides. (6) They take the form of thin lamella type crystals. Unlike poly(ethylene), the exact nature of the packing of the molecules and their method of chain folding has not been definitely established.

The presence of folded chain molecules has been established in single crystals of 6 nylon from crystal diffraction patterns. The alternate inverted chains in the crystal structure of 6 nylon readily suggests the formation of chain folds. However, the diffraction patterns of 6 nylon single crystals suggests that the molecules are not arranged in the monoclinic α form. Instead, hydrogen bonding is thought to occur between parallel chains.

Geil has shown that the hydrogen-bonded planes of the molecules are parallel to the short diagonal of the rhombohedral crystal. If the molecules fold parallel to the growth faces, as is presumed to occur, then the hydrogen bonding must occur between two different molecules in adjacent fold planes rather than with molecules in the same fold plane. (6)

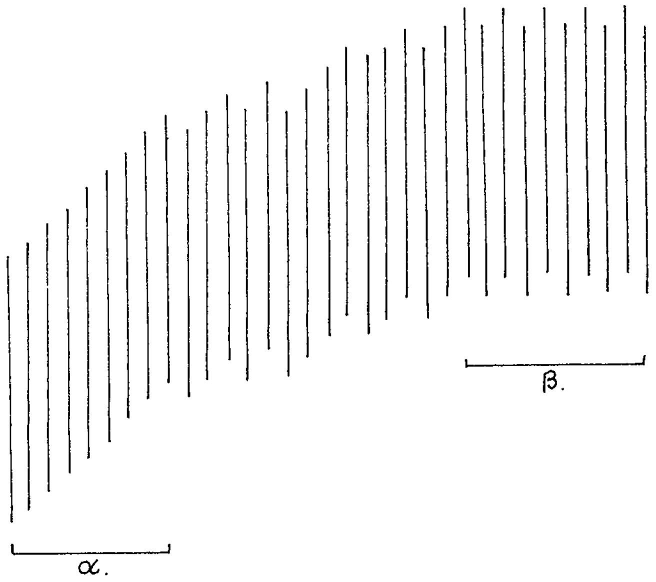


Diagram 3. The α; β; and intermediate forms of 66 Nylon. The lines represent hydrogen-bonded sheets of molecules seen edgewise. (After Bunn and Garner(129).)

Single crystals of 66 nylon have been described as either rolled or folded lamella (134) or as thin platelets. (135)

In the lamella form, (134) the molecules are believed to have a α triclinic lattice, with the long axis of the lamella being parallel to the hydrogen bonded planes of the molecules. Hence the molecules will be inclined at an angle to the thickness of the lamella, since the hydrogen bond plane is tilted with respect to the molecular axis in the triclinic cell.

In the platelets however, the molecules were said to be oriented parallel to the long axis of the lamella (135) unlike poly(ethylene) single crystals in which the molecules are essentially normal to the lamella.

Spherulites have been reported for many polyamides. (6) Different types of spherulites form under different crystallization conditions, ie. positive, negative and non-birefringent in 66 nylon. (35,36) These are thought to most probably have the same basic crystalline unit cell but different morphologies, although no morphological studies have been reported on them.

The polyamides spherulites show the now characteristic fibrillar nature associated with spherulites. Keller using micro X-ray techniques has shown that the molecules were arranged tangential to the spherulite radius. (132) He has shown, for instance, in 610 nylon, two different types of spherulite were formed, in both of which, the molecules were oriented tangentially. In one, however, the hydrogen bonded planes were radial, in the other tangential.

Keller also examined the ribbon like lamella that form spherulites in 610 nylon. (133) From electron diffraction patterns of the lamellae he deduced that the molecules were inclined at an angle of 65^{o}-75^{o} to the ribbon axis and therefore must be folded. The <u>a</u> axis of the triclinic cell lay in the direction of the ribbon axis. The requirement, that all possible hydrogen bonds should be formed, together with a definite fold period, would result in the molecules making an angle of this order with the ribbon axis. He suggests that the fold could occur in either the (100) or the (010) planes of the unit cell. The (010) plane would contain the hydrogen bonds and favour folding. This folding would automatically explain the antiparallel (alternate, inverted) arrangements of molecules in the structure of 6 nylon, but is not so obvious in the case of the parallel chains of 66 or 610 nylon. The (100) plane folding would mean folds occur between adjacent sheets of molecules, and therefore the sheets of molecules would be antiparallel with respect to each other. This is more feasible for 66 and 610 nylon, since no hydrogen bonding occurs between the sheets and reversing the molecular direction of alternate sheets would not alter the triclinic cell.

Although it seems certain that chain folding occurs in polyamides, no definite ideas have been proposed for the way in which a fold was formed or the number of atoms necessary for a fold to occur. Unlike poly(ethylene) where folds can occur anywhere along the chain, the hydrogen bonding in polyamides would restrict the possibility of folds occurring to specific regions of the polymer chain.

Poly(ethylene) requires approximately five backbone carbon atoms (6) to form a fold. If a similar number of carbon atoms were required in the polyamide system, folds would only occur in parts of the polyamide molecule where there were 5 or more carbon atoms, i.e. between the amide groups, if the final structure was still to contain the maximum number of hydrogen bonds.

3. APPARATUS AND TECHNIQUES.

In the following section, the apparatus and experimental techniques, which were used during the course of this research work, will be described.

3:1 D.T.A. APPARATUS.

3:1:1 KEAVNEY AND EBERLIN (136) D.T.A. CELL.

A block diagram of the apparatus is given on page 24 (Diagram 4).

The D.T.A. cell was the same design as that of Keavney and Eberlin, (136) with the following modifications to the sample holders and the thermocouple system. (Diagram 5 page 26). The sample and reference were contained in glass cells made to fit the sample and reference holes in the lower aluminium block (Diagram 5,a). These served to contain the molten polymer and made it easier to change samples. Similar glass cells were used by Barrall and Rogers. (137) An inert atmosphere, to reduce possible sample degradation, was obtained by allowing nitrogen to flow around the sample and reference cells. The nitrogen was fed into the apparatus by using the original thermocouple channels (Diagram 5,b).

Two holes were drilled in the upper block to centre over the sample and reference cells, to take two holed porcelain insulating rods. (3"x$\frac{1}{4}$" O.D., holes 1/16" diam.) Each rod was located in the hole in the upper block by means of a fireclay cement collar (Sankey's "Pyruma" Cement). (Diagram 5,c).

The Chromel/Alumel thermocouple junctions were made with a Capacitor Discharge Welding Apparatus (Spembly Ltd., Chatham, Kent.) The wire was then coated with "Megasil 1400" silicone insulating varnish, (Hopkins and Williams) and stoved in an air oven at 270°C. for 30 minutes. The thermocouple wires were then fixed in the porcelain rods by means of a bead of "Pyruma" cement, (Diagram 5,d) so that all thermocouple junctions projected equally. When the cement bead had set, the rest of the space around the thermocouple wires in the porcelain tubes was filled with more "Megasil" varnish and the whole thermocouple system restoved at 270°C. for 30 minutes.

This method of preparing the thermocouples gave the most stable ΔT trace.

The Bristol recorder was zeroed by putting the temperature

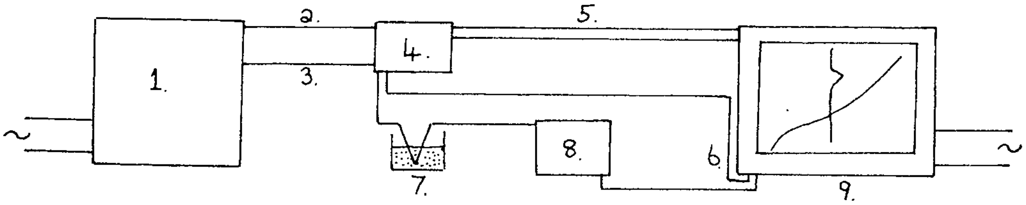


Diagram 4. Block diagram of apparatus using the modified Keavney and Eberlin D.T.A. Cell.

1. Temperature programmer.(Guardsman Indicating Pyrometric Controller(J.S.B.-2),West Instruments Ltd.) The heating rate was controlled by a pre-cut cam, which gave a rate of approximately 10°C./min. up to 200°C., and then, 1·9°--1·6°C./min. between 240°-270°C.

2. Control thermocouple leads.(the thermocouple was located between the upper and lower blocks of the D.T.A. cell.)

3. Power leads to cell heaters.

4. D.T.A. cell.

5. ΔT. thermocouple leads. } 26 s.w.g. Chromel/Alumel.

6. T°C. thermocouple leads. }

7. Ice/water cold junction.

8. Variable millivoltage suppression(P4 Thermocouple Potentiometer,Croydon Precision Instrument Co.)

9. Bristol "Dynamaster" Recorder.(2 pen, centre deflection, ±0·5 mv.(ΔT), ±5·0 mv.(T°C); chart speed 12"/hr.)

To measure sample temperature's between 100°--300°C. (4·1--12·1 mv.), it was necessary to apply a back e.m.f. to the T°C. signal. This was done by using the injection circuit of the thermocouple potentiometer.(8)

thermocouple in the ice/water cold junction at 0°C. and adjusting the thermocouple potentiometer (diagram 4; 8) until zero was recorded. During a run when a temperature of about 100°C. had been reached, the thermocouple potentiometer was re-adjusted to enable the complete temperature range to be covered.

A known amount of sample was placed in the glass sample cell, and a known quantity of 100-120 mesh Ballotini glass beads placed in the reference cell. The thermocouples were placed in position in the top block which was carefully put onto the bottom one. The nitrogen flow was turned on and the apparatus purged for several minutes before starting the temperature programmer.

For samples of 30/10 drawn 66 nylon yarn, a different technique for filling the sample cell was used. The yarn was formed into a small bobbin by winding it onto a spindle. The spindle was made from a drawn down glass rod with two rubber discs, cut from a small rubber bung, to limit the overall length of the bobbin. The spindle was held in the chuck of an electric motor and the yarn wound on at about 600 r.p.m.. Care was taken to avoid stretching the yarn in forming the bobbin, so as not to change the draw ratio.

The bobbin of yarn was removed from the spindle and weighed. Several bobbins were packed into the cell, arranged so that the thermocouples in the sample cell went down the centre of a yarn bobbin, when the apparatus was assembled.

Using the technique described, resolution of the differential trace into two melting peaks (1) was not satisfactory. This was attributed to poor thermal conductivity through the system, block → glass sample cell → nylon sample → thermocouple. To overcome this, silicone oil was used to increase the thermal conductivity of the system.

Further modifications of the D.T.A. cell were therefore necessary. The thermocouple lead channels (diagram 5,b) were closed with a plug of "Pyruma" cement just below the glass cells. The space between the aluminium block and the glass cells was filled with silicone oil and so were the actual sample and reference cells. The silicone oil acted as as inert atmosphere and very little degradation of the sample was observed. Since the silicone oil was used in both the sample and

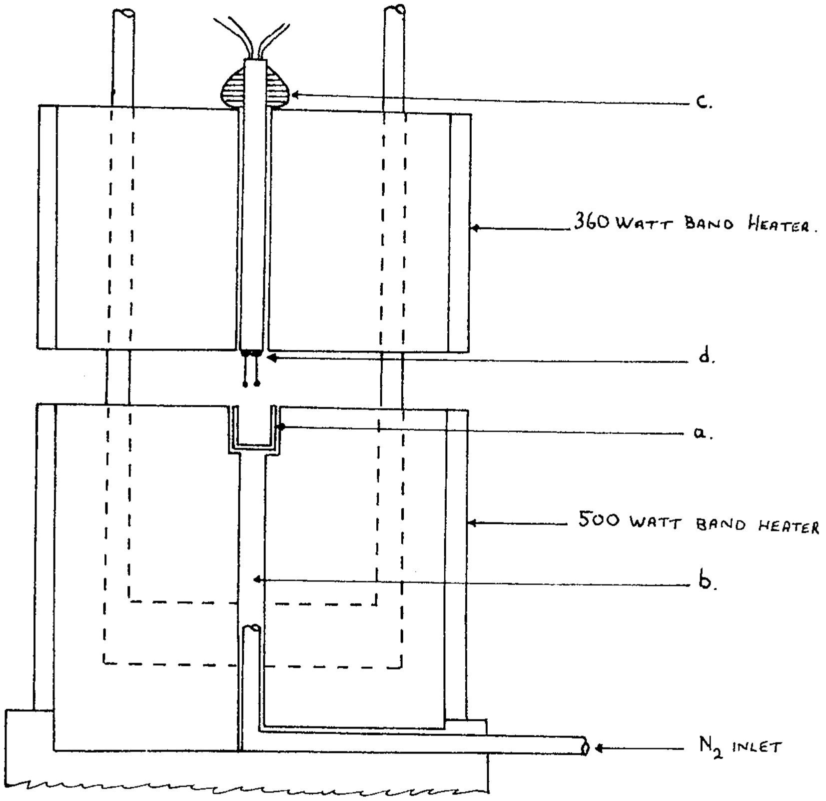


Diagram. 5. Modified Keavney and Eberlin D.T.A. Cell.

a = glass sample cell.

b = original thermocouple channels.

c = fireclay cement collar.

d = thermocouple wires secured by fireclay cement bead.

reference cells, any thermal transitions in the oil would tend to cancel each other out and not be observed on the Δ T trace. Subsequent thermograms showed better endotherm resolution than before.

3:1:2 THE DU PONT 900 THERMAL ANALYSER.

This instrument was made by the Instrument Products Division of E.I. Du Pont de Nemours and Co. It used a D.T.A. cell assembly previously described by Chiu (138) and a temperature programmer, amplifier and recorder similar to those described by Vassallo and Harden. (139) A complete description of the apparatus and its mode of operation is given in the Du Pont instruction manual. (140) Therefore, only a brief description of the apparatus will be given here.

A schematic diagram of the apparatus is shown (diagram 6, page 28). The letters, S, R, and C, refer to the sample, reference and control thermocouples respectively, and H, to the cartridge heater in the D.T.A. cell block.

The recording system was designed so that the differential temperature (Δ T) signal was fed, via a high gain, low noise pre-amplifier to the Y-axis of a variable sensitivity recorder whilst the sample temperature was fed to the X-axis. This gave a direct plot of Δ T as a function of T. The ΔT preamplifier was necessary, on account of the magnitude of the Δ T signal from the very small sample size used.

The Δ T (Y-axis) range of the recorder was from 0.04 mv./inch ($\simeq$ 0.1°C/inch for the Chromel/Alumel thermocouples used) to 0.4 mv./ inch ($\simeq$ 10°C/inch). The T(X-axis) range was from 0.4 mv./inch ($\simeq$ 10°C/inch) to 8mv./inch. ($\simeq$ 200°C/inch). The record on the chart was accurately linear in millivolts; minor corrections had to be made to the temperature scale to correct for the non-linearity of the Chromel/Alumel thermocouples.

The temperature programmer-controller gave infinitely variable heating/cooling rates between 1° and 30°C/minute. The control thermocouple was incorporated in a "feed back" circuit with a proportionally controlled linear temperature programmer. Temperature programming from any selected temperature was achieved by a "bucking" reference voltage, from a reference thermocouple placed in an ice/ water bath. (139) Isothermal operation was also possible. (see 3:1:3)

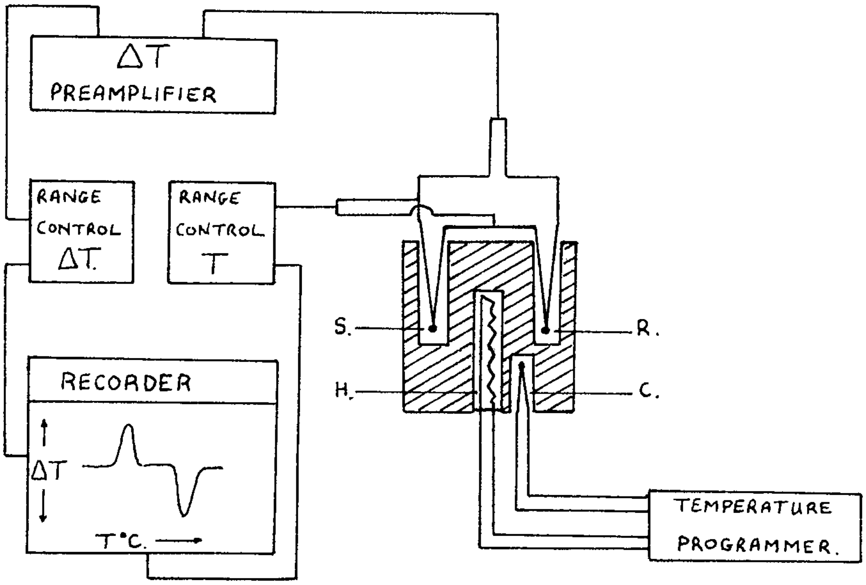


Diagram. 6. Schematic diagram of the Du Pont 900 Thermal Analyser.(by kind permission Du Pont(U.K.),Ltd.,London.)

s = sample thermocouple

r = reference thermocouple

c = control thermocouple

h = D.T.A. cell block heater.

The instrument was connected to a vacuum system (a Genevac Rotary Piston Vacuum Pump (single stage) type G.R.S.2) and an inert gas supply ("White Spot" Nitrogen); to allow control of the D.T.A. cell atmosphere. There was also a connection to cool the D.T.A. cell by drawing liquid nitrogen into it.

3:1:2a THE DU PONT STANDARD CELL (-100°C. → 500°C.)

This was identical to the cell designed by Chiu. (138) The micro heating block (2 mm. glass sample tubes) was used and the cooling jacket was fitted to the cell. This was connected up to the vacuum and coolant ports on the cell baseplate, and allowed rapid cooling of the cell. It also acted as a further thermal shield particularly when the instrument was being used isothermally. Glass beads (supplied by Du Pont) were used as reference.

3:1:2b THE DU PONT VISUAL CELL.

The micro form of this cell as described by Chiu (141) was used. During the run, the sample tube was illuminated by an ordinary tungsten filament lamp. It was necessary to interpose between the cell and the lamp a large beaker of water. This acted as a heat filter and prevented spurious thermal effects due to the heat output of the bulb, being recorded on the thermogram. The sample was observed throughout an experiment by means of a bench cathetometer.

3:1:3 OPERATION OF THE DU PONT 900 THERMAL ANALYSER.

The operating procedure, described in the instruction manual supplied with the instrument (140) was used to obtain thermograms of the various polymer samples. The following text describes operating techniques not covered by the instruction manual that were found to be useful.

A) SAMPLE PREPARATION.

The sample tube was filled with either thin slivers of polymer cut from a chip or a piece of film, or short lengths cut from a piece of bristle, and a thermocouple carefully inserted into the centre of the sample. When the 30 denier, 10 filament, 66 nylon yarn was used, approximately 90 cms. (0.003gm.) were wound directly on to the thermocouple, which was then inserted into a sample tube.

At the end of a run, the thermocouple was removed from the sample tube by gently warming the tube in a bunsen flame. Once the polymer melted, the thermocouple could be removed from the sample tube. Any remaining polymer was carefully burnt off the thermocouple, leaving it clean and ready for re-use, whilst the used sample tube was discarded.

B) REPLACEMENT OF THE D.T.A. CELL'S ATMOSPHERE.

The assembled cell unit was tightened down onto its mounting on top of the instrument console. The air in the cell was replaced with nitrogen, by alternately applying a vacuum (29" of Mercury, as indicated by the instrument's vacuum gauge), and subsequently releasing it with nitrogen. This procedure was repeated at least 4 times to ensure that the air had been removed from the sample tubes as completely as possible. When the vacuum was finally released, the cell was purged continuously with a slow stream of nitrogen (1.5 ft. ^{3}/hr.) throughout a run.

C) HEATING RATES.

For most experiments, a rapid heating rate of 30°C./minute was used to within 40°C. of the temperature of the transition being studied. Then the programmer-controller was stopped and reset to the desired heating rate, usually 5°C./minute, and the run restarted. With practice, the cell heater voltage could be adjusted, when resetting the heating rate, to minimise any thermal effects caused by the change in the heating rate.

D) INSTRUMENT CONTROL SETTINGS.

The X-Y recorder sensitivity controls were adjusted as follows:- X axis (T°C.) 20°C./inch; Y axis (Δ T) 0.2°C./inch.

During the initial heating up period, the X axis (T°C.) zero shift control was used to offset the recorder zero by an appropriate amount to enable the desired transition to be recorded on the highest T sensitivity possible. For thermograms of 66 nylon samples, a T zero shift of -5 or -10 inches (-100°C. or -200°C. for an X axis setting of 20°C./inch.) was used, thus obtaining the maximum chart utilization.

E) COOLING.

Only unprogrammed cooling was used in this work. The natural cooling rate for the standard Du Pont D.T.A. cell complete with cooling jacket, over the temperature range 275°C.---200°C., was

11° to 12° C./minute.

After a sample under investigation had been maintained in the molten state for a preselected time (see F below), the programmer was switched off. The position of the recorder pen was reset with the ΔT zero shift control and relowered onto the chart paper to record the cooling thermogram.

Satisfactory programmed cooling rates, using the method suggested in the Du Pont manual (140) were never achieved. Rapid unprogrammed cooling was only used to cool the cell to room temperature so that a fresh sample could be examined without too much delay.

F) ISOTHERMAL OPERATION.

The "isothermal" setting of the temperature programmer-controller enables the temperature of the cell block to be held at a given temperature for long periods of time.

The temperature of the block was controlled by the setting of the "starting temperature" dial. The relationship between the "starting temperature" dial setting and the isothermal control temperature is shown in diagram 7. (page 32).

The graph shown, only relates to the Du Pont standard cell fitted with the cooling shield with a flow of nitrogen (1.5 ft. ^{3}/hr.) through the cell. Should other apparatus, such as the Calorimeter cell be used, or the programmer-controller replaced, recalibration is necessary. However, an approximate value of the setting required for a given temperature, can still be obtained from the graph given.

Slight alterations in the "starting temperature" dial may be necessary during an isothermal run, due to external temperature variations.

The isothermal temperature was reached in one of two ways. Firstly, during a run when the required temperature had been reached, the programmer-controller was switched to "off", the "starting temperature" dial set to the required value and the programmer switched to "isothermal". The block was then controlled at the required temperature.

Secondly, the isothermal setting could be used directly from the start of a run, ie. when a sample was annealed prior to melting. The "starting temperature" dial was set to the required value and the

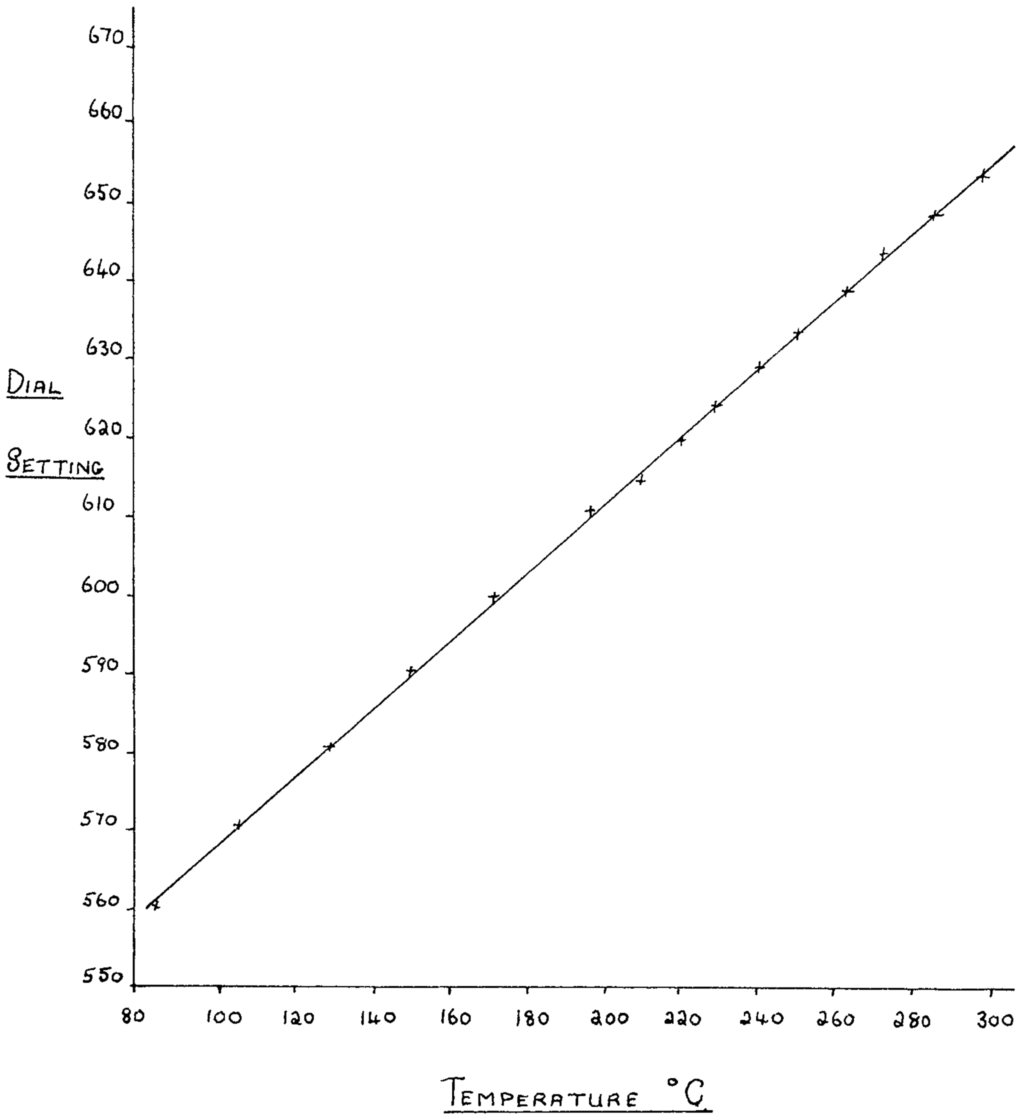


Diagram 7. The relationship between the starting temperature dial setting and the isothermal control temperature.

programmer-controller switched to "isothermal". The D.T.A. cell block was then heated up at maximum heater voltage (110v.) until about 50°C. before the required isothermal temperature was reached. Then, automatically, the voltage was slowly reduced until the cell reached the required isothermal temperature. The heater voltage then remained constant to maintain the cell block at this temperature. Using this method, 240°C. could be reached from room temperature in approximately 3½ minutes.

To continue a run after a sample had been held isothermally at a given temperature, all that was necessary was to reset the temperature programmer-controller as described in the instruction manual and restart it.

G) EXPERIMENTAL OPERATING PARAMETERS.

Before any experiments were carried out in the D.T.A. instrument, the effects of several operating parameters on the thermogram had to be considered. In his book on "Thermal Analysis", Wendlandt, (61) considered a number of these parameters, several of which have already been fixed by the design of the commercial instrument. Only four such parameters were considered here, the cell atmosphere, the effects of the heating rate, the sample weight, and its physical form.

Control of the D.T.A. cell's atmosphere was important to prevent oxidative degradation of the polymer samples. The close fit of the thermocouple sleeve into the glass sample tube prevented a rapid exchange of the air trapped around the sample and the remainder of the cell atmosphere. It was assumed that any exchange that occurred during an experiment was the result of mainly thermal expansion of the gas around the sample and also by natural diffusion processes through the porous ceramic thermocouple sleeves. The fact that some exchange did occur was indicated by the detection of the odour of pyridine outside the D.T.A. cell unit as a nickel pyridine complex thermally decomposed.

By initially applying a vacuum to the whole cell unit, and then releasing it several times with nitrogen, it was assumed that the air around the sample was completely replaced with nitrogen. The final slow flow of nitrogen was to prevent any back diffusion of air into the cell. The flow rate of 1·5 $ft.^3/hr.$ was chosen arbitrarily, the only consideration being that it should not cause any significant cooling of the cell block. The method proved to be quite satisfactory, and only occasionally after prolonged experiments at high temperatures was there any slight detectable degradation.

The effect of the heating rate on thermal transition has been considered by several workers.(61) In this work there were two conflicting problems. Firstly, to obtain the maximum resolution of any multiple melting peaks, and secondly to prevent any significant thermal modifications to the polymer occurring during the D.T.A. run.

Maximum peak resolution will occur at slow heating rates, which allow a sample to thermally re-equilibrate between two transitions. Slow heating rates result in reduction of the overall peak size, which necessitates increased recorder sensitivity to detect small effects. The increased recorder sensitivity often results in a higher electronic noise level on the thermogram, thus giving the possibility of spurious thermal effects being observed, when looking for a small genuine effect. However, multiple peak resolution is reduced by faster heating rates, although the overall peak size is larger and a lower recorder sensitivity is therefore required.

It was not possible to detect any differences between thermograms recorded at a slow heating rate over the whole range, and those where a rapid heating rate was used to within 50°C. of the expected transition, and then the slower rate used.

Diagram 8 (page 36) shows the effects of different heating rates on the melting thermograms of the same weight of drawn 66 nylon yarn. The thermograms were obtained by using a heating rate of 30°C./minute to 200°C. and then using the required heating rate for the actual transition range. This technique, using the 5°C./minute slow heating rate, which gave suitable peak resolution in a reasonable time period, was used for all subsequent work.

The effect of sample weight on the thermogram was much as expected. The larger the sample used, the greater the thermal effect observed. Diagram 9 (page 37) shows this behaviour for different weights of drawn 66 nylon yarn run under identical operating conditions. Normally, samples in the range 0.003-0.005g. were used, although their weights were not accurately determined.

Uniform packing of the sample in the sample cell was virtually impossible to achieve because of the widely differing physical forms of the polymer samples used. This could explain the differences noted between the initial melting thermogram of a sample and subsequent thermograms on the same sample. Presumably once the sample had been melted and flowed round the thermocouple, its packing became more uniform and so the subsequent thermograms were more reproducible.

H) TEMPERATURE CALIBRATION CHECK.

To allow familiarization with the operation of the instrument and as a calibration check, melting runs were carried out on several substances, using the procedure suggested in the Du Pont Instrument Manual,(140) in a nitrogen atmosphere. (1.5 std.ft.^{3}/hr.)

The results are tabulated below.

Sample	Heating Rate °C./Min.	Transition	Found °C	Quoted °C
Benzoic Acid	10°	Melting	121.9	121.8
Sulphur	20°	Rhombic/Monoclinic	110	111
		Monoclinic melt	122	122
		π to λ form	194	190
		Bpt.*	440	444.6
Indium	5°	Melting	156	157
Tin	—"—	—"—	230.5	231.9
Bismuth	—"—	—"—	268.6	271

*Depends on the atmospheric pressure.

These results indicate the accuracy of temperature measurement obtainable with the instrument.

3:1:4 THE DU PONT CALORIMETER CELL.

This is a "plug-in" module for the Du Pont 900 Thermal Analyser, and uses the same temperature programmer and X-Y recorder system. A separate 10 mv. time base recorder may be used in conjunction with the X-Y recorder to facilitate the measurement of peak areas.

The cell was first described by Sarashon (108-110) and is based on principles first suggested by Boersma,(120) of separating the sample and reference from the heat source, thus enabling quantitative

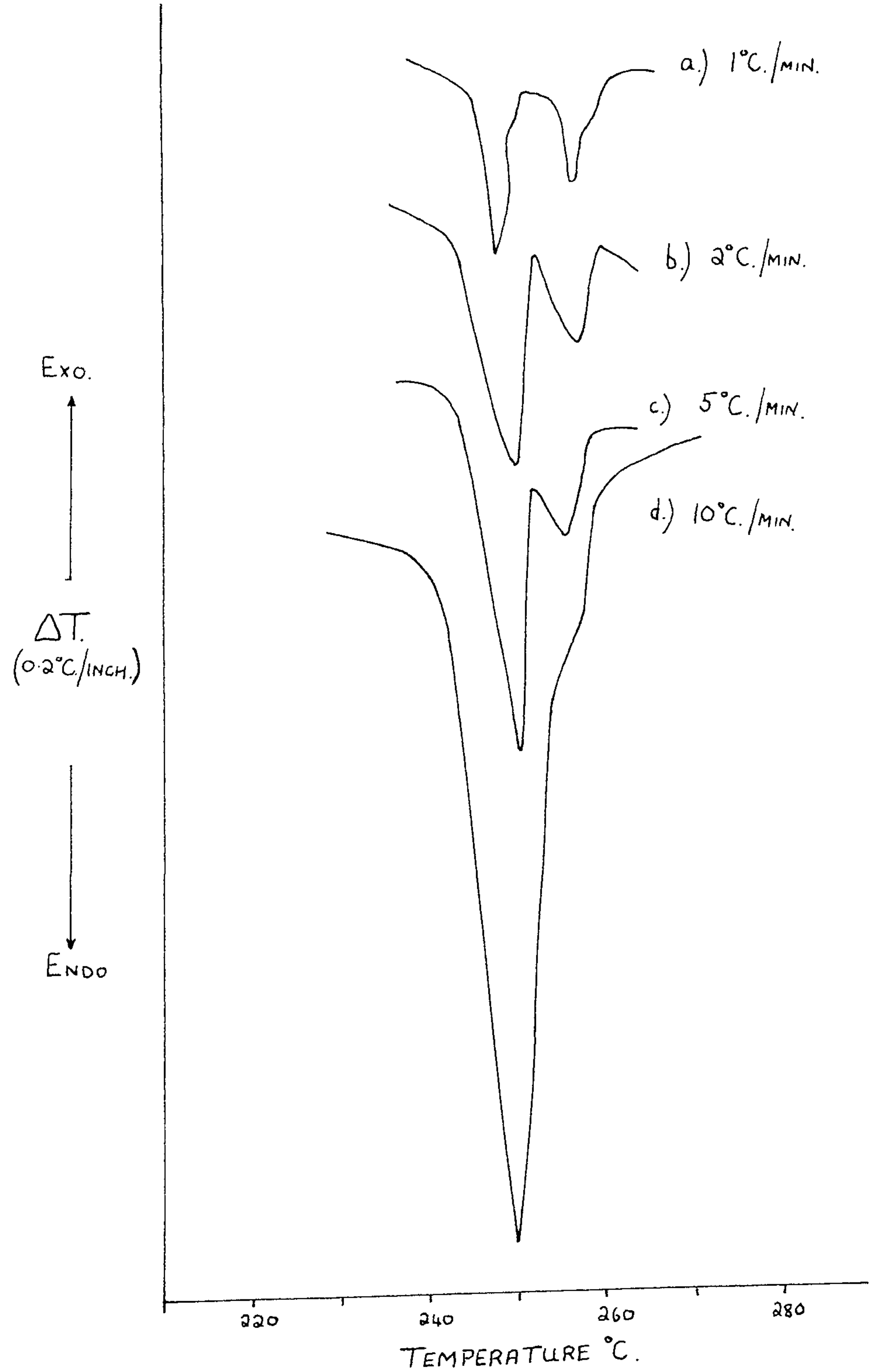


Diagram 8. The effects of different heating rates on the same weight(0·0025 g.) of drawn 66 Nylon yarn.(melting thermograms.)

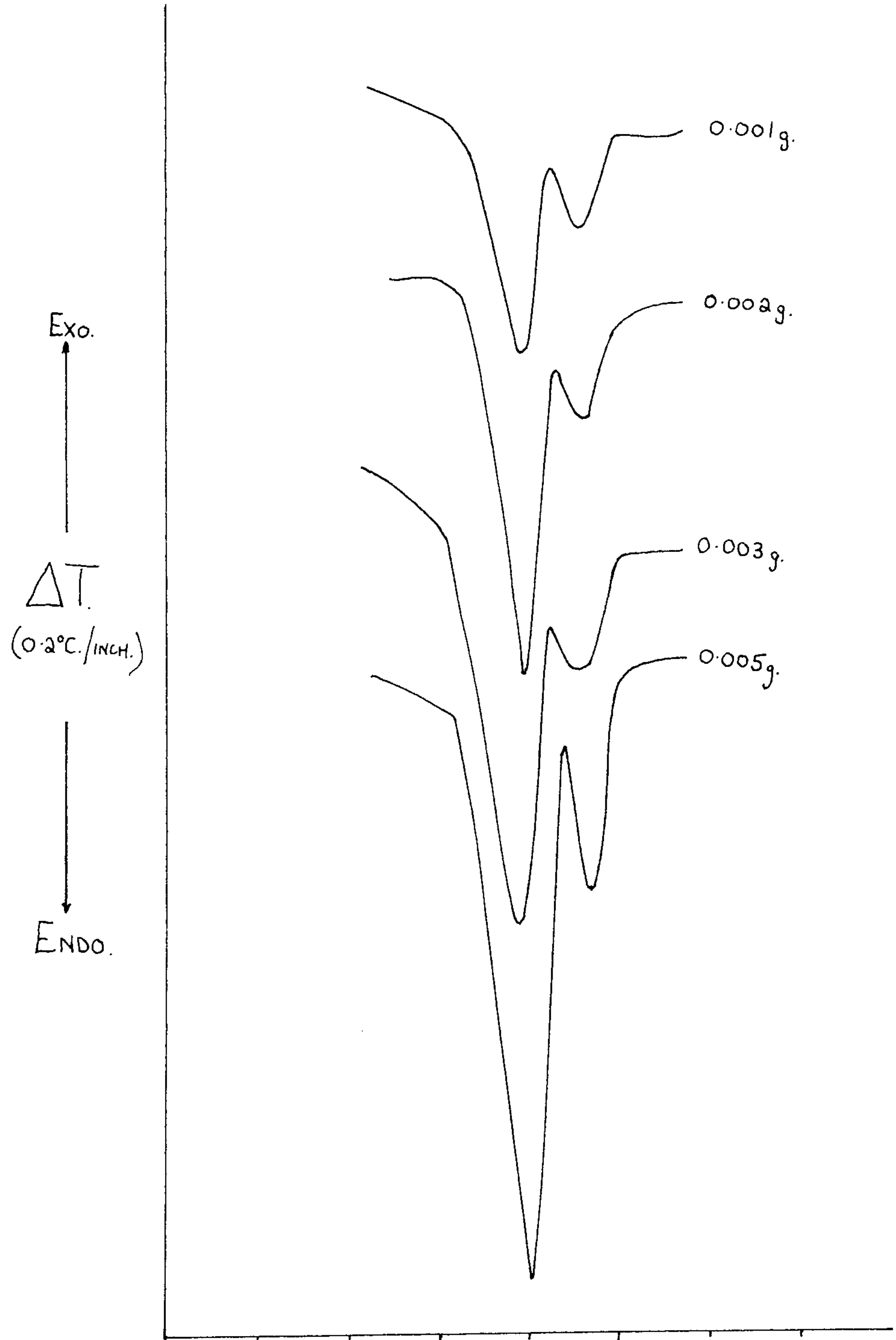


Diagram 9. The effect of sample size on the melting thermograms of drawn 66 Nylon yarn. (heating rate = 5°C/min.)

measurements to be made more readily. Diagram 10 (page 39) shows the main details of the cell and the small modifications made to it and described below.

The initial experiments with 66 nylon samples, following the instructions for the cell, (114) resulted in discoloured samples after an experiment. This degradation was attributed to the presence of oxygen in the air space (Diagram 10,g) above the sample cups. (Diagram 10,j). The closely fitting heating block cover (Diagram 10,a) and the insulating lid (Diagram 10,b) prevented the exchange of air for nitrogen, when the atmosphere of the cell was changed at the start of the experiment, using a technique similar to the described for the standard cell previously.

The cell was modified by inserting two 0.005" steel spacers (Diagram 10,d) between the top of the heating block and its cover (Diagram 10,f and a), and three thin fibreglass spacers (Diagram 10,c) between the edge of the insulating lid and the top of the cell. The small clearances thus produced, enabled a more ready exchange of the atmosphere above the sample cups in the heating block and that of the remainder of the cell to occur. As a result, samples no longer showed any visible signs of degradation at the end of an experiment.

Once the cell atmosphere had been replaced, a static nitrogen pressure of 2-5 psi. was applied to the cell. Even with the modifications to the cell, any atmosphere exchange during a run was likely to be very slow and result from thermal expansion effects. The positive nitrogen pressure prevented the possible back diffusion of exygen through any leaks into the cell.

The samples were contained in aluminium or platinum foil liners. Platinum was used for materials which either react with aluminium, ie. zinc, or melt at temperatures approaching,or above that of aluminium. The liners were made by cutting out a disc of foil with a suitable sized cork borer. This disc was then formed by hand, over a dowel pin, to make the liner.

The liner, after being washed with acetone and ether, was weighed on a Stanton "Unimatic" balance. The sample was then weighed into the liner, which was then carefully transferred to the sample cup

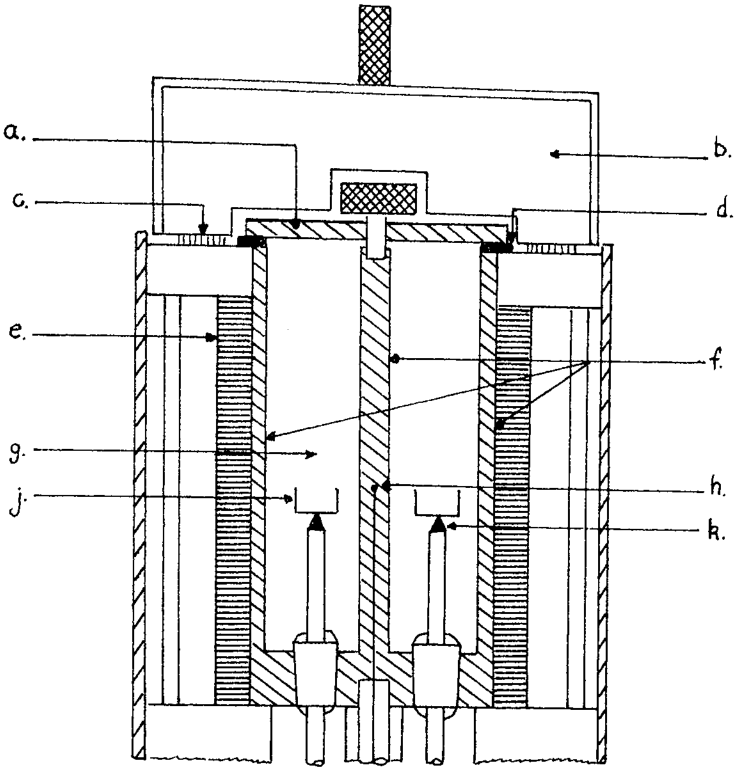


Diagram 10. The Modified Du Pont Calorimeter Cell.

a) Heating block cover.
b) Insulating lid.
c) Fibreglass spacer.
d) Steel spacer (0·005".)
e) Heater.
f) Heating block.
g) Air space.
h) Control thermocouple.
j) Sample/Reference cups.
k) Thermocouple.

The cell is enclosed by a glass bell-jar.

using a pair of pointed tweezers. Care was taken to ensure good contact between the base of the liner and the bottom of the sample cup. Neither liner nor reference material were required in the reference cup.

The modified Calorimeter cell was then assembled. The cell atmosphere was replaced with nitrogen, and the run commenced by setting the temperature programmer into operation.

For a similar sample size and heating rate, the total peak area and the degree of resolution obtained with the Calorimeter Cell was less than that from the standard D.T.A. cell. Hence samples of the order of 10 mgms. and heating rates of 2° to 3° C./minute were used to obtain reasonably satisfactory results.

The areas of the peaks plotted on the X-Y recorder were difficult to measure accurately with a polar planimeter (Ott type 17 planimeter-No. 96457. - loaned from Mechanical Engineering Dept.). A 10 mv. time base recorder was therefore used to record peaks, whose areas could be measured more accurately.

Three different 10 mv. recorders were used during the course of this work. Firstly, a Bristol 6 channel "Multipoint" recorder with all 6 inputs connected in parallel, to give a virtually continuous trace. However several curves could be drawn through one set of points thus giving variable peak areas.

Secondly, a "Vitatron" recorder with an integral peak integrator, was used. (Supplied by Fisons Scientific Apparatus Ltd.) The integrator system proved to be unreliable and so finally a Bristol single pen recorder was used. With all three recorders, the X-Y recorder was operated simultaneously to record reference temperatures.

The "Zero" and " ΔT" sensitivity controls on the calorimeter cell were used in conjunction with the external recorder; the " ΔT" sensitivity being adjusted to give the maximum peak area it was possible to record. It was essential to earth the cell when an external recorder was used, otherwise a noisy trace resulted.

It was impossible to cool the Calorimeter cell at a faster predetermined rate than its natural one, without destroying its atmosphere. The increased thermal mass of the cell reduced its natural cooling rate compared to the standard D.T.A. cell. Between 280° and 200°C., the normal cooling rate was approximately 5°C./minute.

3:1:5 OPERATION OF THE CALORIMETER CELL WITH WATER PRESENT IN THE CELL.

A schematic layout of the apparatus used to provide the cell with an aqueous atmosphere is shown in Diagram 11 (page 42). The volume of the calorimeter cell bell-jar (790 mls.) and the amount of water required to fill this volume with a pressure of 5 psi. at 260°C. was calculated. (0.4356 g.) This quantity of water was distributed equally between the two pockets of the heating block using an "Agla" micrometer syringe.

After the sample had been placed in the sample holder, and the bell-jar replaced, the cell was connected to a vacuum line and evacuated. Moist nitrogen was allowed to flow into the cell to replace the vacuum, until a pressure of 5 psi., indicated by the pressure gauge on the nitrogen cylinder was reached. The mercury manometer was then connected to the system and the height of the mercury noted.

The atmosphere of the cell was completely replaced with moist nitrogen using the previously described technique. The vacuum line was disconnected, and the nitrogen pressure adjusted until the previous manometer reading was reached.

The run was commenced. As the temperature rose, the cell atmosphere pressure, as shown by the manometer, was kept constant by carefully venting off the excess pressure. During a run, beads of moisture tended to form on the cooler parts of the bell-jar.

On crystallization, as the temperature fell, the pressure was maintained constant, by admitting small quantities of moist nitrogen to the cell until the manometer again reached the required value.

By this process, the cell's pressure and its moisture content was kept reasonably constant throughout a series of quantitative determinations. The amount of pressure fluctuation during a 14 hours annealing run (ie. overnight.) was not known. After such a run, it is likely that the cell's moisture content had decreased on account of a) leakage, or b) further condensation of moisture on cooler parts

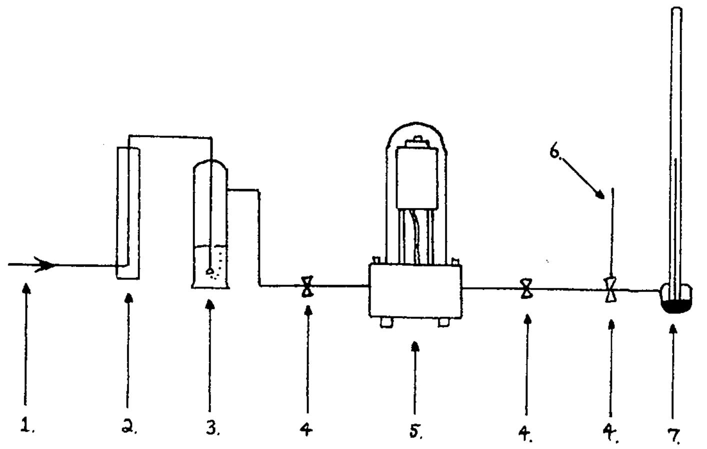


Diagram. 11. Schematic layout of apparatus used to operate the Du Pont Calorimeter Cell with water present in the cell.

1 = from nitrogen cylinder.

2 = flowmeter.

3 = gas washing bottle(containing water.)

4 = glass taps.

5 = Calorimeter Cell.

6 = to vacuum line or atmosphere.

7 = mercury manometer.

of the cell.

3:2 ANNEALING.

The annealing of polymer samples was carried out by two different methods. Firstly, samples were annealed in the Du Pont D.T.A. cell, using the "isothermal" mode of operation (3:1:3F). Secondly, they were annealed in a silicone oil bath, when larger samples could be used, thus enabling further examination of the samples after annealing, to be carried out.

The oil bath consisted of a 4 litre (approx.) transparent walled Dewar vessel filled with Silicone Oil. The oil was stirred by a propeller stirrer driven by a variable speed motor. It was heated by two "blade" type immersion heaters of 500 and 250 watts respectively. The temperature of the oil was controlled by a mercury in glass thermostat fitted with a proportional control head, (Sunvic Controls Ltd. type Tol 38) linked through a suitable switching system to the 500 watt control heater. The 250 watt heater was used to rapidly raise the temperature of the bath or to maintain it at temperatures above 200°C. The control thermostat was placed "downstream" of the two heaters with respect to the oil movement in the bath.

The temperature of the bath was measured by a mercury thermometer adjacent to apparatus in the oil bath. It was possible to thermostat the bath to ± 1°C. at 242°C.

The apparatus used to anneal polymer samples at 242°C. in an inert atmosphere, to prevent oxidation is shown in diagram 12 (page 44). It attempted to replicate annealing conditions in the D.T.A. cell, by having restricted nitrogen access to the sample during the annealing process.

The apparatus was used as follows. The sample was placed in the sample container and the apparatus connected up to a vacuum line (1) and a nitrogen cylinder. (2) Tap (3) was turned to enable the sample container to be evacuated to about 0.5 mm. Hg. The vacuum line was then closed, the nitrogen turned on and tap (3) turned slowly clockwise until the vacuum had been released and the sample was under pressure. (1-2 psi). This procedure was repeated 4 or 5 times. Finally tap (3) was turned anticlockwise to keep the sample in a nitrogen atmosphere whilst it was transferred to the annealing bath.

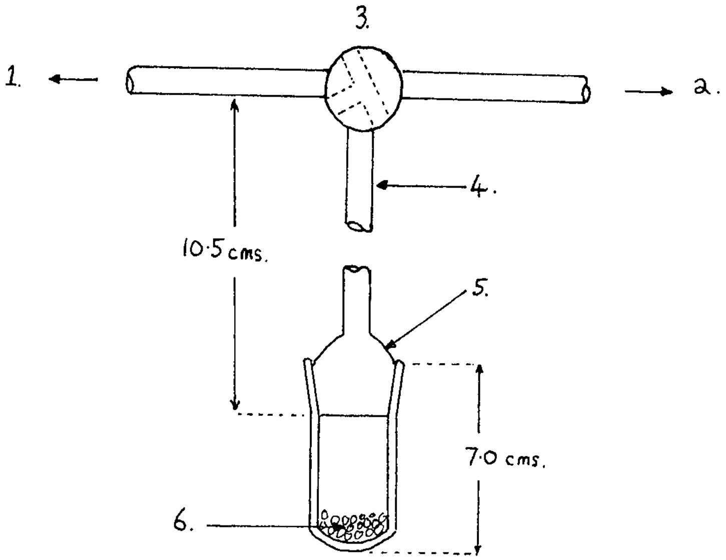


Diagram 12. Apparatus for the annealing of polymer samples in an oil bath.(not to scale.)

1. To vacuum line.

2. To nitrogen cylinder.

3. 3-way glass tap (4 mm. bore).

4. 6 mm. O.D. glass tube.

5. B14. cone and socket joint.(held together by springs).

6. Polymer sample.

Tap (3) was then purged with a slow flow of nitrogen before being turned through 180° clockwise, so that the nitrogen flowed over the top of the tube leading to the sample. The apparatus was then placed in the oil bath. After the desired annealing time, it was removed from the bath and allowed to cool before the nitrogen flow was turned off.

The thermograms of the initial samples annealed in the apparatus, suggested that they were not attaining thermal equilibrium with the oil bath. This was attributed to poor thermal conductivity between the glass apparatus and the sample. By immersing the samples in previously de-gassed silicone oil in the sample holder to increase the system's thermal conductivity, more satisfactory results were obtained.

66 Nylon bristle was annealed in a similar manner. The sample holder consisted of a length of 6mm. O. D. glass tubing (approx. 8 cms. long), sealed at one end. The bristle, cut to a suitable length, was packed into the tube so as to fill it as completely and uniformly as possible. The tube was then connected to the 3-way tap, by a piece of P.V.C. tubing and the procedure described previously to replace the sample atmosphere with nitrogen carried out. On account of the smaller dimensions of the sample holder, and the tighter sample packing obtained with bristle, silicone oil was not necessary to improve the thermal conductivity of the system.

3:3 PRECIPITATION.

In the first method, a dilute solution of the polymer in a suitable solvent was added to a rapidly stirred excess of a non solvent, and the polymer then isolated. In the second, the polymer was dissolved by gently refluxing in a relatively poor solvent. When the polymer had dissolved completely the solution was allowed to cool. The dissolved polymer reprecipitated and was subsequently isolated.

METHOD. 1.

A 5% solution of 66 nylon in 98% formic acid (Hopkin and Williams, G.P.R. grade.) was prepared by mechanical shaking. 10 mls. of this solution were placed in a dropping funnel and run slowly into an excess of rapidly stirred methanol contained in a beaker. A magnetic stirrer was found to be the most suitable for stirring the non solvent, since it did not clog up so readily with the more fibrous precipitates as a propeller stirrer. By using a magnetic stirrer incorporated in an electric hot plate, it was possible to alter the precipitation temperature.

Initially a 4:1 non solvent/solvent ratio was used, but, samples precipitated in this system tended to coalesce on drying in vacuo, probably due to residual formic acid. The non solvent/solvent ratio was then increased to 10:1, but coalescence still occurred during drying.

Some of the early precipitated samples were difficult to filter, since they rapidly blocked a sintered glass crucible (porosity 3). The addition of water to the methanol produced a more fibrous precipitate. (Precipitation directly into water gives a very fibrous precipitate.) At room temperatures, a methanol/water ratio of 2:3 gave the most promising results. Larger percentages of water produced a more fibrous material, whereas lower percentages; ie. 1:1 still resulted in fine precipitates which clogged filters and coalesced on drying in vacuo. The increasing fibrous nature of the precipitate, as the percentage of water increased, was readily observeable in a low powered microscope.

The original washing procedure, of decantation; filtration; redispersion in fresh non solvent; refiltration; followed by further washing with non solvent on the filter, did not succeed in removing the final traces of formic acid from the precipitate, since coalescence occurred on drying at 40°C. in vacuo. Washing the precipitate with a variety of methanol/water mixtures; distilled water or a 1:1 methanol/10% sodium carbonate solution did not prevent the coalescence from occurring.

Precipitated polymer particles, not compacted by filtration, were observed to remain as individual particles on drying naturally. By using a Rotary Film Evaporator (R.F.E.), it was possible to wash the precipitate several times without compacting it. This method should have removed more of the formic acid and yielded a smaller volume of liquid to filter.

The washing procedure using the R.F.E. was as follows. The solution containing the precipitate was placed in the R.F.E. flask and its volume reduced by applying a water pump vacuum, whilst gently warming the flask. When a thick slurry had formed, about 100 mls. of distilled water were added. The slurry was redispersed in the water before reapplying the vacuum to reduce the volume again. This process was then repeated. Finally the slurry was transferred to a sintered glass crucible with the minimum quantity of distilled water, filtered with the minimum of compaction and dried in vacuo. The precipitate, still tended to coalesce slightly on drying.

In an attempt to remove the formic acid completely, the precipitation was carried out in excess methanol containing sufficient sodium hydroxide to neutralize the acid. (8.6 gms. Na OH/10 gms. HCOOH.) The sodium formate formed is readily soluble in both methanol and water and can therefore be washed from the precipitate easily. During the precipitation, the temperature of the non solvent rose from room temperature to 41°C.

The methanol was removed using the R.F.E. technique and replaced with 50 mls. of distilled water. This solution was then centrifuged at 4,000 rpm. for 15 minutes; the supernatant liquid decanted; replaced with fresh distilled water, and the polymer redispersed in the water prior to recentrifuging. This was repeated, and the polymer finally filtered on a sintered glass crucible before drying it at 40°C. in vacuo. The polymer obtained by this method was fine and white, and did not coalesce on drying. However its D.T.A. thermogram suggested that the alkali had attacked the polymer, and therefore the method was not repeated.

The precipitation method described by Haslam and Willis (142) was also used. 10 mls. of a 10% solution of 66 nylon in 98% formic acid were placed in a 50 ml. conical flask immersed in a 25°C. thermostat. Sufficient methanol was added with shaking until a faint turbidity was produced. ($\simeq$7.5 mls.) The solution was allowed to stand for 30 minutes when precipitation appeared to be complete. Sufficient distilled water was then added to the precipitate to transfer it to centrifuge tubes. It was then centrifuged at 3,000 rpm. for 10 minutes. The supernatant liquid was decanted off; replaced with more distilled water and the polymer redispersed before recentrifuging. This was repeated 4 times, before the solid was transferred to a sintered glass crucible and filtered. It was then washed first with acetone and the 2 or 3 times with diethyl ether before drying in vacuo at 40°C. This sample did not coalesce on drying and its D.T.A. thermogram had two melting endotherms.

(5:2:3) A second identical experiment was carried out at 40°C.

The method was examined in greater detail. A 1.0%, by weight solution of 66 nylon in 98% formic acid was prepared. To 100 mls. aliquots of this solution, were added with shaking, a) 10 mls., b) 20 mls., c) 30 mls., and d) 40 mls. of methanol before the samples were placed in a 25°C. thermostat. Sample d) precipitated within 30 minutes, but was left in the thermostat overnight. After 16 hours, c), had also precipitated out, but b) appeared to have only partially precipitated, whilst a) remained clear.

Sample b) was centrifuged for 10 minutes at 3,000 rpm., the supernatant liquid decanted off, and 200 mls. of distilled water added to it. Some further precipitation occurred and this polymer was also recovered.

Methanol was added slowly to a),initially an extra 5 mls., then a further 2.5 and finally another 2.5 to bring the methanol concentration up to 20 mls. In between each addition, the sample was shaken and allowed to stand overnight, but no precipitation occurred until a total of 20 mls. of methanol had been reached.

All the samples were subsequently recovered from solution using the isolation and washing techniques described previously.

A sample was prepared by the direct precipitation of a formic acid solution into excess stirred methanol, and then isolated using the centrifuging technique. The thermogram of this sample only contained a single endotherm, thus demonstrating that the isolation procedure did not cause the formation of polymer showing two melting endotherms.

METHOD. 11.

A 2%, by weight, solution of 66 nylon in benzyl alcohol (Perfumers grade, Bush Chemicals Ltd.) was prepared by dissolving the polymer chip in the refluxing solvent (177°C. maximum.), in a nitrogen atmosphere. Samples were removed from the hot solution by pouring into test tubes. These were then allowed to cool naturally, or else were placed in silicone oil baths (see 3:2 for details.), at various temperatures, to give different crystallization conditions. All crystallizations were carried out in air, no attempt was made to prevent sample degradation, and none was observed.

In further experiments, after the 66 nylon solution had cooled to room temperatures, samples were reheated, either to the minimum temperature at which a homogeneous solution formed ($\simeq 150^{\circ}$C.) or alternatively to 167-170°C., when refluxing commenced, before any further crystallizations were carried out.

After crystallization, the solutions were allowed to cool to room temperature, before isolating the polymer. The benzyl alcohol solution set to a rigid gel when cold. Acetone was added and the gel stirred to break it up before it was filtered through a sintered crucible (porosity 3) at a water pump. The filter cake was broken up; redispersed in acetone and then refiltered. It was then washed with more acetone and finally 2 or 3 times with diethyl ether, before drying in vacuo at 40°C. for at least an hour.

3:4 DENSITY MEASUREMENTS.

The density of samples were determined using a density gradient column (supplied by Davenports (London) Ltd.), thermostatted at 23°C.

The columns were prepared by the "slip under" technique (143) from suitable mixtures of carbon tetrachloride (s.g. 1.595 g./ml.) and toluene (s.g. 0.8669 g./ml.). The ratio of carbon tetrachloride to toluene to give solutions of density approximately 1.10 g./ml. and 1.20 g./ml. were 1:2.1 and 1:1 respectively. The density of the solution was checked by means of a suitable hydrometer before the column was prepared.

The columns were calibrated by means of glass floats precalibrated to 0.0001 g./ml. (also from Davenports.) To avoid disturbing the gradient, the floats were slowly lowered into the column by mechanical means. Their positions in the column were measured by means of a cathetometer mounted on the side of the apparatus.

The density of samples were determined as follows. The sample was immersed in the more dense solvent to prevent the formation of air bubbles, then placed carefully on the top of the column and allowed to fall to its equilibrium position, usually overnight. The calibration of the column would then be checked, the position of the samples noted, and a graph of density against column height plotted. Hence the density of the sample could be obtained.

3:5 THE HOT STAGE MICROSCOPE.

The apparatus was used to prepare thin films of 66 nylon polymer of a specific morphology, ie. containing negative spherulites. (35,36.) It consisted of a Köfler hot-stage mounted on a Reichert R.C.H. polarising microscope (magnification 100X), fitted with substage illumination, supplied by Shandon Scientific Instruments Ltd.

The single Reichert (type 7905) rotary transformer supplied with the hot-stage did not control the temperature of the hot-stage to the required degree of accuracy. A second rotary transformer (Berco Rotary Regavolt type 72A) was connected in series with the Reichert transformer to give a finer degree of temperature control. With suitable precautions against draughts, the hot-stage could be thermostated to ± 1°C. as measured by a mercury thermometer mounted in the hot stage itself.

A Townson and Mercer Thermostat Hotplate, adjacent to the microscope was used as a melt thermostat to prepare the polymer films.

Photographs were taken in polarised light, directly through the eyepiece of the microscope, on Kodak Tri-X Pan. film, using an Exakta Varex IIA 35mm. camera. (Exposure, 10 secs.) The film was then developed in Kodak D. 76 developer (1:1 dilution with distilled water), and then half plate enlargements ($\simeq$ 4.2 magnification) of appropriate negatives were made by Visual Aids Department.

A glass microscope slide (1"x1½" approximately) was placed on the hot-stage, covered with the glass cover plate and allowed to reach thermal equilibrium. It was found necessary, experimentally, to keep the hot-stage (as indicated by the stage thermometer), some 2-3°C. above the actual desired crystallization temperature. Otherwise, the negative spherulites, as described in the literature (35,36) did not form. This was because the polymer film on top of the microscope slide was not at the required temperature, due to the decreasing thermal gradient between the hot-stage and the polymer film.

The polymer films were prepared on the adjacent hotplate as follows. The hotplate was set at the desired temperature (263°-270°C.), measured by a thermometer inserted in the hotplate. A glass microscope slide cut to size, and a coverslip were placed on the hotplate and allowed to reach thermal equilibrium.

A small chip of polymer was placed on the hot slide and spotted with silicone oil, to prevent degradation of the polymer as much as possible. The coverslip was then placed on top of the chip and carefully pressed down with the edge of another microscope slide, so that the molten polymer formed a thin film. Successful films were as uniform and free of bubbles as possible, with no visible sign of degradation (a slight brown discolouration) in the body of the film.

The blank microscope slide was removed from the microscope hot-stage just prior to the rapid transference of the molten polymer film from the melt hotplate to the microscope hot-stage. This transfer was normally carried out after the film had been molten for approximately five minutes. The time of a),the transference, b), the first appearance of spherulites and c), at which any photographs were taken, was noted. At the end of crystallization runs,the slide was removed from the hot-stage, and cooled in air, or quenched in liquid nitrogen if further crystallization was to be prevented.

Samples were annealed on the hot-stage to compare with similar samples annealed in the Du Pont 900 D.T.A. apparatus. For this the microscope hot-stage was set to the required temperature, again with a blank microscope slide in place. Once the desired temperature had been reached and thermal equilibrium established, the blank slide was removed and the previously prepared one inserted in its place. Timing of the annealing period was started when the hot-stage thermometer regained the desired annealing temperature. Observations of the melting of samples of known morphology were also carried out. These were done, by slowly increasing the temperature of the microscope hot-stage (approximately 1^{o}C./min.) and taking photographs at suitable temperature intervals throughout the melting range.

3:6 X-RAYS.

X-ray photographs were taken to determine qualitatively whether samples of 66 nylon which had different D.T.A. melting endotherms, also haddifferent X-ray diffraction photographs.

Powder photographs of precipitated 66 nylon were taken with nickel filtered X-rays generated from a Copper target. The nickel filter ensured only Copper Kα radiation was used. The X-rays were generated at 40 Kv. and 10 m.amps., using a Solus-Schall generator. The samples were mounted in lithium beryllium borate glass tubes in a Phillips 10.5 cm. diameter powder camera, fitted with a 0.5 mm. collimator. After 12 hours exposure to the X-ray beam, the film was removed, processed and examined.

Fibre diagrams were obtained for samples of 66 nylon bristle, both before and after they had been annealed at 242°C. for various periods of time, using the following method.

The bristle was mounted in a special clamp. Diagram 13 (page 53) shows the clamp in more detail. It was made to hold the bristle taut with its fibre axis vertical and at 90° to the X-ray beam.

The clamp was fitted in place of the goniometer head in a Unicam SP 25 Oscillation camera. The design of the clamp was such that the bristle was offset from the centre of the camera towards the 0.5 mm. collimator. This was not important originally since the photographs were only intended to be used for qualitative comparison purposes, rather than detailed analysis. The bristle was not oscillated during its exposure to the X-ray beam.

After 12 hours exposure to the X-ray beam, the film was removed from the camera, processed and examined.

Apparatus was not available in the University to obtain low angle X-ray diffraction patterns. Some samples of precipitated polymer and annealed film were sent to I.C.I. Fibres Ltd., Pontypool, Monmouthshire who were able to take such low angle photographs, and kindly did so.

The photographs they obtained were taken on a Kiessig low angle camera, using 0.7 mm. circular collimation. The film to specimen distances were:- wide angle 10 cm; low angle 20 cms. (The film samples were about 1 mm. closer to the X-ray film than the powder samples.) An aluminium screen was used in front of the wide angle X-ray film to reduce the amount of back scattering, causing overall fogging of the X-ray film.

Eight thicknesses of the polymer film were used in each case with the extrusion direction of the film vertical. The precipitated polymer samples were about 1 mm. thick in each case.

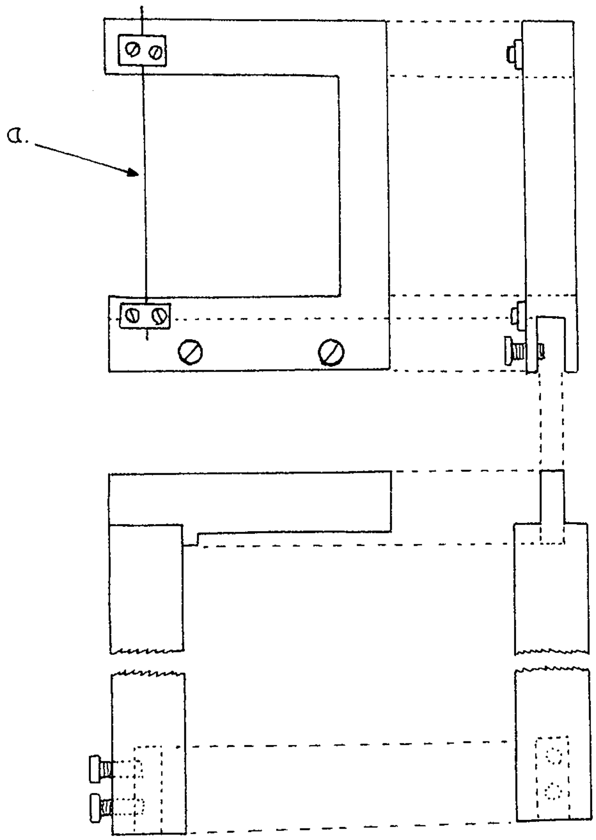


Diagram 13. Brass clamp used to mount 66 nylon bristle(a) in an X-ray oscillation camera.(not drawn to scale.)

4. MATERIALS.

In this section, details (when available) are given for the various polymers, solvents etc., that were used in this work.

4:1 66 NYLON.

4:1:1 YARN.

30 denier (10 filament), standard production yarn, from I.C.I. Fibres Ltd., Pontypool, Monmouthshire.

TiO_2 Content, 0.3%

Average tenacity, 4.5g./ denier.

Relative viscosity, 35. (Relative viscosity is defined as the solution viscosity ratio for 8.4% by weight of 66 nylon in 90% formic acid.)

4:1:2 BRISTLE.

"Brulon 240" standard monofilament, from I.C.I.(Plastics Division) Ltd., Welwyn Garden City, Hertfordshire.

Diameter, 0.010".

TiO_2 Content, 0.0%

Draw ratio, 4.0:1.0.

Molecular weight, approximately 13,000.

4:1:3 CHIP.

Samples of polymer chip of different degrees of polymerization were supplied by I.C.I. Fibres Ltd., Pontypool, Monmouthshire. Details are given in Table 4:1 (page 55). All samples were TiO_2 free.

Sample 1 (Table 4:1) was used for the majority of the experiments carried out using 66 nylon chip. It contained 0.5 mole % of acetic acid incorporated into the 66 nylon during polymerisation to control the molecular weight.

Sample 4 was made from sample 3 by solid state polymerisation in atmospheric steam at 240°C. for 2 hours. It was treated as a thin layer of chip and quenched with cold distilled water on removal from the finishing apparatus to prevent air oxidation.

4:1:4 FILM.

This was supplied by I.C.I. (Plastics Division) Ltd., Welwyn Garden City, Hertfordshire. It was made from "Maranyl A150" grade 66 nylon and contained no additives. It was slightly orientated in the extrusion direction.

TABLE 4:1. PHYSICAL CONSTANTS OF 66 NYLON CHIP SAMPLES.

Sample Number	I.C.I. Reference Number.	Relative Viscosity	Amine End Groups (μ.eq./g.)	Carboxyl End Groups (μ.eq./g.)	Molecular Weight. ⊕ X 10^4
1	XP10257	35	44	58	1.72
2	--"--	31.7	43	81.5	1.23
3	XP11099	43	50.5	70	1.43
4	--"--	74.6	32.1	54	1.85

⊕ Calculated from the carboxyl end group value, as follows.

66 Nylon is made from equimolecular amounts of adipic acid and hexamethylene diamine. Acetic acid is added to control the molecular weight. Unless the number of acetyl end groups are known, the exact number average molecular weight (Mn) can not be calculated. However, twice the number of the carboxyl end groups is a reasonable approximation to the total number of chain end groups. Therefore, an approximate value for the molecular weight can be obtained from the equation;

$$Mn = 2 \times 10^6 / 2 \times (\text{Carboxyl End Groups.})$$

4:2. 6 NYLON.

4:2:1 YARN.

This was supplied by Dr. Holliday of Courtaulds Ltd., Coventry. It was made from semi matt "Celon" (BX8294) containing anatase. It had a draw ratio of 3.09:1.

4:2:2 CHIP.

Two samples of chip were used. 1) A sample from which the yarn (4:2:1) was prepared, 2) A sample from I.C.I. Fibres Ltd., Pontypool, Monmouthshire, which contained no TiO_2 or additives, no other details being available.

4:2:3 IONIC POLYMERIZED.

No details were available for this experimental sample which was made by B.A.S.F.

4:3 11 NYLON.

The sample of 11 nylon was supplied by I.C.I. Fibres Ltd., Pontypool, Monmouthshire. Apart from being free from TiO_2 and other additives no other details were available.

4:4 610 NYLON.

4:4:1 BRISTLE.

"Brulon 266" standard monofilament from I.C.I. (Plastics Div.) Ltd., Welwyn Garden City, Herts. It was 0.010" in diameter, contained no TiO_2 and had a draw ratio of 4.0:1.

4:4:2 CHIP.

This was supplied by I.C.I. Fibres Ltd., Pontypool, Monmouthshire. It was free from TiO_2, and unstablised. No other details were available. (I.C.I. reference number ON/541/51/L).

4:5 OTHER POLYAMIDES.

The samples of 7, 76, 77 and 68 nylon were experimental samples supplied by I.C.I. Dyestuffs Div. Ltd., Manchester. The sample of 68 nylon was supplied as "prepolymer". This was subsequently heated for four hours at 229°C. under a vacuum of 0.1 mm.Hg., to allow further polymerization to take place before any experiments were performed. No further details were available.

4:6 LOW DENSITY POLY(ETHYLENE).

This was a sample of "Alkathene ZJF46" made by I.C.I. Plastics Div., Welwyn Garden City, Herts, as used for polyethylene film.

4:7 HIGH DENSITY POLY(ETHYLENE).

This was supplied by Dr. Holliday of Courtaulds Ltd., Coventry.

4:7:1 "MONOFILAMENT".

This was "Courlene X3", 0.010" in diameter made from polymer chip (4:7:2 for details). It had a draw down ratio of approximately 2:1 and a stretch ratio of 8:1.

4:7:2 CHIP.

This was a sample of "Rigidex" type 3 (ex British Resin Products) batch number 8/4177/4 and had a melt index of 0.3.

4:8 POLY(PROPYLENE).

Samples of polymer granules, drawn and undrawn fibre were supplied by I.C.I. Fibres Ltd., Harrogate, Yorkshire. No information about these samples was available.

A sample of unstablised powder (PLZ109) made by Shell was also used.

4:9 POLY(ETHYLENE OXIDE).

This was a sample of "Carbowax 6000", the highest molecular weight polyethylene glycol made by Union Carbide, Ltd. No specific details were available for this particular sample.

4:10 ISOTATIC POLY(PROPYLENE OXIDE.)

This was supplied by Dr. D. E. Eaves, Dunlop Research Centre, Birmingham. It was prepared with a $FeCl_3/H_2O$ catalyst and is further described in a paper by Cooper, Eaves and Vaughan.(95)

4:11 POLY(4-METHYL PENTENE-1).

This sample was supplied by I.C.I. Plastics Division Ltd., Welwyn Garden City, Hertfordshire. No further details were known about it.

4:12 POLY(ETHYLENE TEREPHTHALATE).

These samples were supplied by I.C.I. Fibres Ltd., Harrogate, Yorkshire.

4:12:1 FIBRE.

No details were supplied. The birefringence observed when it was examined in a microscope between crossed polarizers suggested it was a drawn sample.

4:12:2 CHIP.

I.C.I. Fibres Ltd., reference, "Terylene" chip type B3, no other details available.

4:13 POLY(FORMALDEHYDE).

This was a sample of "Delrin" polymer that was available in the laboratory. No details were known about it.

4:14 SOLVENTS AND CHEMICALS.

The ordinary laboratory grade solvents and chemicals were used in this work, unless stated otherwise.

4:15 INERT GAS.

"White Spot" grade nitrogen supplied by the British Oxygen Company was used in all instances where an inert atmosphere was required.

4:16 SILICONE OIL.

Silicone oil (Midland Silicones MS 550) was used in the silicone oil annealing baths (3:2). It was also used as a heat transfer agent to aid the annealing of polymer samples, and to prevent oxidative degradation of molten polymer films which were being crystallized on the hot stage microscope.

5. EXPERIMENTAL RESULTS.

5:1. EXPERIMENTS CARRIED OUT ON 66 NYLON POLYMERS.

For further details of the particular samples used see 4:1. Some of these experimental results have been published in the Journal of Applied Polymer Science. (144)

5:1:1. OBSERVATIONS ON THE MELTING OF 66 NYLON USING THE MODIFIED KEAVNEY AND EBERLIN D.T.A. CELL. (See 3:1:1.)

An attempt to calibrate the cell was made using benzoic acid. The results are given in table 5:1 (page 60).

Initially the ΔT baseline was very unsteady with a marked slope. Diluting the sample with glass beads (the inert reference material) reduced the slope. The large discrepancy between the quoted and measured melting points of benzoic acid was most probably due to the poor thermal conductivity of the cell design. (See 6:1). No attempt was made to improve the temperature calibration of the cell, since at this time, it was not known whether it was capable of resolving multiple melting endotherms.

The initial thermograms of drawn fibre and polymer chip were very unsatisfactory. The thermocouple wires shorted giving rise to a noisy ΔT trace. The method by which this was overcome is described in 3:1:1.

The resolution of the cell was improved by the use of silicone oil in the sample and reference cells. This resulted in the satisfactory resolution of the two melting endotherms of drawn 66 nylon yarn. Table 5:2 (page 61) and Diagram 14 (page 62) give the results of some of the experiments carried out with 66 nylon samples in the cell.

At this stage of the work, the Du Pont 900 Thermal Analyser became available. It gave better and more reproducible thermograms than the modified Keavney and Eberlin cell, which as a result was no longer used.

5:1:2 OBSERVATIONS ON THE MELTING OF 66 NYLON SAMPLES USING THE DU PONT 900 THERMAL ANALYSER.

All these results were obtained using a heating rate of 5°C./minute over the melting range (220° - 270°C.) unless otherwise stated. The experiments were carried out in an atmosphere of nitrogen. The temperatures quoted refer to the tip of the exothermic or endothermic

TABLE 5:1 CALIBRATION OF THE MODIFIED KEAVNEY AND EBERLIN D.T.A. CELL. MELTING POINT OF BENZOIC ACID (121.9°C.) AS DETERMINED IN THE ABOVE CELL, WITH GLASS BEADS USED AS THE INERT REFERENCE MATERIAL.

HEATING RATE °C/MIN	EXPERIMENTAL CONDITIONS	SAMPLE/INERT (g.).	INITIAL DEVIATION °C.	ENDOTHERM TIP °C.
5	In N_2 Flow (a)	0.4/0	127	137
10	—"— (a)	Remelt of above	127	142
5	Still Air. (a)	0.2/0.5	127	143
5	—"— (b)	0.1/0.75	125	138

(a) Temperature measured in sample

(b) Temperature measured in inert reference.

Diluting the sample with the inert reference improved the base line stability of the cell but did not improve the temperature measurement.

TABLE 5:2 TYPICAL RESULTS FOR THE MELTING OF SAMPLES OF DRAWN 66 NYLON YARN OBTAINED WITH THE MODIFIED KEAVNEY AND EBERLIN D.T.A. CELL.

SAMPLE GMS.	ATMOSPHERE	HEATING RATE °C./MIN.	1ST PEAK °C.	2ND PEAK °C.
0.25	N_2 flow	2.3	247-266	266-278
0.24	-"-	4.7	245-262	263-277
0.2	Si Oil	1.6	253-264	264-260
0.04	-"-	1.6	251-259	259-268
0.075	-"-	2.0	247-261	261-267

The overall peak resolution was improved considerably when silicone oil instead of nitrogen was used to give an inert atmosphere around the sample. (See diagram 14, page 62). This was partly due to the increased thermal conductivity of the cell system with silicone oil present and also from the use of smaller samples. These allowed the thermal equilibrium of the system to be regained more rapidly after a transition had occurred.

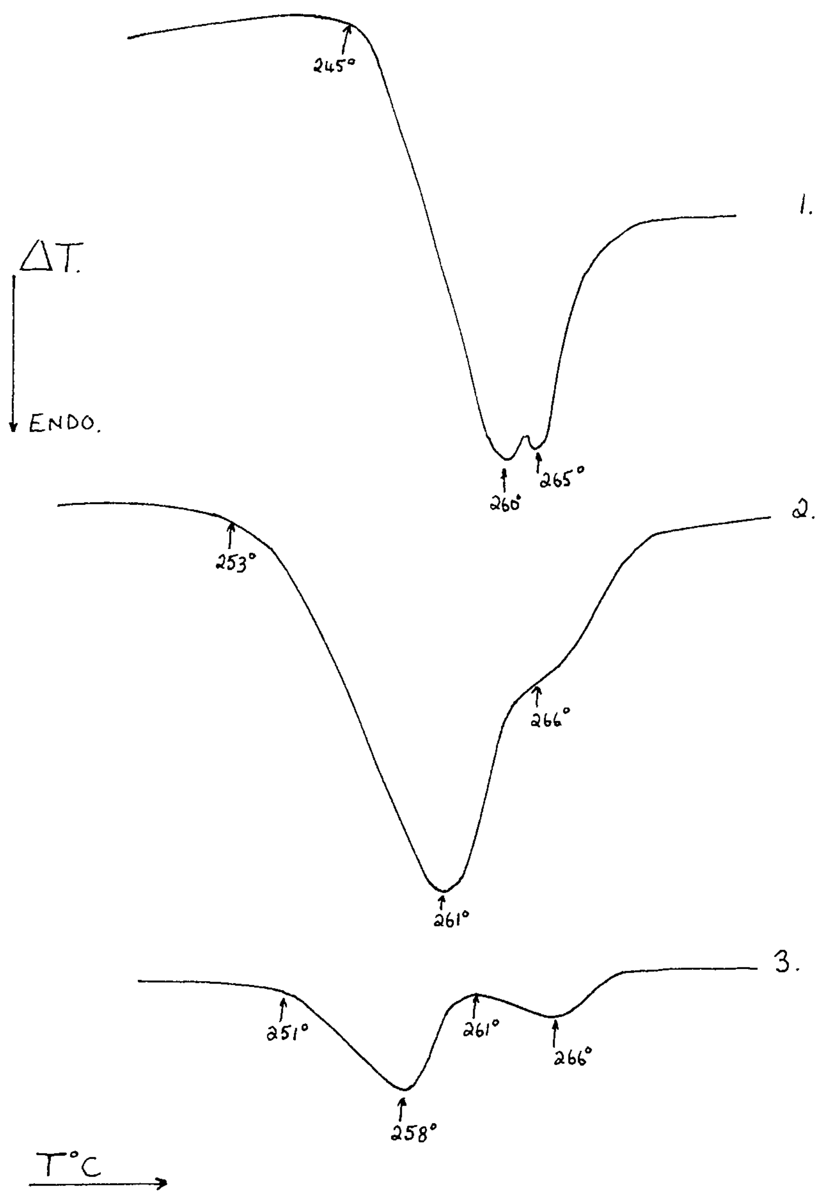


Diagram 14. Melting thermograms of drawn 66 Nylon yarn obtained using the modified Keavney and Eberlin D.T.A. cell.

1. 0·2 g. sample, nitrogen atmosphere.
2. 0·2 g. sample, } Silicone Oil present.
3. 0·04 g. sample, }

peak unless stated otherwise. (See 3:1:2 for further details.) The melting of pieces of 66 nylon chip or film resulted in a single broad melting endotherm with its peak at 258° ± 1°C. for chip, or 256° ± 1°C. for film. (Diagram 15a, page 64). The melting of a drawn fibre or bristle resulted in two melting endotherms at 250° ± 1°C. and 258° ± 1°C. respectively, comparable with White's original observations (1) (Diagram 15b, page 64). Observation of the melting of a drawn fibre in the visual cell (3:1:2b), showed that the fibre characteristics did not disappear until almost 258°C. had been reached.

After the initial melting run, or prior to any subsequent thermal treatment, a sample was usually held isothermally in the molten state at 270°C. for ten minutes. It was then allowed to cool naturally in the apparatus. The unprogrammed cooling rate for the instrument over the temperature range 270° → 200°C. was 11° to 12°C. per minute. This resulted in a crystallization exotherm in the temperature range 228° - 238°C.

Subsequent remelting of the sample always resulted in a thermogram with a small endotherm between 242°C. and 249°C. followed by a much larger one between 254° and 259°C. (Diagram 15c, page 64). This characteristic double endotherm was always observed on the remelting of a sample which had been held at 270°C. for ten minutes and allowed to cool naturally. These remelting endotherms were not detectably affected by the sample's previous morphology or thermal history. It was therefore assumed that previous physical structure was destroyed in the ten minute period at 270°C.

The effects of different heating rates and different sample weights on the melting thermograms of 66 nylon have already been described. (3:1:3).

The effect of molecular weight changes on the melting thermograms of 66 nylon is shown in table 5:3 (page 65).

5:1:3 EFFECT OF MELT TEMPERATURES ON THE CRYSTALLIZATION AND REHEAT THERMOGRAMS OF 66 NYLON.

A sample of 66 nylon chip was heated at 5°C./minute (above 200°C.) in a nitrogen atmosphere, to a series of different melt temperatures between 260°C. and 290°C. in the Du Pont standard D.T.A. cell. After

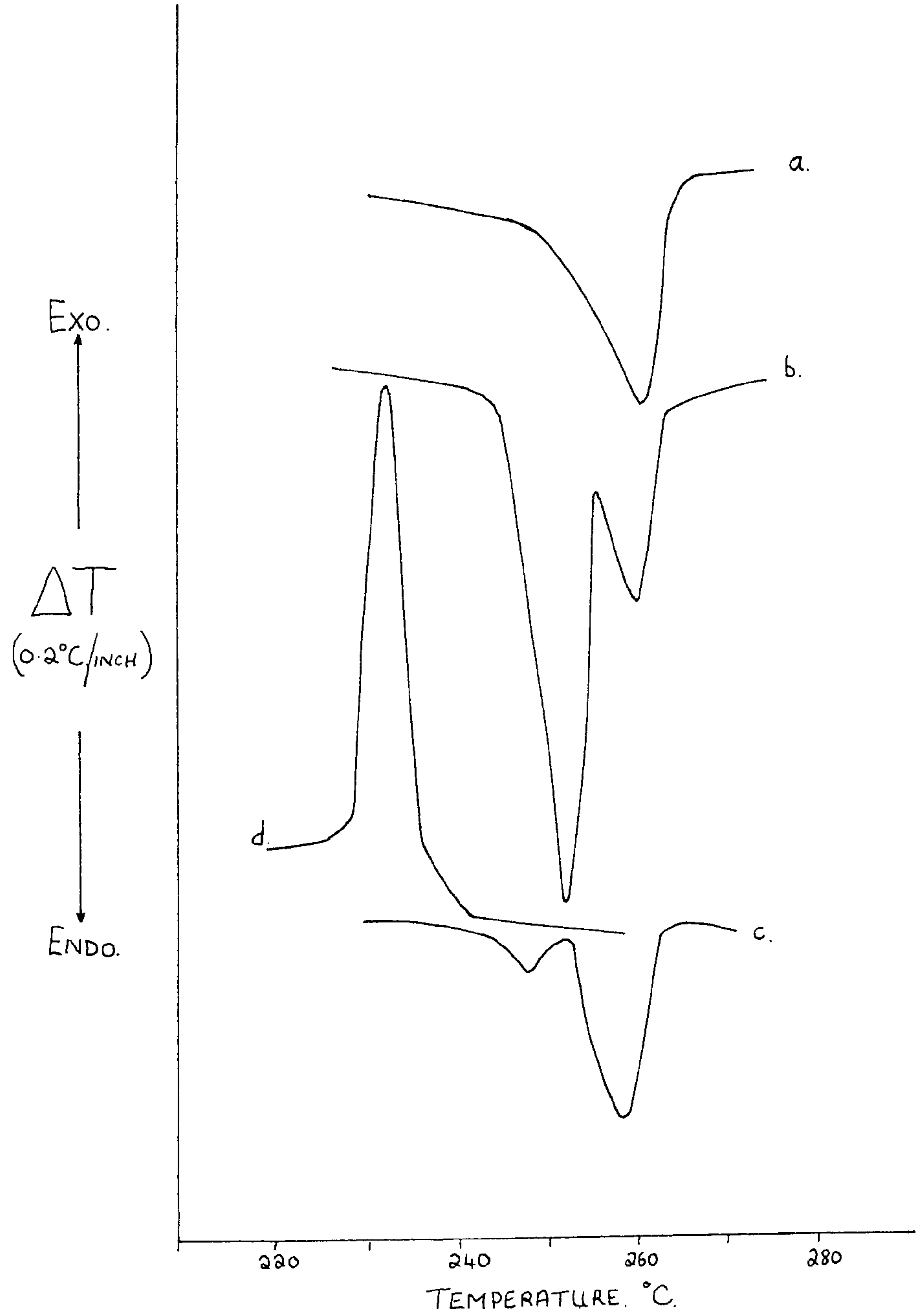


Diagram 15. Thermograms of various 66 Nylon samples.

a. chip.
b. drawn yarn. } melting thermograms.

c. remelt of a. or b. after crystallization

d. crystallization of a. or b.

TABLE 5:3 THE EFFECT OF MOLECULAR WEIGHT CHANGES ON THE MELTING THERMOGRAMS OF 66 NYLON.

No.	Sample	Relative x viscosity	Initial Melting °C.		Remelting °C.	
			1st Peak	2nd Peak	1st Peak	2nd Peak
1	XP10257	31.7	----	258	248	258
2	XP11099	44.3	----	260	249	259
3	XP11099	74.6	242	258	248	258

x For the definition of relative viscosity see 4:1:1.

The new first peak observed with sample 3 on its initial melting, probably resulted from the thermal treatment the sample received during its preparation from sample 2 by solid state polymerisation. Apart from this instance, changes in the 66 Nylon samples' molecular weight or molecular weight distribution had no real effect on the melting thermograms.

holding the sample for 10 minutes at the respective melt temperature, it was allowed to cool naturally to 120°C. before reheating commenced.

The results are given in diagrams 16/17 pages 67 and 68 and table 5:4 below.

TABLE 5:4 EFFECT OF MELT TEMPERATURE ON CRYSTALLIZATION THERMOGRAMS OF 66 NYLON.

Run no.	Melt Temp °C.	Crystallization Peak. °C.			Peak Height(cms)
		Start	Finish	Tip	
1	262	250	226	238	4.3
2	267	245	226	235.5	8.4
3	272	240	230	234	11.1
4	277	239	226	233	12.5
5	282	237	218	230	6.6
6	289	236	216	220	3.5

They show that as the melt temperature increased so the temperature of both the crystallization and remelting endotherms decreased. The effect was most pronounced on the crystallization temperature and the temperature of the first remelting endotherm.

To check the reproducibility of the thermograms a sample of 66 nylon was cycled in the standard D.T.A. cell between 220° and 275°C. The melting and crystallization thermograms obtained from several cycles were completely superimposable.

5:1:4 THE MELTING OF 66 NYLON SAMPLES OF SPECIFIC MORPHOLOGY.

5:1:4a) SINGLE CRYSTALS.

These were prepared by modifications of methods described by Geil (134) and Badami and Harris. (135) These modifications were necessary to obtain sufficient quantities of polymer without having to process large volumes of solutions. Geil's method was modified by dissolving 0.1 g. of polymer in refluxing glycerine. The resulting yellowish solution was allowed to cool overnight, the polymer isolated by filtration, washed with acetone and ether and dried under vacuum. (see 3:3 for details of washing techniques.) The polymer had discoloured, suggesting some degradation had occurred. This was

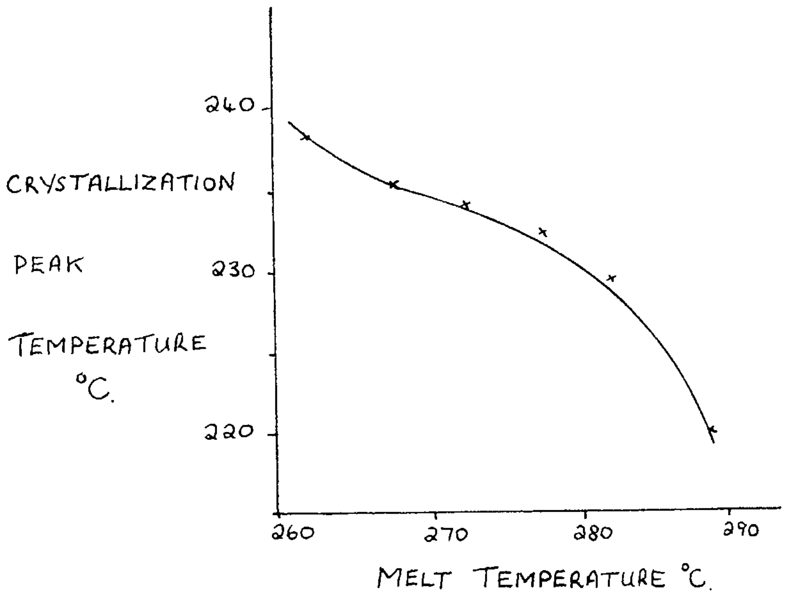


Diagram 16. The effect of the melt temperature on the subsequent crystallization exotherm of 66 Nylon.

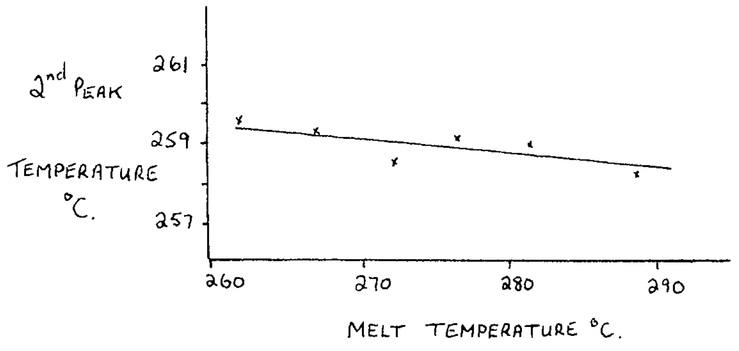


Diagram 17A. The effect of the melt temperature on the temperature of the second remelting endotherm of 66 Nylon.

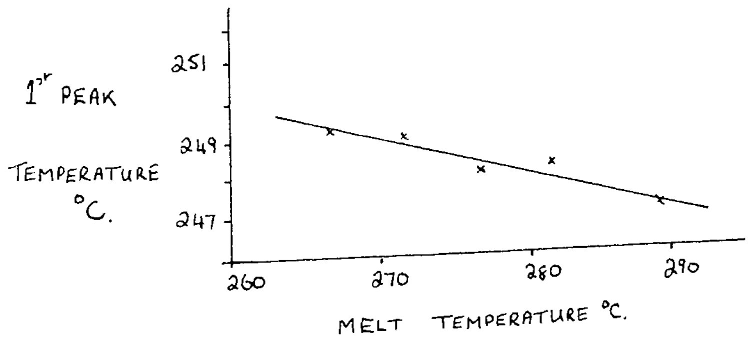


Diagram 17B. The effect of the melt temperature on the temperature of the first remelting endotherm of 66 Nylon.

confirmed by the D.T.A. thermograms (Diagram 18a, page 70) which had a final melting endotherm at 244°C. some 15°C. lower than normally observed.

The remelting endotherm of this sample, further confirmed that some sample degradation had occurred. The thermogram was poorly resolved but it was possible there was a small endotherm at 233°C. preceeding the final melting endotherm at 242°C. compared to the usual remelting thermogram of 66 nylon (5:1:2). The D.T.A. run was continued up to 270°C. but no further endotherms were observed. No further experiments were carried out using this method for preparing single crystals.

Badami and Harris's (135) method of precipitation by preferential slow volatilization of the formic acid from a 90.5% solution of 66 nylon in aqueous (90%) formic acid was repeated exactly. The volatilization was carried out on a water bath, the polymer solution being contained in an evaporating basin. The D.T.A. thermogram of polymer recovered from this is shown in diagram 18b, page 70, the two endotherms occur at 252°C. and 260°C. respectively.

The slower method of precipitation described by Badami and Harris (135) was also used. More concentrated solutions were used (0.25 g. of 66 nylon instead of 0.0025g.) but otherwise the experimental conditions were similar (see 3:3). The initial melting and remelting thermograms of polymer prepared by this method are shown on diagram 18c, page 70. Two initial melting endotherms were observed, at 252°C. and 260°C. The remelting endotherms are similar to those normally observed. (Diagram 18c, page 70).

Samples of polymer prepared by the methods of Badami and Harris were also examined using an electron microscope. No morphological structures similar to those described in the original paper were observed. Their absence was attributed to the incorrect method of preparing the samples for the electron microscope rather than their actual non existence.

5:1:4b 66 NYLON SPHERULITES.

66 nylon normally crystallizes in the form of positive spherulites. Large fibrous birefringent, and negative spherulites were prepared, similar to those described by Khoury (36) and Boasson and Woestenenk, (35)

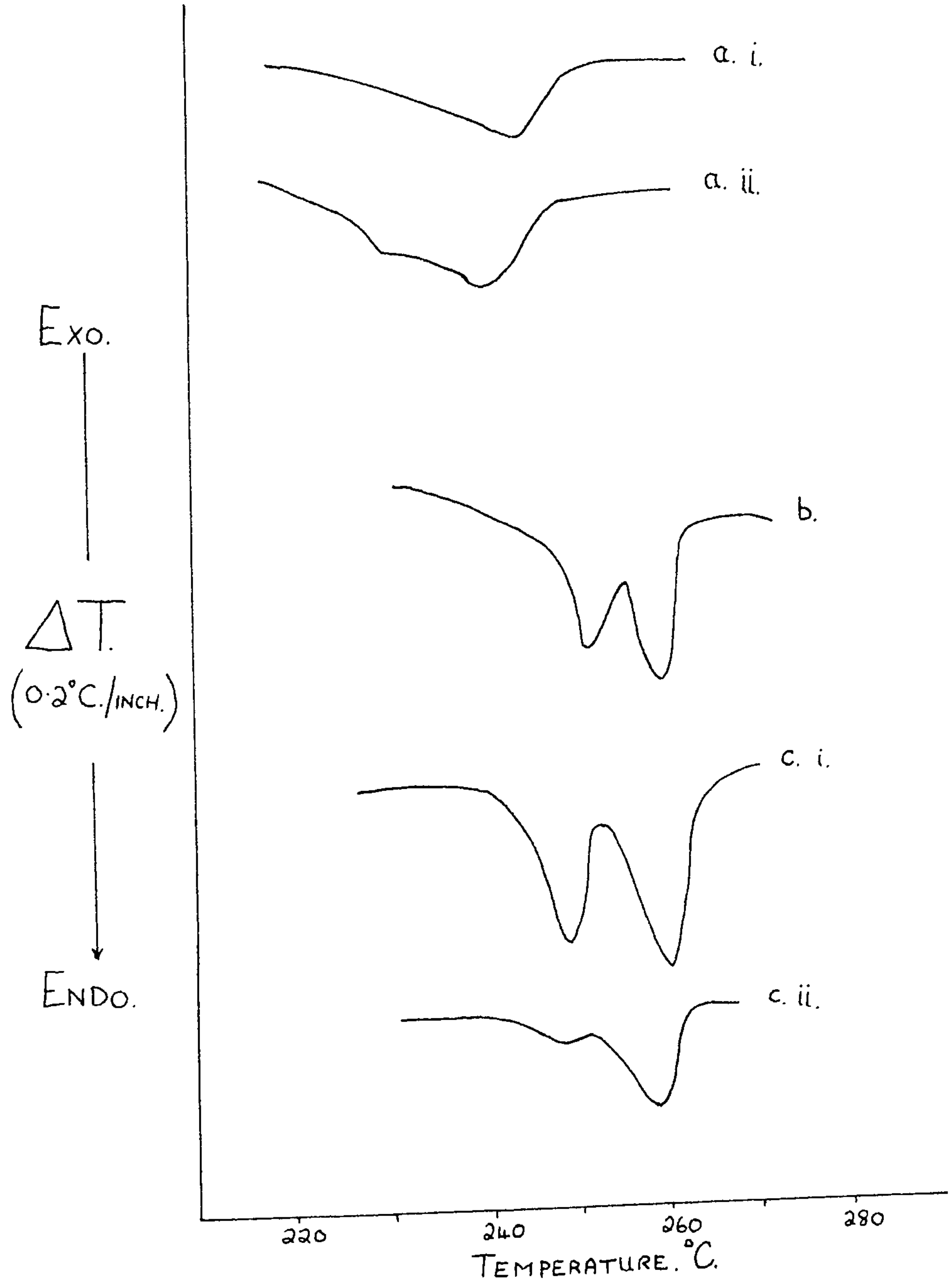


Diagram 18. The melting thermograms of 66 Nylon single crystals.

a. Geil's method.(134)--i.,initial melting.
ii.,remelting.

b. Badami and Harris(135), preferential evaporation.

c. Badami and Harris(135), precipitation,
i.,initial melting.
ii.,remelting.

on a hot stage microscope. (see 3:5). At the end of an experiment, the hot glass slide with the polymer film containing the spherulites was plunged into liquid nitrogen to prevent further crystallization from occurring. The polymer film was then cut up to yield a sample for D.T.A. examination. By using a polarising microscope to select the pieces of film, it was possible to obtain a sample containing 95-100% of the polymer in the desired spherulitic form.

D.T.A. thermograms of the fibrous birefringent and negative spherulites were then obtained. (Diagram 19, page 72). The melting points obtained from the thermograms agreed with those quoted for similar spherulites given in the original papers. (35,36)

TABLE 5:5 MELTING POINTS OF VARIOUS 66 NYLON SPHERULITES.

Spherulite Type	Mpt. °C. D.T.A.	Mpt. °C. Literature	References.
Large fibrous	265	265	(35)
Negative	267	268-270	(35,36)

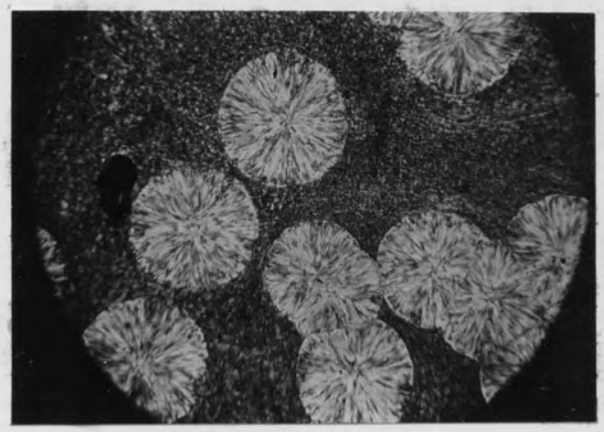
The lower temperature peaks at 256-257°C. in the D.T.A. thermograms were thought to be caused by the melting of the 66 nylon which had not crystallized into the particular spherulitic form.

Photographs of the two types of spherulite, taken between crossed polaroids are shown between pages 71 and 72.

The melting of the fibrous birefringent spherulites was also observed using the hot stage microscope. A previously prepared polymer film containing the desired spherulitic morphology was placed on the hot stage of the microscope. The hot-stage was then rapidly heated to approximately 240°C. The rate of heating was then adjusted to give an approximate temperature rise of 1°C./minute. The temperature at which the birefringence of the sample finally disappeared was taken as the melting point. (272°C.).

Photographs were taken at 245°C. and then at 2°C. intervals up to 255°C. and then at 1°C. intervals until melting took place. The

PHOTOGRAPHS OF 66 NYLON SPHERULITES TAKEN THROUGH CROSSED "POLAROIDS".



1) Large fibrous birefringent spherulites in "granular" background. (magnification ≏ 230x.)

2) Negative spherulites with occasional fibrous spherulites. (magnification ≏ 230x.)

temperatures quoted were those indicated by the hot stage thermometer.

Between 260° and 266°C. the polymer, which was not in the form of the fibrous spherulites, melted. From 267°C. onwards, the spherulites started to melt, until at 272°C. the optical birefringence disappeared. The photographs between pages 73 & 74 show these observations.

The melting of the non fibrous spherulitic polymer between 260° and 266°C. was probably responsible for the low temperature peak in the D.T.A. thermograms. (Diagram 19 page 72). The difference in temperature was due to the thermometer inserted in the hot stage being at a higher temperature than the polymer film resting on a glass slide on the surface of the hot stage.

After the optical birefringence had disappeared at 272°C. the hot stage was switched off and the film allowed to cool on it. A photograph taken after crystallization was complete (at 20°C.) showed the presence of spherulites. Comparison with a photograph of the film before melting, showed that recrystallization had occurred in the exact form of the original spherulites. The internal details of these spherulites were not as detailed as the original ones, nor were they so birefringent. (See photographs 1 and 6 between pages 73 and 74.

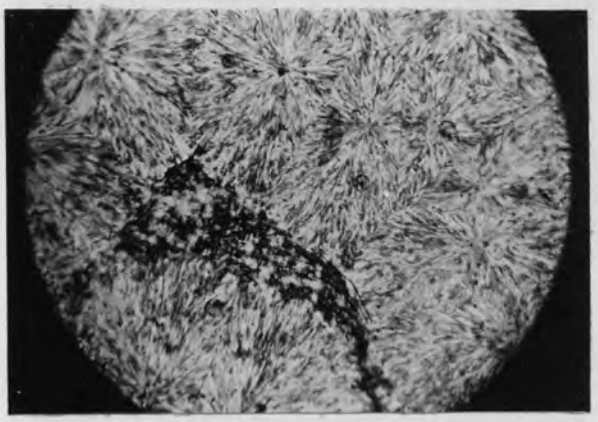
This observation showed that if the sample was only just melted, rather than fused for some time at a temperature above its melting point, the original spherulitic nuclei were not destroyed. Recrystallization could take place again therefore to give the forms of the original spherulites present before melting occurred.

5:1:5 THE MELTING OF 66 NYLON CRYSTALLIZED ISOTHERMALLY FROM THE MELT.

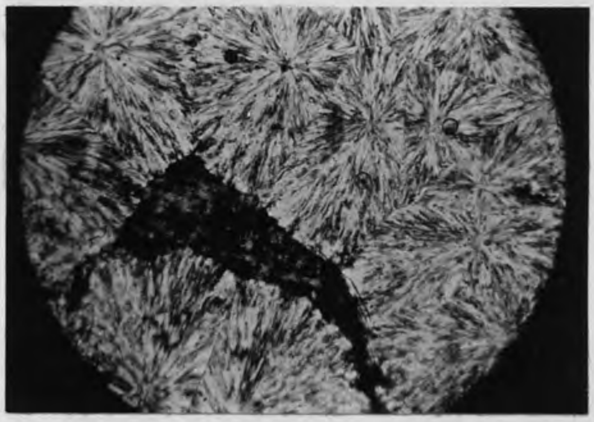
66 Nylon yarn samples, after their initial melting, were heated for 10 minutes at 270°C. before being rapidly cooled to the desired isothermal crystallization temperature. Cooling to the crystallization temperature took approximately 2½ minutes and the cooling thermograms showed no indication of crystallization occurring in this time. Crystallization was carried out at the following temperatures, 238, 240, 242, 245, 250, 255°C. for varying periods of time.

Diagram 20 (page 74) shows the thermograms, obtained by the direct

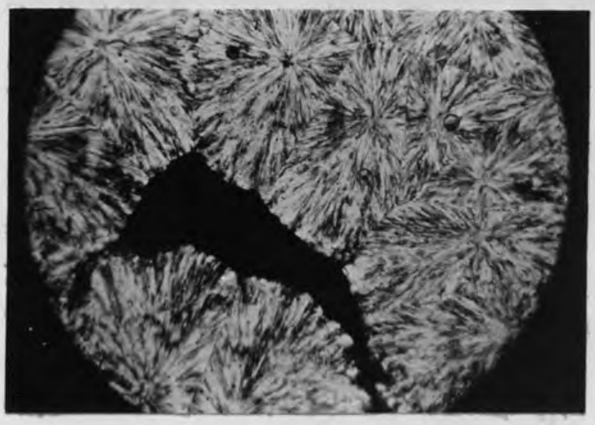
PHOTOGRAPHS TAKEN AT DIFFERENT TEMPERATURES DURING THE MELTING OF LARGE, FIBROUS BIREFRINGENT 66 NYLON SPHERULITES ON A KOFLER HOT STAGE. (Taken through crossed "polaroids"; magnification ≏230x.)



1) 240°C. Non spherulitic polymer surrounded by fibrous spherulites.

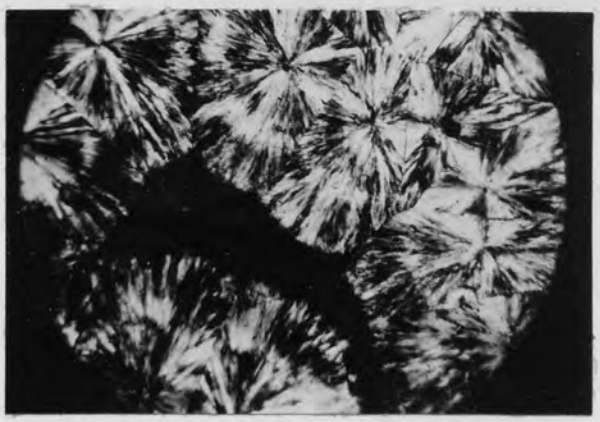


2) 260°C. Non spherulitic polymer partially molten.



3) 265°C. Non spherulitic polymer molten.

(Sequence continued overleaf)



4) 269°C. Fibrous spherulites start to melt.

5) 271°C. Birefringence almost disappeared prior to complete melting at 272°C.

6) 20°C. After natural cooling from 272°C. Sample has recrystallized in the outlines of the original fibrous spherulites, but with an apparently different internal morphology.

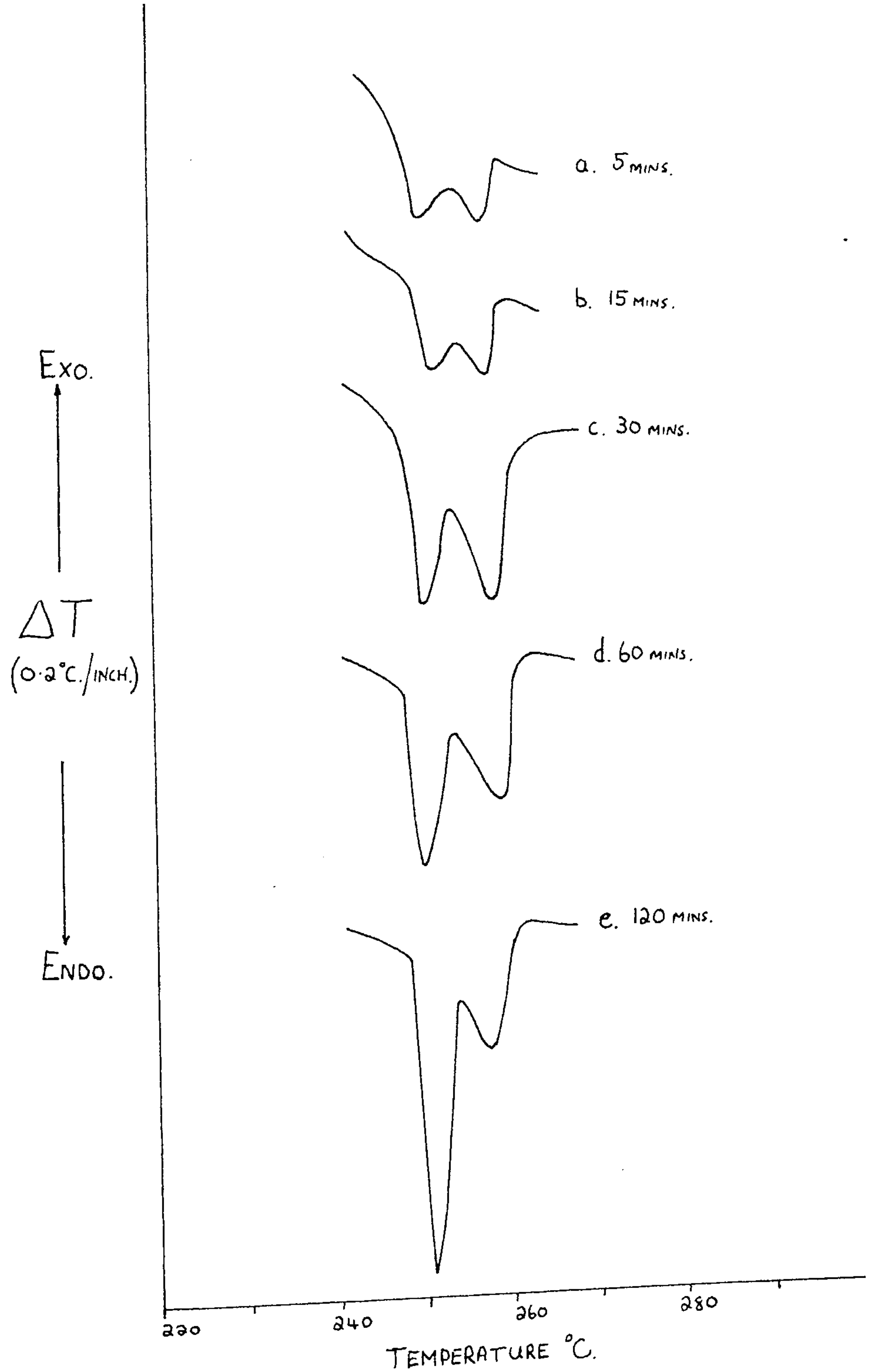


Diagram 20. The isothermal crystallization of molten 66 Nylon at 242°C. Direct reheat from the crystallization temperature.

reheating from the crystallization temperature, of samples which had been crystallized at 242°C. for 5,15,30,60, and 120 minutes respectively. As the crystallization time increased, the size of the first melting endotherm also increased, whilst the second decreased. The size of the first continues to increase after 15 minutes crystallization whereas Magill's work suggests that crystallization should be complete within 10 minutes at 242°C. (145)

The crystallizations were repeated except the sample was now cooled to 200°C. so that any residual molten polymer would crystallize, and a crystallization endotherm would be observed. The resulting thermograms, (Diagram 21 page 76) show that at 242°C. the crystallization was completed within 5 to 10 minutes. Hence, the increase in the size of the first melting endotherm after this time must be the result of a secondary crystallization or annealing process.

Cooling the sample prior to reheating, rather than direct reheating from the crystallization temperature, affected the degree of resolution of the two melting endotherms. This was possibly due to presence of solid non crystalline material resulting from the cooling process, which affected the subsequent remelting.

Diagram 22 (page 77) shows the remelting thermograms of samples crystallized at 240°C. Similar results were obtained from samples crystallized at 238°C.

Diagrams 23, 24 (pages 78 and 79) show the results obtained by crystallization at 245°C. 250°C. and 255°C. respectively. The development of the first melting endotherm is not so pronounced and the time for complete crystallization is considerably greater at these crystallization temperatures than the lower ones.

At these higher crystallization temperatures (245°;250°;255°C.), the first melting endotherm was not observed unless the sample was allowed to cool prior to remelting.

In certain samples, crystallization at 255°C. resulted in an additional melting endotherm. This occurred at a higher temperature, than the normal melting one (ie. 262°C. instead of 259°C.). It was comparable in temperature with the endotherm observed on the melting of samples containing negative spherulites (Diagram 20 page 74).

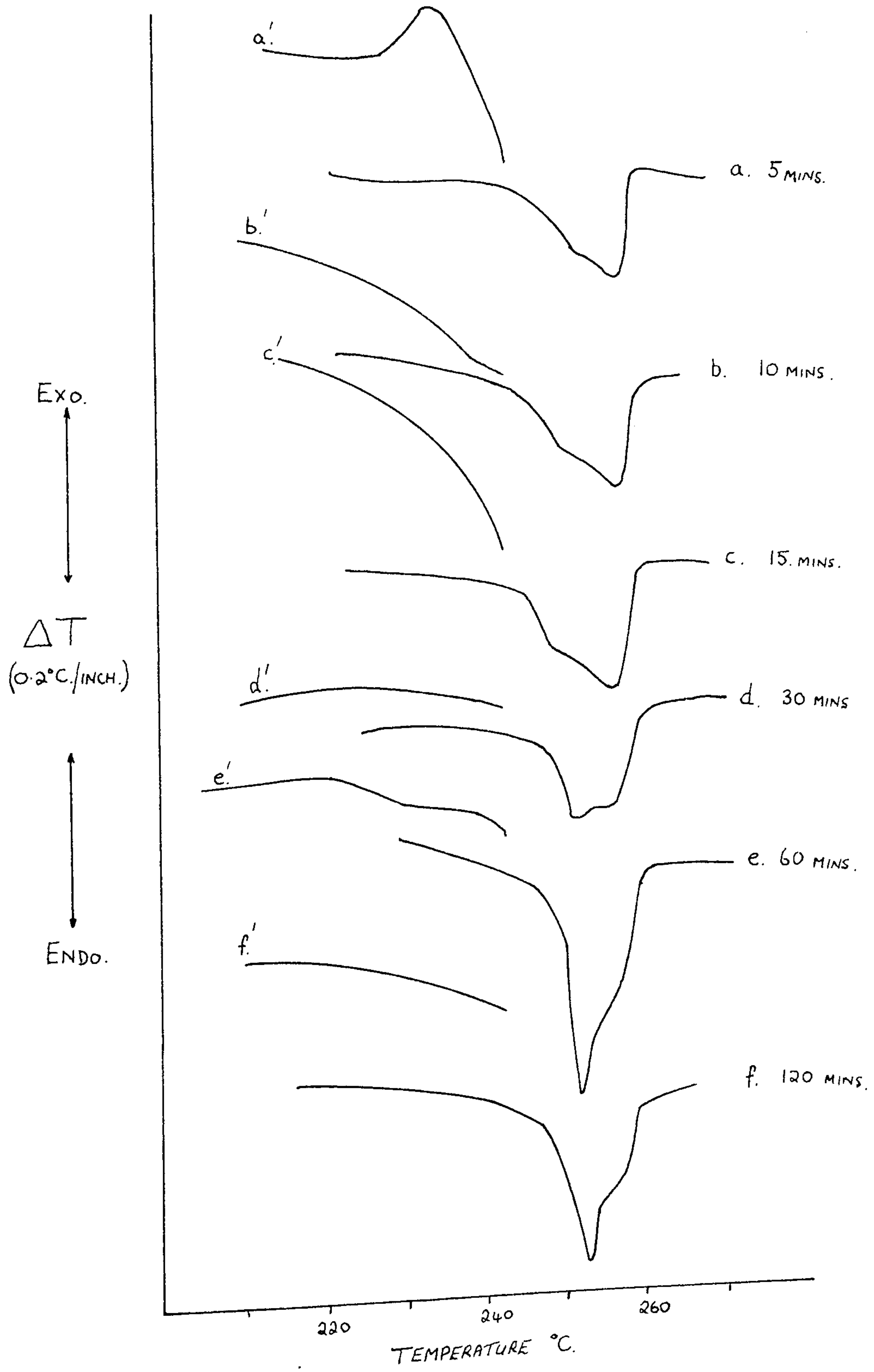


Diagram 21 The isothermal crystallization of molten 66 Nylon at 242°C.
a' is the crystallization thermogram after 5 mins. at 242°C., prior to the melting thermogram a. etc.

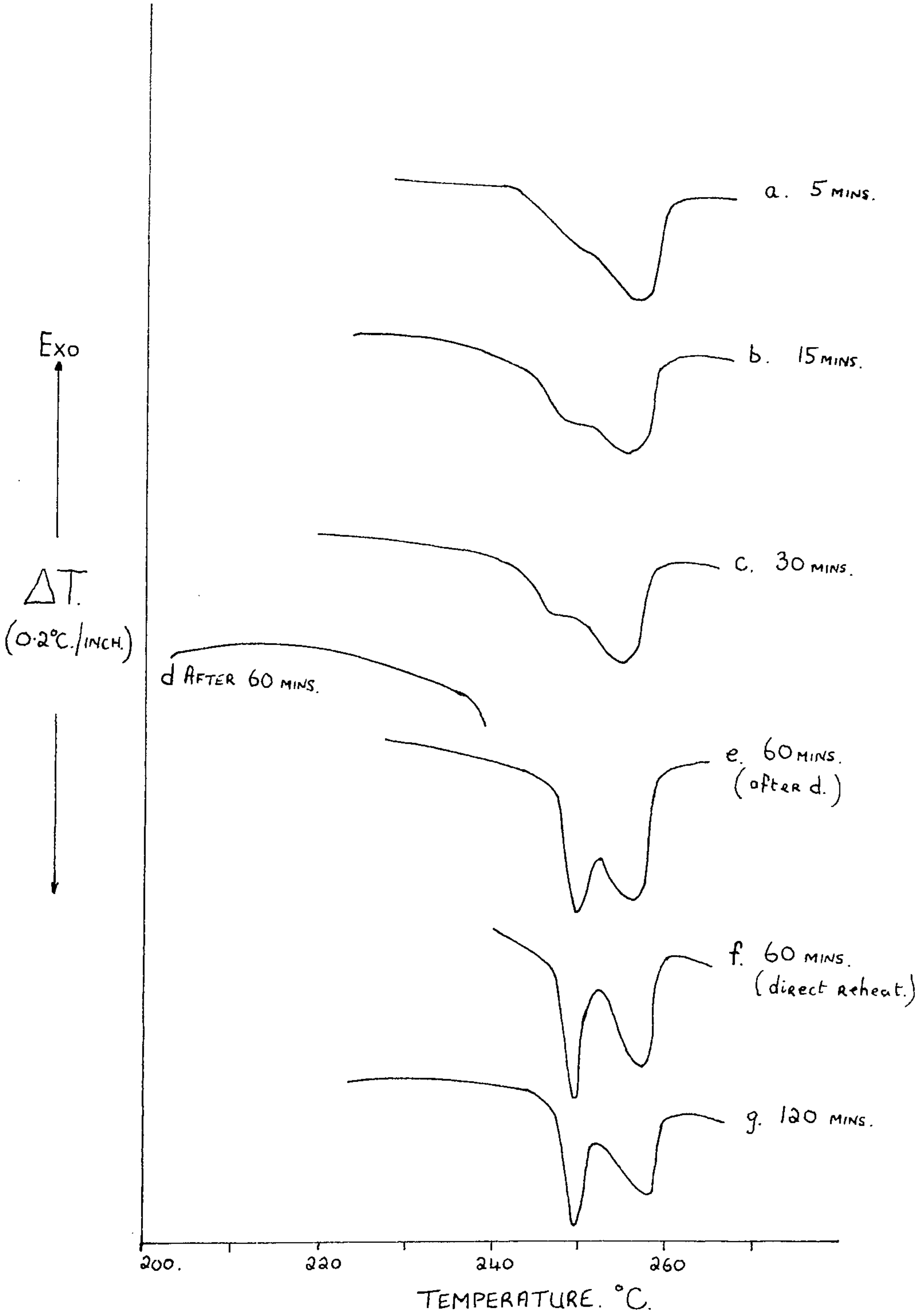


Diagram 22. The isothermal crystallization of molten 66 Nylon at 240°C.

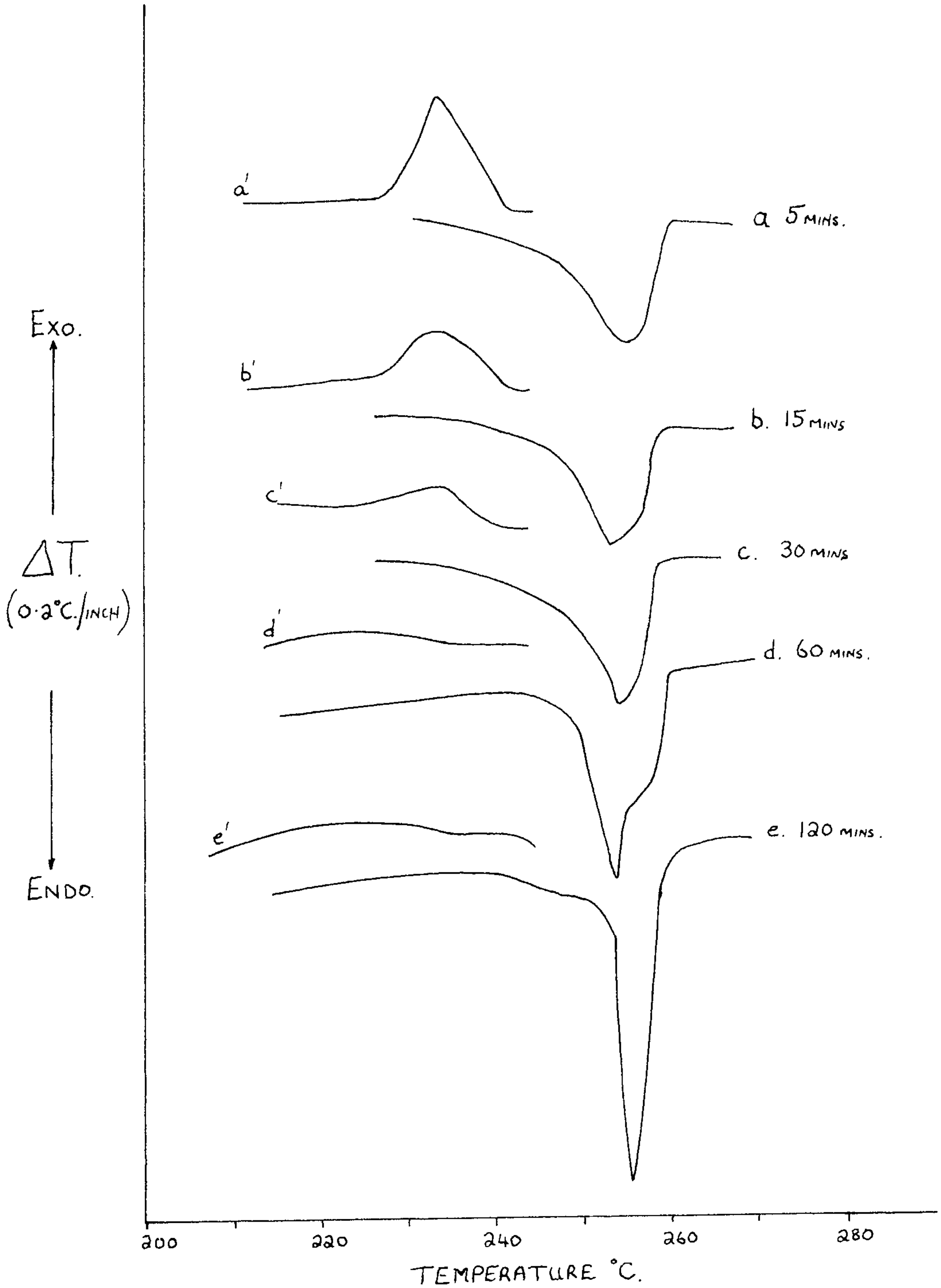


Diagram 23. The isothermal crystallization of molten 66 Nylon at 245°C.
a' is the crystallization thermogram after 5 mins. at 245°C., prior to the melting thermogram a, etc.

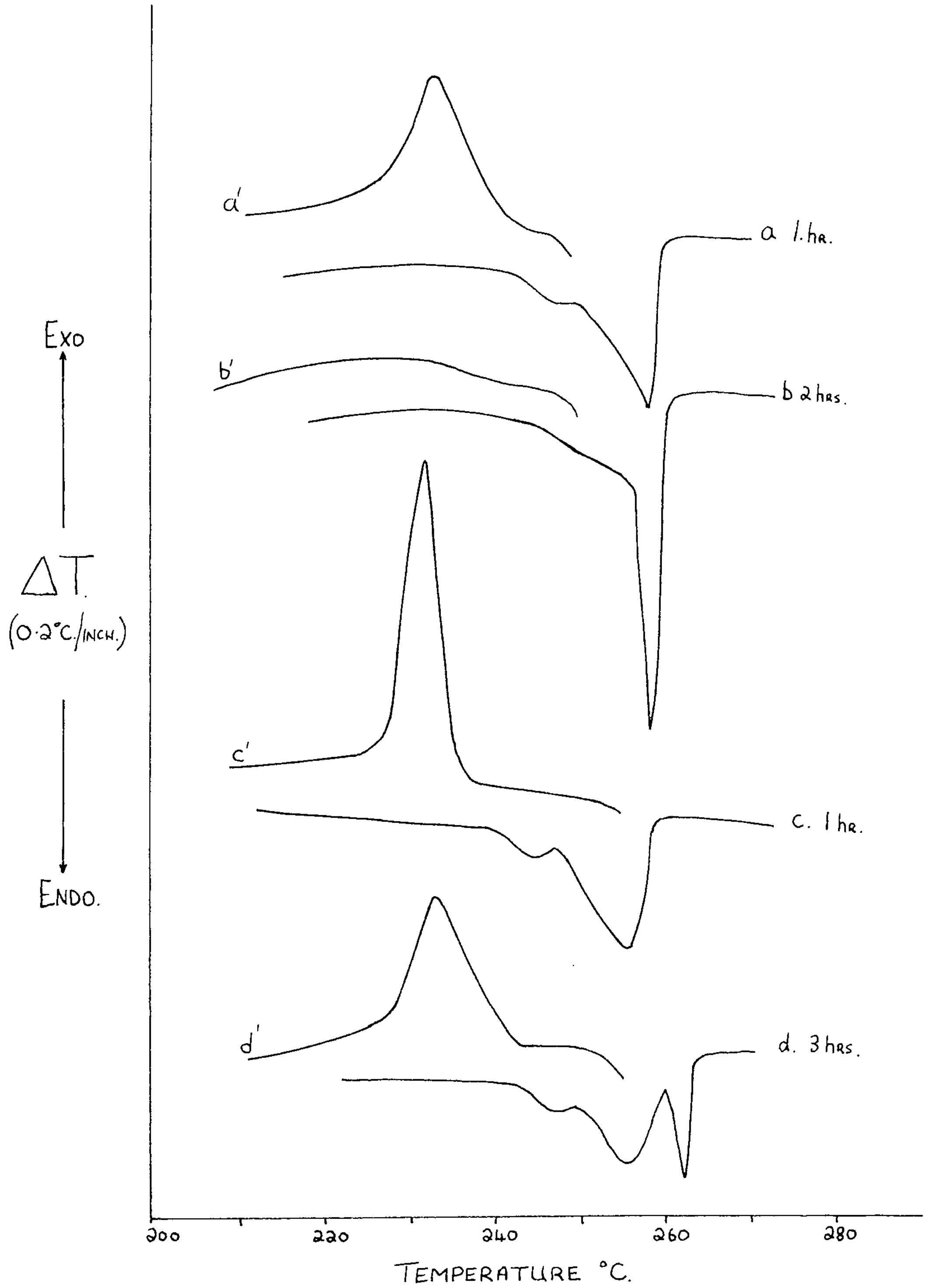


Diagram 24. The isothermal crystallization of molten 66 Nylon at 250°C.(a,b,) and 255°C.(c, d,) a' is the crystallization thermogram after 1 hrs. at 250°C. prior to the melting thermogram a., etc.

5:1:6 THE ANNEALING OF 66 NYLON.

The thermograms of 66 nylon polymer, melt crystallized at 242°C., showed that the primary crystallization process was complete within 10 minutes at this temperature. However, they also showed that the development of two melting endotherms still continued when the samples were held for longer than 10 minutes at 242°C. Some secondary process, such as annealing, must have occurred after the crystallization was complete. The following experiments were performed to determine whether annealing was the probable cause of this behaviour.

Ground polymer was annealed for varying periods of time at 242°C. in the D.T.A. apparatus, prior to melting. Diagram 25 (page 81) shows the thermograms of samples which had been annealed for $\frac{1}{2}$, 1, 2, 4 and 8 hours, prior to melting.

Unannealed polymer chip gave a single melting endotherm at 259°C. (Diagram 15 page 64). On annealing, a new lower temperature melting endotherm appeared, at 247°C. which increased in size as the annealing time increased. After a sufficiently long annealing time, only a single melting endotherm remained at 254°C.

Annealing ground polymer at temperatures other than 242°C. produced similar results. At temperatures below 242°C. longer annealing times were required to obtain comparable results. At temperatures above 242°C. the annealing process occurred far more rapidly. The results of these experiments are given in Table 5:6 (page 82).

These results showed that the annealing of 66 nylon giving rise to two melting endotherms occurred at temperatures other than 242°C. The rate for formation of the new low temperature endotherm was dependent on the annealing temperature up to 248°C. Above 248°C. the phenomenon causing the first melting endotherm was apparently thermally unstable and the first endotherm was not observed.

Since 66 nylon is a condensation polymer, it is feasible that during the annealing process, the molecular weight might change due to some further thermal polymerisation or re-equilibration process. The results of annealing samples of different initial molecular weights at 242°C. for different lengths of time, are given in Table 5:7 (page 84).

66 nylon film was annealed in a silicone oil bath at 240°-242°C.

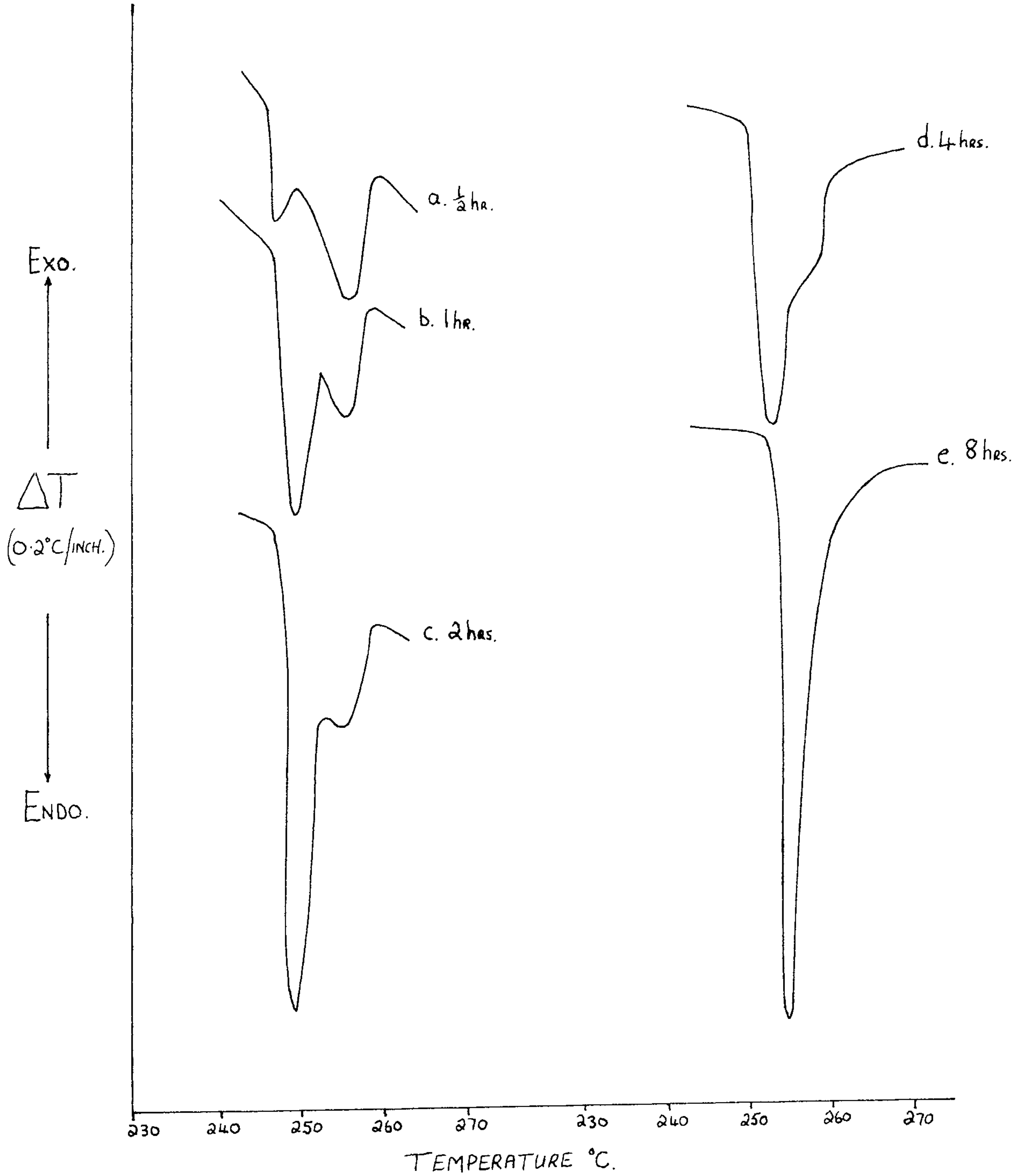


Diagram 25. The annealing of ground 66 Nylon chip for various times at 242°C.

TABLE 5:6 ANNEALING OF 66 NYLON AT TEMPERATURES OTHER THAN 242°C.

Annealing temperature (°C.)	Annealing time (hrs.)	Temperature 1st Peak (°C.)	Temperature 2nd Peak (°C.)	Comments
220	2	—	257	Slight shoulder 252°
220	4	242	257	
230	2	243	256)	Similar to Diagram
230	4	247	257)	25a. and b.(page 81)
246	1	—	254	Sharp
248	10 mins.	255	258)	2nd Peak only a
248	0.25	253	257)	shoulder.
248	0.5	—	254	Sharp
248	1	—	254	—"—
250	1	—	259	—"—
250	2	—	257	—"—
254	1	—	259	Slight shoulder 258°

using the technique described in 3:2, so that changes in other properties such as density could be determined. After annealing, it was removed from the apparatus and carefully wiped free of silicone oil. Infra red spectra were obtained of the film samples before and after the annealing process, using a Perkin Elmer 225 Infra Red Spectrophotometer. The attenuated total reflection technique was used since the films were too thick to obtain satisfactory transmission spectra. The spectrum of the film did not appear to have changed as a result of the annealing process.

The characteristic strong absorption of silicone compounds at 1260 cms.$^{-1}$ was absent in the annealed samples. This showed that the silicone oil was not reacting with or pentrating the 66 nylon even after 18 hours at 242°C.

The resulting thermograms of film annealed for ½, 1, 2, 4, and 18 hours in silicone oil were very similar to those for annealed ground polymer chip shown in diagram 25 (page 81).

66 nylon bristle was annealed at 240°-242°C., in both the Du Pont instrument and in a silicone oil bath, to discover whether the double melting endotherm produced by annealing, depended on the method of annealing used. After equivalent experiments, the temperatures of the two melting endotherms were identical, independent of the annealing method used.

As the annealing time increased, the two original endotherms of the bristle at 250°C. and 259°C. reverted to a single sharp peak at 253°-54°C. However, the degree of resolution of the two endotherms was much greater with the bristle samples than that observed with the annealed ground polymer, even after fairly long annealing times. Table 5:8 (page 85) shows the results obtained on melting 66 nylon bristle annealed in an oil bath at 240°-242°C.

Annealing of drawn 66 nylon fibres gave results similar to those observed with bristle. One sample was annealed on a glass former at constant length, in a silicone oil bath at 242°C. for an hour. The resulting melting thermogram only showed a single sharp melting endotherm at 252.5°C. with a slight trace of a second endotherm at 257°C.

When precipitated polymer, having two melting endotherms was annealed at 242°C. in the Du Pont cell, the characteristic change in

TABLE 5:7 THE EFFECT OF CHANGES OF MOLECULAR WEIGHT ON ANNEALING THERMOGRAMS OF 66 NYLON.

No.	Sample	Relative⊕ Viscosity	Annealing Time hrs.	Endotherm 1^{o}C.	Endotherm 2^{o}C.	Comments
1	XP10257	31.7	½	250	258	See diagram 25.
2	(Standard)		1	250	258	" "
3	— " —		2	251	258	" "
4	XP11099	44.3	½	251	258	2nd peak not so well resolved as 7
5	— " —		1	251	257	2nd peak only just resolved
6	— " —		2	253	257	257 peak is slight shoulder
7	XP11099	74.6	½	248	257	Very sharp 1st peak
8	— " —		1	249	257	2nd peak reasonably resolved
9	— " —		2	253	---	Single peak no shoulder

⊕ See 4:1:1 for definition of relative viscosity.

These results show that the annealing of 66 nylon polymer giving rise to two melting endotherms, was independent of any changes in the molecular weight distribution of individual polymer samples.

TABLE 5:8 ANNEALING OF 66 NYLON BRISTLE AT 242°C. IN A SILICONE OIL BATH.

No.	Annealing Time (mins.)	1st Endotherm °C.	2nd Endotherm °C.	3rd Endotherm °C.	Comments
1	0	246	251	259	First endotherm is really only a slight small peak on the low temperature side of the second endotherm.
2	2.5	248	250	258	
3	5	249	251	258	
4	15	249	251	259	
5	30	251	253	259	
6	45	250.5	252	258	
7	60	250.5	252	259	
8	120	—	252	259	3rd endotherm is very small.

The second endotherm becomes the major one, as the annealing time increased, whilst the third simultaneously decreased.

the melting endotherms occurred. After 6 hours annealing at 242°C., the first endotherm had sharpened considerably, increased in size and its temperature risen from 249°C. to 253°C. The second endotherm remained at 259°C. but had considerably decreased in size.

5:1:7 THE ANNEALING OF SAMPLES OF KNOWN MORPHOLOGY.

Experiments were carried out on 66 nylon samples of known morphology to discover whether annealing altered this morphology. It was hoped that any change which occurred in a thermogram as a result of the annealing would also be detected as a morphological change.

Samples of films of 66 nylon containing 95-100% of either fibrous birefringent, or negative spherulites, prepared on a hot stage microscope (see 3:5) were annealed at 242°C. for 1 hour in the D.T.A. apparatus, prior to melting. The resulting thermograms a and b respectively are shown in diagram 19, (page 72), together with the melting traces prior to the annealing experiment (see 5:1:4b).

Samples containing the fibrous birefringent spherulites were also annealed at 242°C. for 1 hour on the hot stage microscope. Photographs were taken at 5 minute intervals throughout the annealing period to record any slight morphological changes that occurred. No differences were observed between any of the photographs taken throughout the annealing period.

A similar experiment, using a film sample which had been prepared initially by treating the film at 270°C. for 10 minutes and then allowing it to cool to room temperature was carried out. This sample now had approximately the same thermal history as a sample being annealed in the D.T.A. cell. The film consisted of a mass of small positive spherulites, giving the film a granular appearance between crossed polaroids. Again photographs were taken during the annealing but no changes could be detected. A similar film sample was also annealed for 4 hours at 242°C. on the hot stage microscope. Again no differences were detected in photographs taken before and after the annealing process.

Subsequent thermograms of these samples annealed on the hot stage microscope for 1 hour at 242°C. showed that their melting endotherms were similar to similar samples annealed directly in the D.T.A. apparatus. The endotherms occurred at 247°, 257°, 264°C. and 246°, 258°C. for the fibrous birefringent, and the granular positive spherulites, respectively.

The thermogram of the sample annealed for 4 hours at 242°C. contained two well resolved melting endotherms at 252° and 264°C. respectively. The endotherm at 264°C. was the larger one of the two.

These results show that the changes which occur in the D.T.A. melting thermograms of samples of known morphology as a result of annealing could not be related to any visible morphological changes.

5:2 THE PRECIPITATION OF 66 NYLON FROM SOLUTION.

5:2:1 PRECIPITATION INTO EXCESS NON SOLVENT.

The thermograms of all the samples precipitated by the addition of a formic acid solution of the polymer to methanol or methanol/water mixtures, showed a single broad melting endotherm, similar to that of the original polymer. (See Diagram 26,a, page 88).

5:2:2 PRECIPITATION BY THE ADDITION OF THE MINIMUM QUANTITY OF NON SOLVENT TO THE POLYMER SOLUTION.

Samples were precipitated by the method of Haslam and Willis (142) (see 3:3). Their melting thermograms all contained two endotherms at 250°C. and 260°C. (See Diagram 26,b, page 88).

Water was added to the supernatant liquid remaining from the above precipitations. In only one instance was any further polymer recovered. (3:3) A thermogram of this sample only contained a single melting endotherm, similar to that of the original chip.

Visual observation of the melting of the precipitated samples which had two melting endotherms, showed that no obvious melting occurred until about 258°C. although a slight shrinkage of the sample might occur before this temperature was reached.

5:2:3 PRECIPITATION FROM HOT BENZYL ALCOHOL SOLUTIONS.

Samples precipitated from these solutions have different melting endotherms, depending on whether precipitation occurred from a freshly prepared solution, or from one that had been allowed to cool and was reheated until a homogeneous solution was again obtained.

The results are given in the form of two tables, 5:9a and 5:9b. Table 5:9a., lists results obtained from freshly prepared solutions, table 5:9b., from reheated solutions. (see pages 89 and 90).

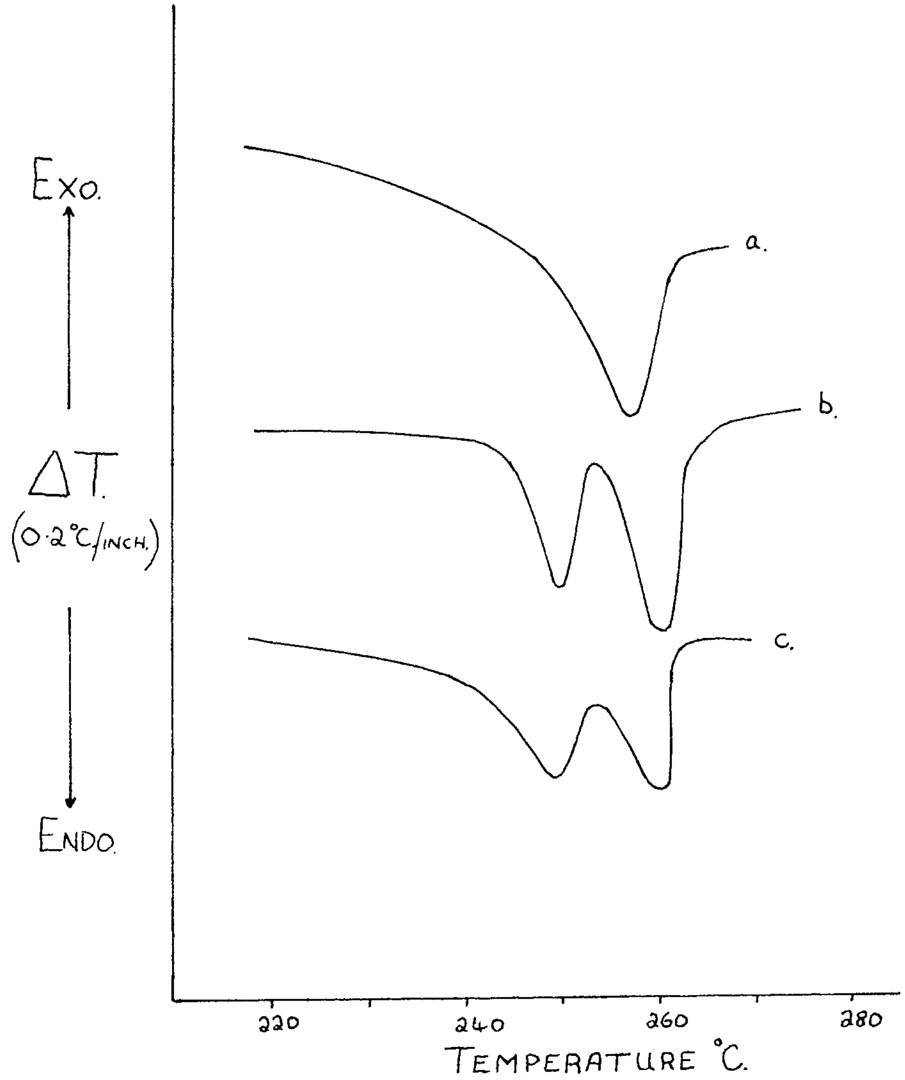


Diagram 26. Melting thermograms of precipitated 66 Nylon.

Precipitation methods as follows :-
a), Addition of a formic acid soln. to excess stirred methanol.
b), Addition of the minimum quantity of methanol to start precipitation to a formic acid soln..
c), Cooling a hot 2·0% benzyl alcohol soln..

TABLE 5:9a. PRECIPITATION FROM FRESHLY PREPARED HOT BENZYL ALCOHOL SOLUTIONS. (A AND B, REFER TO DIFFERENT SOLNS.)

CRYSTALLIZATION CONDITIONS	SOLN. CONC.	ENDOTHERM 1(°C.)	ENDOTHERM 2(°C.)	COMMENTS
Natural cool	2.0%A	245	257	1st ≃ 2nd
100°C/1 hr.	2.0%A	247	258	-"-
120°C/1 hr.	2.0%A	247	258	-"-
130°C/1 hr.	2.0%B	247	258	1st ∠ 2nd not so well resolved.
130°C/3 hrs.	2.0%B	249	258	1st ∠ 2nd resolution reasonable.

Precipitation from freshly prepared benzyl alcohol solutions always resulted in samples with two melting endotherms, independent of the precipitation temperature.

TABLE 5:9b PRECIPITATION FROM REHEATED BENZYL ALCOHOL SOLUTIONS.

CRYSTALLIZATION CONDITIONS.	SOLN. CONC.	REHEAT TEMP. °C.	ENDOTHERM 1(°C.)	ENDOTHERM 2(°C.)	COMMENTS
Natural cool.	2.0%	147	249	258	1st < 2nd Broad, poorly resolved 1st
-"-	-"-	170	247	257	
100°C/ 1 hr.	-"-	---	248	258	1st slightly smaller.
120°C/ 1 hr.	-"-	---	249	258	1st < 2nd, poorly resolved 1st.
130°C/ 1 hr.	-"-	---	---	259	
130°C/ 3 hrs.	3.0%	---	---	257	
130°C/ 3 hrs.	2.0%	---	246-47	257	1st < 2nd poor trace.
130°C/ 3 hrs.	-"-	---	---	258	Broad single peaks
130°C/ 3 hrs.	-"-	147	---	258	
130°C/ 3 hrs.	-"-	170	---	257	

These results show that the temperature to which the benzyl alcohol solutions were reheated to redissolve the 66 nylon, had no effect on its subsequent melting thermogram. Reprecipitation at 130°C., after reheating the benzyl alcohol solution, however, resulted in samples which had only a single melting endotherm.

Diagram 26,c, (page 88) shows a thermogram of a 66 nylon sample, precipitated from benzyl alcohol solution, which has two melting endotherms.

Natural cooling of the benzyl alcohol solutions from 170°C. to 55°C. took 25 minutes and the polymer first appeared to precipitate at 77°-80°C., after about 10 minutes. At the other temperatures, precipitation started at the earliest, 15 to 20 minutes after the sample was placed in the silicone oil bath, and appeared to be completed, sometime within 35 and 60 minutes.

Samples of 66 nylon were suspended in benzyl alcohol and silicone oil respectively, for two hours at 100°C., to discover whether the presence of benzyl alcohol aided any degradation or annealing process during a prolonged precipitation.

They were then filtered and washed free from benzyl alcohol or silicone oil with either acetone or benzene respectively using previously described techniques (3:3) before finally drying.

The subsequent melting thermograms were identical, each with a single broad endotherm at 259°C., with a very slight shoulder at 256°C. This shoulder was not characteristic of annealing having occurred during the experiment. At these temperatures, if any annealing had occurred, a small endotherm at a lower temperature than 256°C. would have been expected.

5:3 DENSITY MEASUREMENTS ON 66 NYLON SAMPLES.

The density of various 66 nylon samples were determined using a density gradient column (3:4). The columns, once prepared, remained stable for several weeks. Typical calibration figures, and a calibration graph are given on page 92, diagram 27.

The densities of various forms of 66 nylon are given below.

Sample	Density (g./ml.)
Drawn Yarn (30/10 denier)	1.1448
Polymer Chip	1.1406-1.1420
Bristle (0.010")	1.1476
Film (unorientated)	1.1448-1.1470
Precipitated Polymer(single melting endotherm)	1.1478-1.1520
-"- (double melting endotherm)	1.1780

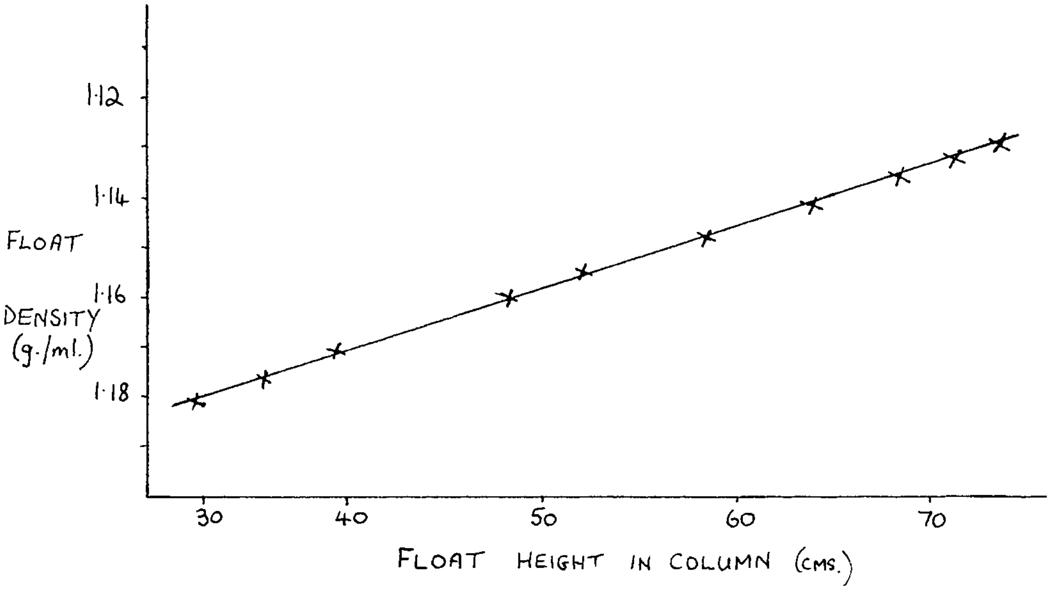


Diagram 27. Density Column Calibration.

density (g./ml.)	height (cms.)
1·1800	29·95
1·1760	32·95
1·1714	36·55
1·1600	45·15
1·1558	49·20
1·1478	55·30
1·1411	60·90
1·1355	65·40
1·1322	68·00
1·1272	71·25

All the 66 nylon samples which have double melting endotherms have higher densities, than those with only a single one. Density is normally taken as a measure of crystallinity and therefore samples with double melting endotherms were likely to be more crystalline than those without.

The change in density that occurred on the annealing of 66 nylon film and bristle at 242°C. in a silicone oil bath is shown in diagrams 28 and 29, respectively. (Page 94). As the annealing time increased, the density increased, indicating a corresponding increase in crystallinity.

Diagram 28 (page 94) also shows the increase in temperature of the first melting endotherm as the film was annealed for increasing lengths of time at 242°C. Table 5:8 (page 85) gives the corresponding temperature increases for annealed 66 nylon bristle.

5:4 QUANTITATIVE MEASUREMENTS OF THE ANNEALING AND MELTING OF 66 NYLON POLYMER.

Experiments were performed to obtain quantitative data about the changes that occurred in the thermograms of 66 nylon as a result of various thermal treatments, as already observed by the normal D.T.A. techniques.

5:4:1 USING THE DU PONT STANDARD D.T.A. CELL.

A large number of experiments were carried out using 90 cms. of 30 denier, 10 filament drawn 66 nylon yarn (0.003 g.) under as near identical operating conditions as possible. By measuring the areas of the melting peaks in the thermograms, it should have been possible to obtain some quantitative data on the two melting endotherms.

A base line was drawn across the two melting endotherms. The peak area was carefully traced onto paper of a known mass/unit area, cut out and weighed. Table 5:10 (page 95) gives typical results obtained.

5:4:2 USING THE DU PONT CALORIMETER CELL. (SEE 3:1:4 FOR A DESCRIPTION OF THE APPARATUS.

5:4:2A CALIBRATION.

It was necessary to calibrate the calorimeter cell. As the cell's temperature increased, so did the heat transfer coefficient between the sample holder and the remainder of the cell. Therefore the the calibration coefficient E (see eqn. 5:4:1) which includes the

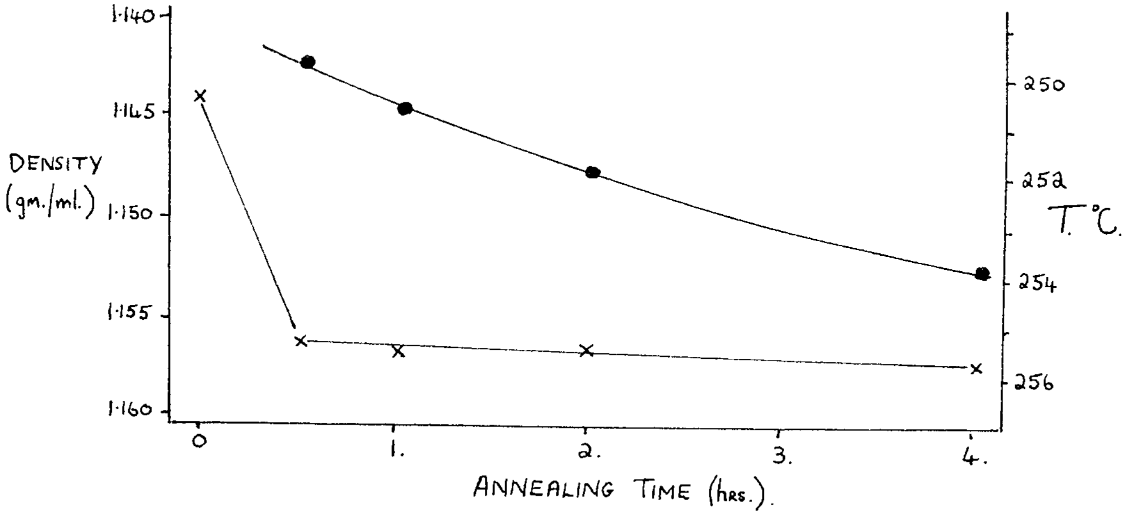


Diagram 28. The increase in the density(×) and also in the temperature of the first melting endotherm(•), on the annealing of 66 Nylon film at 242°C.

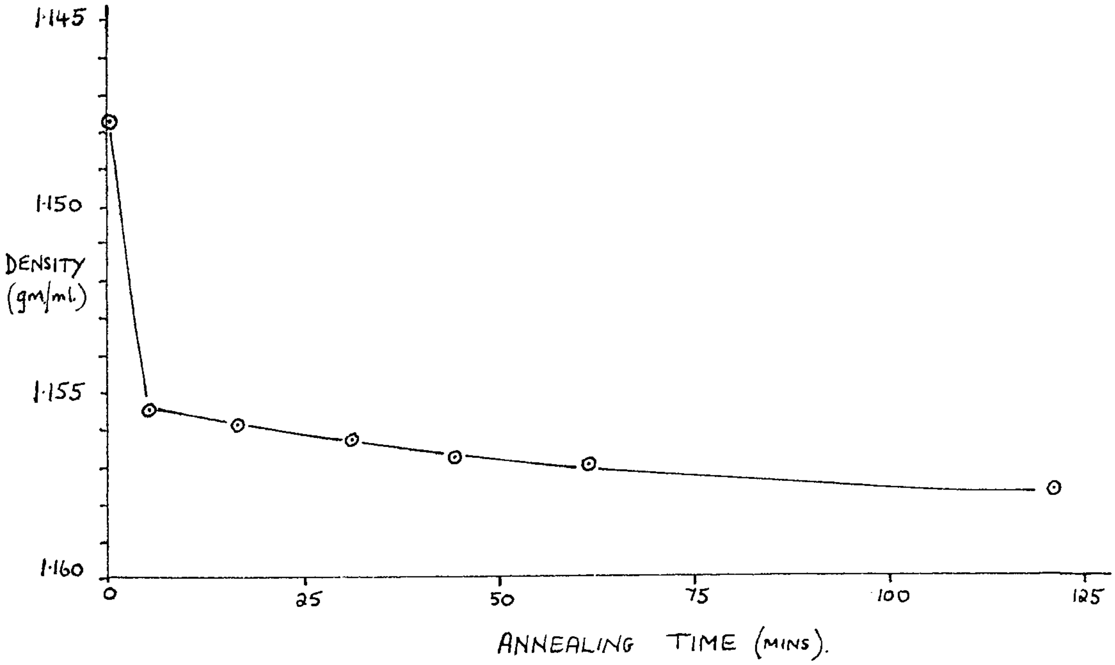


Diagram 29. The increase in density of 66 Nylon bristle after annealing for various times at 242°C.

TABLE 5:10 THE AREA OF THE TWO MELTING ENDOTHERMS OF DRAWN 66 NYLON YARN, WHEN SAMPLES OF IDENTICAL WEIGHT WERE HEATED UNDER IDENTICAL CONDITIONS, (30°C./MIN TO 200°C; 5°C./MIN THEREAFTER.) IN THE DU PONT STANDARD D.T.A. CELL.

Total Peak Area. ins.^{2}	Area of 1st Peak. A_1 ins.^{2}	Area of 2nd Peak. A_2 ins.^{2}	A_1/A_2
0.96	0.71	0.25	2.84
0.92	0.71	0.21	3.38
0.95	0.81	0.14	5.77
0.87	0.57	0.30	1.9
0.83	0.69	0.15	4.6
0.88	0.70	0.17	4.1
0.84	0.69	0.14	4.9

The mean total peak area of these experiments was 0.89 ins.^{2} ± 5.4% (stdn. devn.). These errors were thought to be rather too high to give useful results and the method was abandoned.

value of the heat transfer coefficient, also varied with temperature.

Pure metals, such as Gallium, Indium, Tin, Zinc and Aluminium were used to calibrate the cell. They are obtainable in high states of purity and have known heats of fusion and melting points. Using the results obtained from these standards, (supplied by Du Pont with the cell) it was possible to obtain a graph of the calibration coefficient against temperature for given operating conditions. From this graph, the calibration coefficient could be obtained for any temperature, provided the cell was operated under similar conditions to those in which the calibration standards were run.

Equation 5:4:1 relates the heat of fusion of the sample to the peak area when using the X-Y recorder of the Du Pont instrument. (114)

$$\Delta H_f = \frac{E.\ A\ \Delta T_s\ .T_s}{Ma} \qquad \text{Eqn.5:4:1}$$

ΔH_f = Heat of fusion (m. cals./g.)

E = Calibration Coefficient (m.cals./°C.min.)

A = Peak area (ins.^{2}.)

ΔT_s = Y axis sensitivity (°C./in.)

T_s = X axis sensitivity (°C./in.)

M = Sample weight (mg.)

a = Heating rate (°C./min.)

The peak areas were measured with an Ott polar planimeter (type 17). The following gives four different planimeter readings on the same melting endotherm of Bismuth; 9.67; 9.64; 9.67; 9.63 ins^2. The mean peak area was 9.65 ± 0.02 ins^2.; ie. an error of ± 0.3%. This was typical of the results obtained. Readings were taken until at least three consecutive readings differed by less than ± 0.5%.

Table 5:11 (page 97) gives the values of the calibration coefficient calculated using eqn. 5:4:1; a heating rate of 10°C./min.; before the cell was modified.

It was thought that by using a time base recorder instead of the Du Pont X-Y recorder, it might be possible to reduce the errors in area measurement shown in Table 5:11 (page 97). A time base recorder,

TABLE 5:11 CALIBRATION COEFFICIENTS OBTAINED USING THE X-Y RECORDER.

Metal.	Mpt.°C.	ΔH_f (Cals/g.)	Sample wt. (mg.)	Area (in^2) ⊗		E(m.cals/°C min.)	
				min	max	min	max
Ga	29.8	19.9	5.9	1.55	1.61	37.9	36.5
In	156	6.79	14.1	0.84	0.85	57.0	56.3
Sn	232	14.2	6.9	1.63	1.66	60.1	59.2
Zn	419	27.0	7.3	0.73	0.74	108.0	106.0
Al	660	95.3	6.1	0.77	0.84	150.0	138.0

ΔT, for Ga, and Al = 1°C./in. for, In, Sn, Zn = 0.5°C./in.

⊗ These maximum and minimun values for the peak area refer to the same peak in a thermogram. They arose because it was possible to draw more than one baseline across the same endotherm. Therefore it was possible to obtain more than one value for the area of a given endotherm.

The error in the value of E ranged from ± 0.5% for Indium to ± 6.7% for Aluminium.

by increasing the peak area would minimise the error in drawing the correct baseline for an endotherm.

Calibration standards were also sought whose thermal characteristics and melting points were nearer those of 66 nylon. Pure materials of known heats of fusion with these requirements are relatively few and were not readily obtainable. Unfortunately, many seemingly suitable organic compounds, ie, p. nitro-benzoic acid, sublime rapidly above their melting points, which render them useless. Silver nitrate, (mpt,221°C.; ΔH_f 16.24 cals./ g.) and Bismuth (mpt. 271°C.; ΔH_f 12.59 cals./g.) (146) were used as calibration standards. Silver nitrate was subsequently abandoned, since it was suspected that it attacked the sample liners.

The equation relating the peak area and the heat of fusion when using an external time base recorder is given by:- (114)

$$\Delta H_f = \frac{E\ A\ \Delta T_s}{MC} \qquad \text{———— eqn.5:4:2}$$

where C equals the chart rate in ins./min., and the other symbols remain as equation 5:4:1. When samples are run under identical operating conditions, the value of the peak area/unit weight was useful for purely comparative purposes since it can be assumed that ΔH_f, E, ΔT_s and C remain effectively constant.

Calibration Coefficients (E values) were determined for Indium, Silver Nitrate and Bismuth from equation 5:4:2 using the Bristol 6 Channel Multipoint recorder, after the Calorimeter cell had been modified (see 3:1:4). The E values obtained were the averages of several determinations on samples of differing weights. They were respectively 64.98 ± 2.5%; 78.64 ± 6.0%; and 81.33 ± 1.0%. The changes in sample weight did not effect the E value in any consistent manner.

Because of the sharp melting range of the calibration standards, it was possible to draw a reasonable curve through the recorder trace. However, when 66 nylon was used, it was not so obvious where to draw the mean curve through the more scattered points. Therefore, this recorder was abandoned.

A comparison of the peak area/mg. of samples of Indium determined under identical conditions with both the Bristol "Multipoint" and "Vitatron" recorder showed no change in the total percentage error between successive determinations. (2.5-3.0%).

However, when the "Vitatron" recorder was used and the same peak area measured, a), by using the built-in integrator and b), the Ott planimeter, and the results compared, it was found that the integrator areas were between 10 and 15% greater than the planimeter areas. (See Table 5:12, page 100).

Finally, a Bristol single pen recorder was used and more satisfactory results were obtained.

The effect of varying the heating rate on the peak area of the same sample of Bismuth (11.7 mg.) are given in table 5:13 (page 100). These show, that even with the same sample, differences in peak area occur. These could not be readily related to changes in heating rate.

The results of all the calibration experiments using the Bristol single pen recorder and Bismuth as the calibration standard are given in table 5:14 (page 101). They serve to show the wide variations obtained for the calibration coefficient of the same metal standard. The mean melting E value of these experiments was 78.43 ± 3.8%.. Without a considerable amount of further work it seemsed unlikely that it would be possible to reduce the % error much below ± 4.0%.

5:4:2B MEASUREMENTS ON 66 NYLON SAMPLES.

The initial experiments utilised the X-Y recorder, and were used to determine the best sample sizes and heating rates to obtain satisfactory traces. 66 nylon yarn was used and it proved difficult to satisfactorily insert a sufficient quantity of yarn into a sample liner. Samples were found to be severely degraded at the end of an experiment and as a result the cell was slightly modified (see 3:1:4) It was necessary to use heating rates of 2.5°C./min. or less to obtain adequate endotherm resolution, but complete resolution into individual peaks was never achieved. On account of the degradation, no attempt was made to obtain quantitative data from these experiments.

Some quantitative data on the melting and annealing of 66 nylon chip at 242°C., was obtained using the modified calorimeter cell and the "Vitatron" integrating recorder. The modifications to the cell had overcome the problem of sample degradation. Analysis of the results,

TABLE 5:12 COMPARISON OF PEAK AREAS OBTAINED FROM THE "VITATRON" RECORDER INTEGRATOR AND AN OTT PLANIMETER.

Sample	Wt.(mg.)	Integrator Area cms.^{2}.	Planimeter area ins^2	Planimeter area cms^2	Ratio Integrator /Planimeter.
Indium	14.6	14.57	2.04	13.16	1.11
		14.37	2.09	13.48	1.067
	21.4	21.66	3.05	19.66	1.10
		21.74	3.15	20.35	1.07
Bismuth	15.7	22.05	3.24	20.87	1.06
		21.42	3.16	20.40	1.05
	29.7	18.1	2.49	16.05	1.13
		18.58	2.61	16.83	1.10

These results show that the integrator and planimeter measurements of identical endotherms did not agree with each other.

TABLE 5:13 THE VARIATION OF THE PEAK AREA AND E VALUE FOR THE SAME SAMPLE OF BISMUTH (11.7 mg.) WHEN THE HEATING RATE WAS VARIED.

Run no.	ΔT	Heating Rate nominal	Heating Rate actual	Mean Peak Area ins.^{2}	E Value (m.cals/$^\circ$C.min.)
1	0.5	10	10.30	4.24	69.49
2	0.5	8	8.00	4.26	69.16
3	0.5	6	5.79	4.02	73.28
4	0.5	5	4.59	4.26	69.16
5	0.5	4	3.53	4.20	70.15
6	0.5	2	1.16	4.33	68.03
7	0.2	2	1.16	10.14	72.63
8	0.5	2	1.19	3.76	78.34

(Mean E value 71.27 ± 3.33, ie. ± 4.67%)

Run No. 6 and 7; ΔT ratio = 2.5:1; Peak area ratio = 2.34:1

TABLE 5:14 PEAK AREAS AND CALIBRATION COEFFICIENTS (E VALUES) OBTAINED USING BISMUTH AS THE CALIBRATION STANDARD.

Exp. No.	Wt. mg.	ΔT °C/in.	Heating rate(A)	Heating rate(A)	No. of runs	Mean peak area (B)	Stdn. Devn. ±	% Error ±	Mean E Value (C)
1	11.9	0.5	5	—	5	4.24	0.03	0.6	70.66
2	11.9	0.2	2	—	4	9.7	0.51	5.25	77.66
3	18.0	0.5	2	1.28	5	5.99	0.20	3.28	75.78
4	11.7	0.5	10→2 (D)	10.3 → 1.16	7	4.15	0.20	4.77	71.27
5	11.7	0.5	3	2.30	5	3.79	0.11	2.9	77.93
6	11.7	0.2	3	2.33	6	9.82	0.25	2.55	74.94
7	11.7	0.5	3	2.50	4	3.87	0.03	0.78	76.12
				—— " ——					
8	11.7	0.5	(F)	5.74	4	4.45	0.1	2.25	66.21

A = °C./min.
B = in.^{2}
C = m.cals./°C.min.
D = See Table 5:13. (page 100).
F = Crystallization.

N.B. Exp.5 and 6; ΔT ratio = 2.5:1
Peak area ratio = 2.59:1

The mean melting calibration coefficient (E value) = 74.83. m.cals/°C min. ± 3.8%.

obtained using the integrator in terms of peak area/mg. of sample, showed errors of 10-15% between similar determinations and led to the discovery of a faulty integrator mechanism. (See 5:4:2A).

The quantitative data obtained using the Bristol single pen recorder, in a 5 psi. nitrogen atmosphere are given in tables 5:15 - 5:18 (pages104/7). Tables 5:15 and 5:16 (pages104/5) refer to determinations of melting and crystallization obtained from a single 66 nylon chip, whereas table 5:17 and 5:18 (pages106/7) give similar figures for different samples.

The heats of fusion (H_f) and crystallization (H_c) of the samples after the various annealing experiments were calculated using equation 5:4:2. The values of the calibration coefficients used in the equation were 74.83 cals./g. for melting and 66.21 cals./g. for crystallization. These values were those obtained using Bismuth as the calibration standard. The melting points of Bismuth and 66 nylon were sufficiently similar to warrant using them directly, especially in view of the errors in the calibration coefficients themselves.

The percentage crystallinity of the samples was then obtained as follows. The heat of fusion for a sample of 100% crystalline 66 nylon was quoted by Inoue, (84) as 46.8 calories/g. The experimentally calculated value of the heat of fusion of the samples was expressed as a percentage of this value.

The "Annealing Time" column in the subsequent tables 5:15 to 5:20 (pages104, 105, 106, 107, 110, 111,) refers to the actual time of annealing. The results refer therefore to the subsequent melting of the sample after it had been cooled to $< 100^\circ$C. for the melting experiments. The crystallization results refer to the crystallization of the sample after it had been annealed for the given time, remelted and held isothermally in the molten state for ten minutes at 285°C.

"T_1" and "T_2" are the temperatures of the first and second melting endotherms respectively. "Ta" is the total area of the melting endotherms and "A_1", and "A_2" were the areas of the first and second endotherms respectively. Since the two endotherms were never completely resolved into separate entities, "A_1" and "A_2" were obtained by a certain amount of reasonable extrapolation of the individual endotherms to the base line. (See diagram 30, page 103).

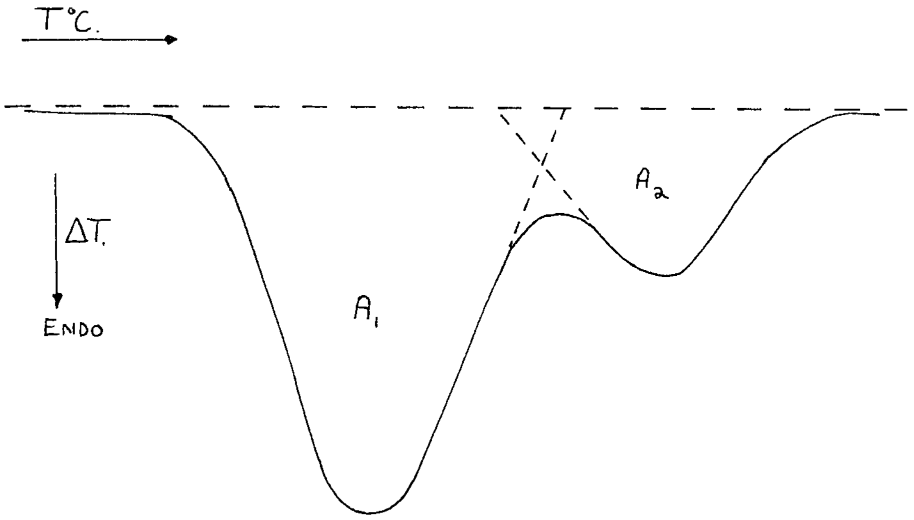


Diagram 30. The sketch shows the method of extrapolating the areas of the two melting endotherms of 66 Nylon after a quantitative annealing experiment.

TABLE 5:15 THE HEATS OF FUSION (H_f) AND THE PERCENTAGE CRYSTALLINITY OF A SINGLE SAMPLE OF 66 NYLON CHIP ANNEALED FOR VARIOUS TIMES AT 242°C.

Annealing Time, hrs.	T_1 * °C	T_2 * °C	T_a * ins^2	A_1 * ins^2	A_2 * ins^2	A_1/T_a %	A_2/T_a %	H_f cals /g.	% Crystallinity.
0	----	256	11.63	----	----	----	----	14.98	31.6
$\frac{1}{4}$	249	257	13.13	3.63	9.24	27.6	70.4	16.41	35.18
1	251	257	12.79	5.09	7.52	39.8	58.2	16.4	35.06
2	253	259	14.59	6.89	7.82	47.2	53.6	18.8	40.1
4	253	260	14.14	9.54	4.48	67.5	31.7	18.1	38.75
14	----	255	14.32	----	----	----	----	18.3	39.1
$\frac{1}{4}$	246	257	9.53	3.43	6.10	36.0	64.0	12.2	26.1
$\frac{1}{2}$	246	257	9.58	2.66	6.92	27.8	72.2	12.3	26.2

Sample wt. 11.7 mg.; ΔT., 0.2°C./in.

Heating rate (200-285°C.) 2.45 ± 0.04°C./min.

Chart speed 1"/min.

* See page 102 for explanation.

TABLE 5:16 THE HEATS OF CRYSTALLIZATION (H_c) AND THE PERCENTAGE CRYSTALLINITY OF A SINGLE SAMPLE OF 66 NYLON CHIP ANNEALED FOR VARIOUS TIMES AT 242°C.

Annealing time hrs.	Exotherm Temp. °C.	Area ins^2	H_c cals/g.	% Crystallinity
0	238	13.48	15.3	32.6
$\frac{1}{4}$	238	12.25	14.5	31.0
1	238	12.08	13.7	29.2
2	236	11.90	13.5	28.8
4	236	11.50	13.0	27.8
14	236	11.20	12.7	27.1
$\frac{1}{4}$	236	10.90	12.4	26.6
$\frac{1}{2}$	237	10.85	12.3	26.3

Sample wt. 11.7 mg., ΔT, 0.2°C/In.

Cooling rate 4.92 ± 0.04°C./min.

Chart speed 1"/min.

TABLE 5:17 THE HEATS OF FUSION (H_f) AND THE PERCENTAGE CRYSTALLINITY OF DIFFERENT SAMPLES OF 66 NYLON CHIP (ALL WEIGHING 11.7MG.) ANNEALED FOR VARIOUS TIMES AT 242°C.

Annealing time, hrs.	T_a * ins^2.	A_1 * ins^2.	A_2 * ins^2.	A_1/T_a %	A_2/T_a %	H_f cals./g.	% Crystallinity
0	10.92	---	---	---	---	14.0	29.9
1	14.37	4.44	9.92	30.9	69.1	18.4	39.3
Reheat	10.46	1.34	9.12	12.8	87.2	13.9	28.6
0	11.8	---	---	---	---	15.1	32.3
14	14.96	---	---	---	---	19.1	40.9
Reheat	9.22	0.81	8.41	8.8	91.2	11.8	25.2
0	10.29	---	---	---	---	13.2	28.1
$\frac{1}{4}$	9.32	2.32	6.82	24.9	73.2	11.9	25.5
0	12.15	---	---	---	---	15.5	33.2
$\frac{1}{4}$	12.25	3.62	8.58	29.6	70.0	15.7	33.5
2	13.52	6.52	6.95	48.2	51.2	17.3	36.9
$\frac{1}{4}$	10.29	2.75	7.54	26.7	73.3	13.2	28.1

Heating rate (200-285°C.), 2.46 ± 0.07°C./min.

ΔT, 0.2°C./in.

Chart speed 1"/min.

* See page 102 for explanation.

TABLE 5:18 THE HEATS OF CRYSTALLIZATION (H_c) AND THE PERCENTAGE CRYSTALLINITY OF DIFFERENT SAMPLES OF 66 NYLON CHIP (ALL WEIGHING 11.7 MGM.) ANNEALED FOR VARIOUS TIMES AT 242°C.

Annealing time hrs.	Area ins^2.	H_c cals./g.	% Crystallinity
0	11.20	12.7	27.1
1	12.22	13.8	29.5
Reheat	11.81	13.4	28.6
0	11.41	12.9	27.6
14	10.10	11.4	24.4
0	12.18	13.8	29.5
$\frac{1}{4}$	8.62	9.8	20.9
0	12.81	14.5	31.0
$\frac{1}{4}$	11.45	13.0	27.7
2	13.2	15.0	31.9
$\frac{1}{4}$	13.12	14.9	31.7

Cooling rate 4.81 ± 0.3°C/min.

ΔT, 0.2°C/in. Chart speed 1"/min.

The results given in tables 5:15, 16, 17, and 18, pages 104, 105, 106, 107, indicated that the heats of fusion and crystallization, and hence, the percentage crystallinity of the samples were related to the annealing time at 242°C. As the annealing time increased, the percentage crystallinity tended to a maximum of approximately 40%, for a given sample. The changes in the shape of the melting thermograms were more pronounced than the corresponding changes in the percentage crystallinity. (See Diagram 25, page 81 for typical changes in the melting thermograms of 66 nylon as the annealing time at 242°C. was increased.)

The heat of crystallization of a single sample of 66 nylon was dependent on the time the sample had been in the molten state (see table 5:16, page 105). In between each run, the sample had been held at 285°C. for 10 minutes. Therefore, by the time the experiment was finally concluded, the sample had been molten for a total of 80 minutes. This suggested that some process was occurring in the molten state which reduced the amount of crystallizeable material in the sample. After shorter periods in the melt, the changes were usually less pronounced. (see Table 5:18, page 107).

5:4:3 MEASUREMENTS ON 66 NYLON WITH WATER PRESENT IN THE CELL.

It has been shown (149) that the presence of water affects the crystallization of drawn 66 nylon filaments. If a molten filament was cooled rapidly in anhydrous conditions, no characteristic spherulite growth or crystallization behaviour was observed. In the presence of moisture, the normal spherulitic growth and crystallization occurred. When filaments, which had been rapidly cooled in anhydrous conditions, were stored in a desicator no changes occurred. Once, they were exposed to moisture, changes in both the birefringence and X-ray diffraction patterns were observed.

In the previous experiments in the calorimeter cell, moisture would have almost certainly been lost from the polymer, either during the annealing, or in the subsequent melt fusion, since 66 nylon is a condensation polymer. This water would condense on cooler parts of the cell and not be present when crystallization took place. The loss of water would not only affect the mass of polymer used, thus altering the H_f value, since the mass is involved in equation 5:4:2. It could have also affected the sample's crystallization, since this also would be occurring in drier conditions.

An attempt was made to carry out some experiments in the calorimeter, in an inert atmosphere containing water. (see 3:1:5 for further experimental details and description of the apparatus). If moisture did affect any of the experiments, then changes in the heats of fusion might be expected. The results of experiments carried out with water present in the calorimeter cell are given in tables 5:19 and 5:20 (pages 110 and 111). The higher values of the heats of fusion and percentage crystallinity of samples annealed in a water containing atmosphere, compared to those of samples annealed in anhydrous conditions, showed that the presence of water in the cell was influencing the results.

5:5 THE EFFECT OF HEATING SAMPLES OF 66 NYLON WHICH SHOW TWO MELTING ENDOTHERMS TO THE TEMPERATURE BETWEEN THE TWO ENDOTHERMS, COOLING AND REMELTING.

Various samples, which showed two melting endotherms, were heated in the Du Pont Standard D.T.A. cell, to the temperature between the endotherms. Immediately this temperature was reached, heating was stopped, and the sample allowed to cool. Once 200°C. had been reached, remelting was commenced.

Diagram 31 and table 5:21 (pages 112 and 113 respectively) give the results obtained.

Crystallization exotherms were observed after annealed polymer (1 hr. @ 242°C.), drawn yarn, and bristle were heated to the temperature between the two endotherms and then cooled. Under similar conditions, no exotherm was observed for polymer precipitated by adding methanol to a formic acid solution (see 3:3) which also has two melting endotherms. It would appear that the phenomenon responsible for the two melting endotherms in the precipitated polymer was different from that in the other samples.

Visual observation of the melting of drawn yarn (see 5:1:2) has already demonstrated that little visual change occurred in the yarn, until almost the temperature of the second melting endotherm was reached. The material that recrystallizes does not become evident as another endotherm, as might be anticipated, on remelting.

TABLE 5:19 THE HEATS OF FUSION (H_f) AND THE PERCENTAGE CRYSTALLINITY OF 66 NYLON SAMPLES ANNEALED AT 242°C. FOR VARIOUS TIMES, WITH WATER PRESENT IN THE CALORIMETER CELL.

Annealing time hrs.	T_1 * °C.	T_2 * °C.	T_a * ins.^{2}	A_1 * ins.^{2}	A_2 * ins.^{2}	A_1/T_a %	A_2/T_a %	H_f cals./g.	% Crystallinity.
0	—	258	10.17	—	—	—	—	13.0	27.8
½	250	258	11.25	3.58	7.67	31.8	68.2	14.4	30.8
0	—	258	11.31	—	—	—	—	14.5	30.9
½	248	257	11.52	3.20	8.35	27.7	72.5	14.7	31.5
14	—	253	16.52	—	—	—	—	21.1	45.2
½	246	257	10.54	2.92	7.54	27.7	71.5	13.5	28.8

Sample wt. 11.7 mg. ΔT, 0.2°C./in.

Heating rate (200-285°C.) 2.37 ± 0.04°C./min.

Chart speed 1"/min.

Atmosphere 5 psi. water saturated nitrogen.

* See page 102 for explanation.

TABLE 5:20 THE HEATS OF CRYSTALLIZATION (H_c) AND THE PERCENTAGE CRYSTALLINITY OF 66 NYLON SAMPLES ANNEALED AT 242°C. FOR VARIOUS TIMES, WITH WATER PRESENT IN THE CALORIMETER CELL.

Annealing time (hrs.)	Exotherm Temp. °C.	Area ins.^{2}	H_c cals./g.	% Crystallinity
0	238	10.99	12.5	26.6
½	238	11.70	13.2	28.3
0	238	12.98	14.7	31.4
½	238	11.53	13.1	27.9
14	238	12.10	13.7	29.3
½	238	10.82	12.3	26.2

Sample wt. 11.7 mg. ΔT, 0.2°C./in.

Cooling rate 4.86 ± 0.07°C./min.

Chart speed 1"/min.

Atmosphere 5 psi. water saturated nitrogen.

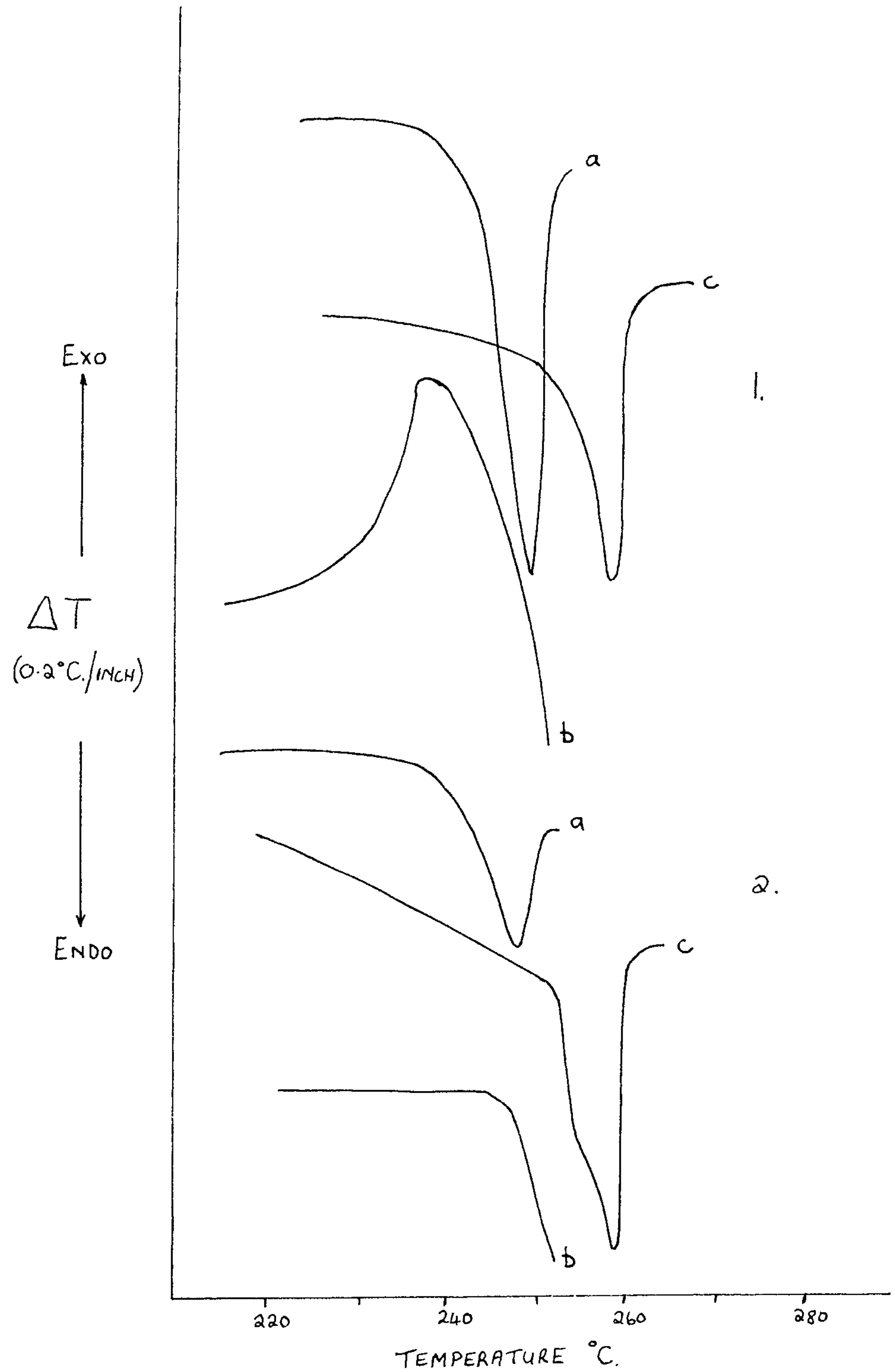


Diagram 31. The heating of samples of 66 Nylon with two melting endotherms to the temperature between the endotherms. 1,drawn yarn or annealed chip, 2,precipitated polymer. a, initial melt b, crystallization c, remelt.

TABLE 5:21 HEATING 66 NYLON SAMPLES WITH 2 MELTING ENDOTHERMS TO THE TEMPERATURE IN BETWEEN THE TWO ENDOTHERMS.

Polymer	1st Peak (Normally) °C.	Heated to °C.	Crystallization Exotherm °C.	Remelt		Comments
				Start °C.	Tip °C.	
Annealed Chip (1 hr. at 242°C.)	252	254	243 (low broad peak)	254	258	Similar to yarn
30/10 yarn (drawn)	249	253	240.5 (large sharpish)	253	257	See Diagram 31 (page 112).
Bristle (0.012" dia.)	251	254	246 (similar yarn)	254	258	Similar to yarn
Ppted (MeOH → HCOOH system)	249	252	———	253	260	Inflexion 256°C See Diagram 31 (page 112).

In all instances, on remelting, the first endotherm was absent and melting did not recommence until the temperature at which the previous heating run had ceased, whether recrystallization had occurred or not.

5:6 DILATOMETRY.

This method of studying the melting, crystallization and annealing of 66 nylon did not yield any further information about the cause of the double melting endotherms.

The samples were carefully dried, and the dilatometers, (based on the design used by Harvey (147)) were then carefully assembled to avoid air or moisture being trapped in them. Despite these precautions, above 200°C., a slow continuous expansion of the mercury occurred. This masked any other volume changes that may have occurred in the sample.

This behaviour was attributed to the presence of moisture either not removed by the drying process, or else arising from further condensation of the type:- (where P = polymer molecule.)

$$P_1 \text{—}NH_2 + HOOC\text{—}P_2 \rightleftharpoons P_1 \text{—}NHOC\text{—}P_2 + H_2O$$

This was confirmed by thermogravimetric analysis in a slow stream of nitrogen, using the Du Pont 950 Thermogravimetric Analyser, with the temperature thermocouple in the "unshielded" position below the sample boat.(148) A sample of 66 nylon lost about 3.0% by wt. up to 150°C., then no further measureable changes took place up to 300°C. During a subsequent 1 hour's annealing at 242°C., a further 0.4% wt. loss occurred.

Approximate calculations, assuming the wt. loss on annealing to be entirely due to water from further condensation showed that it was about 80x greater than the actual increase measured during a corresponding dilatometric annealing experiment at 242°C.

This difference was to be expected, since the thermogravimetric results were obtained in a stream of nitrogen which would aid the forward condensation reaction. In the dilatometer, as the amount of water and hence the pressure increased, the rate of the forward reaction would be retarded.

Without performing a series of experiments to determine if there was a change in the molecular weight of the 66 nylon during annealing, these observations could not be verified. At this point, it was thought that further experiments would not yield more information, and experiments were discontinued.

5:7 THE SHRINKAGE OF DRAWN 66 NYLON BRISTLE ON HEATING.

Samples of 66 nylon bristle were heated to various temperatures across the temperature range of the first melting endotherm, to discover how much shrinkage occurred during this stage of the melting process.

The bristle was cut into short lengths to fit into a Du Pont micro sample tube. One piece was cut so that its length was different from the rest. The length of this piece could then be measured with a travelling microscope, both before and after an experiment. The difference in length between the two readings was expressed as a percentage of the sample's original length. (Table 5:22, page 116).

On cooling, from 246°C., no crystallization exotherm was observed; from 250°C., a small crystallization exotherm occurred at 244°C., and from 254°C., a crystallization exotherm occurred at 245°C., similar to that described in 5:5.

These results show that a large proportion of the observed shrinkage occurs before any actual melting (as shown by the subsequent crystallization exotherm) takes place.

Two samples of bristle were annealed at 242°C. for ½, and 2 hours, respectively, to see whether the annealing process affected the sample shrinkage.

After measuring the sample's length, (as described previously) it was annealed for the desired time at 242°C.; cooled to 100°C., reheated to the temperature between the peaks and then cooled, before remeasuring.

The results are given in table 5:23 (page 116).

In both instances, crystallization exotherms were observed at 244°C., similar to those described in 5:5.

These two results show that annealing did affect the total shrinkage, by reducing it by almost half, but increasing the annealing time caused little further effect.

TABLE 5:22 THE SHRINKAGE OF DRAWN 66 NYLON BRISTLE AFTER IT HAD BEEN HEATED TO DIFFERENT TEMPERATURES WITHIN THE TEMPERATURE RANGE OF THE FIRST MELTING ENDOTHERM.

Temperature to which bristle heated °C.	Original length cms.	Length after heating cms.	Difference	Shrinkage %
246	0.664	0.604	0.06	9.0
250	0.746	0.640	0.106	14.2
254	0.654	0.540	0.114	16.9

TABLE 5:23 THE SHRINKAGE OF DRAWN 66 NYLON BRISTLE AFTER IT HAD BEEN ANNEALED AT 242°C. FOR 45 AND 120 MINS.

Annealing time @ 242°C. mins.	1st Endotherm Temp. °C.	Heated to °C.	Original length cms.	Length after heating cms.	Difference	% Shrinkage
45	251.5	255	0.756	0.694	0.062	8.2
120	253	256	0.766	0.704	0.062	8.1

5:8 THE EFFECT ON THE CRYSTALLIZATION EXOTHERM, WHICH OCCURRED ON COOLING AFTER AN ANNEALED 66 NYLON SAMPLE HAD BEEN HEATED TO THE TEMPERATURE IN BETWEEN THE TWO MELTING ENDOTHERMS, AS THE ANNEALING TIME AT 242°C. WAS INCREASED.

On heating an annealed sample to the temperature between the two melting endotherms, and then allowing it to cool, a crystallization exotherm was observed. (see 5:5) The following experiments were devised to discover whether this crystallization peak observed after such thermal treatment, also increased, as the annealing time increased.

Samples were first annealed for the appropriate time at 242°C., and then cooled. They were then reheated until the first melting endotherm was completed and allowed to cool.

Table 5:24 (page 118) gives the results obtained, and Diagram 32 (page 119) shows the cooling endotherms obtained.

These results show that as the size of the first melting endotherm increased on annealing, so did its associated crystallization exotherm.

Polymer samples, initially annealed at 242°C. for one hour, were held isothermally at 254°C. (the temperature between the two melting endotherms) for 30 and 60 minutes respectively, before being allowed to cool. They were subsequently remelted.

The original first melting endotherm occurred at 252°C. in both instances. On cooling after 30 minutes at 254°C., a broad indistinct crystallization exotherm occurred between 252-240°C., whilst after 60 minutes at 254°C., a smaller but more distinct exotherm at 238°C. was observed. In both instances on remelting, only a single sharp melting endotherm at 262°C. was observed, much higher than the normal final melting endotherm. (Diagram 33 page 120).

5:9 THE EQUILIBRIUM IODINE SORPTION OF PRECIPITATED 66 NYLON SAMPLES.

The iodine sorption of 66 nylon samples can be used to differentiate between samples of varying degrees of crystallinity. The amount of iodine sorption is dependent on the number of amorphous regions in the polymer, where sorption can occur. The lower the iodine sorption value, therefore, the higher the crystallinity or the structural order of the sample.

Dr. T. R. White of I.C.I. Fibres Ltd., Pontypool, Monmouthshire, kindly determined the iodine sorption of two different samples of

TABLE 5:24 THE CHANGES IN THE CRYSTALLIZATION EXOTHERM, OBSERVED AFTER HEATING AN ANNEALED SAMPLE TO THE TEMPERATURE BETWEEN THE TWO ENDOTHERMS AND ALLOWING IT TO COOL, AS THE ORIGINAL ANNEALING TIME OF THE SAMPLE INCREASED.

Annealing Time @ 242°C.	Temp. of 1st endotherm (°C.)	Heated to (°C.)	Crystallization peak °C.	Diagram 32 Trace
5	249	252	No	a
10	249	252	250-51 (doubtful)	b
15	251	254	250-251	c
30	250	254	250-244	d
60	253	256	250-244	e

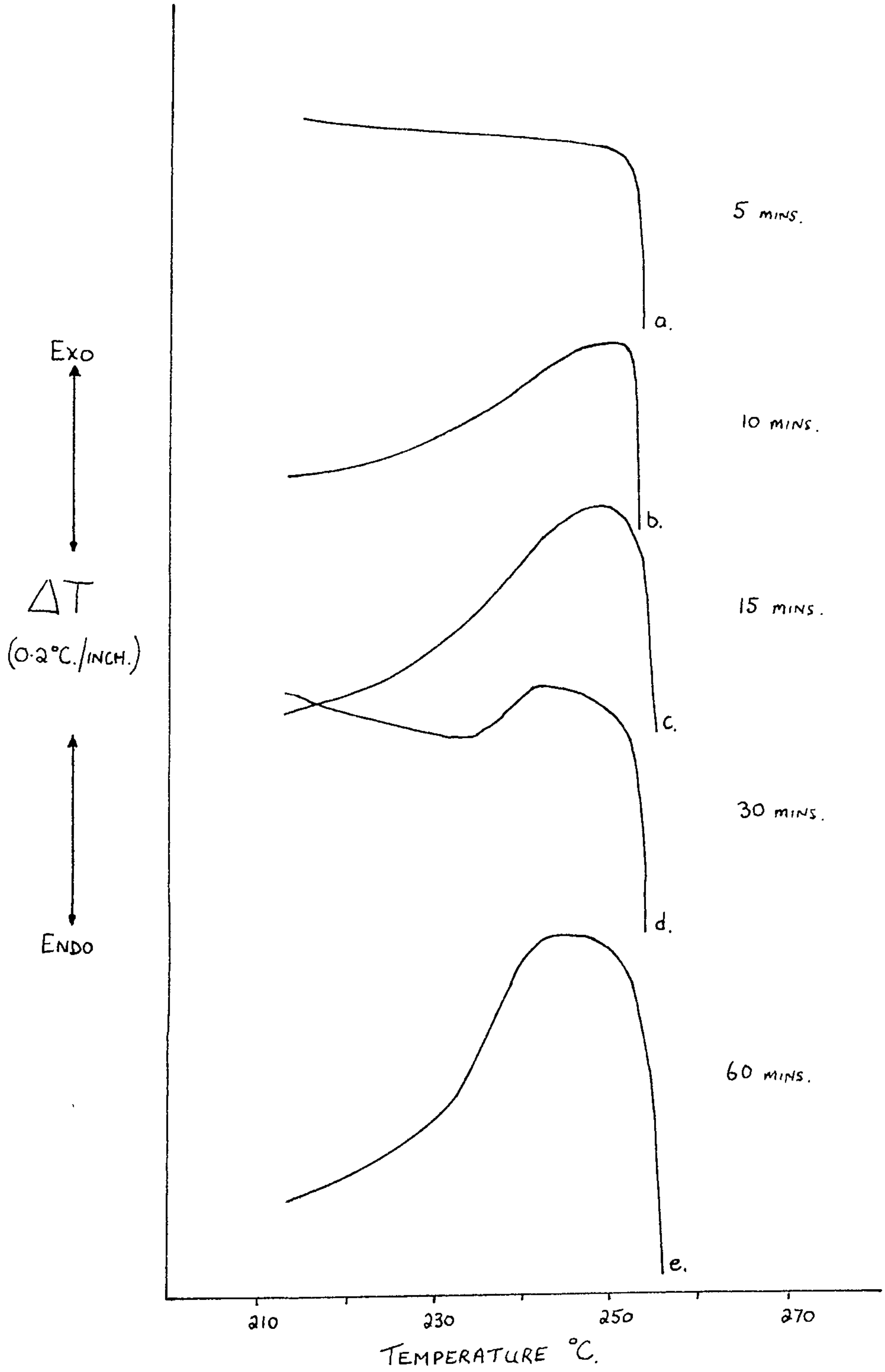


Diagram 32. Cooling thermograms after heating samples of 66 Nylon, previously annealed at 242°C. for various times, to the temperature between the two melting endotherms. The times on the diagram refer to the original annealing times.

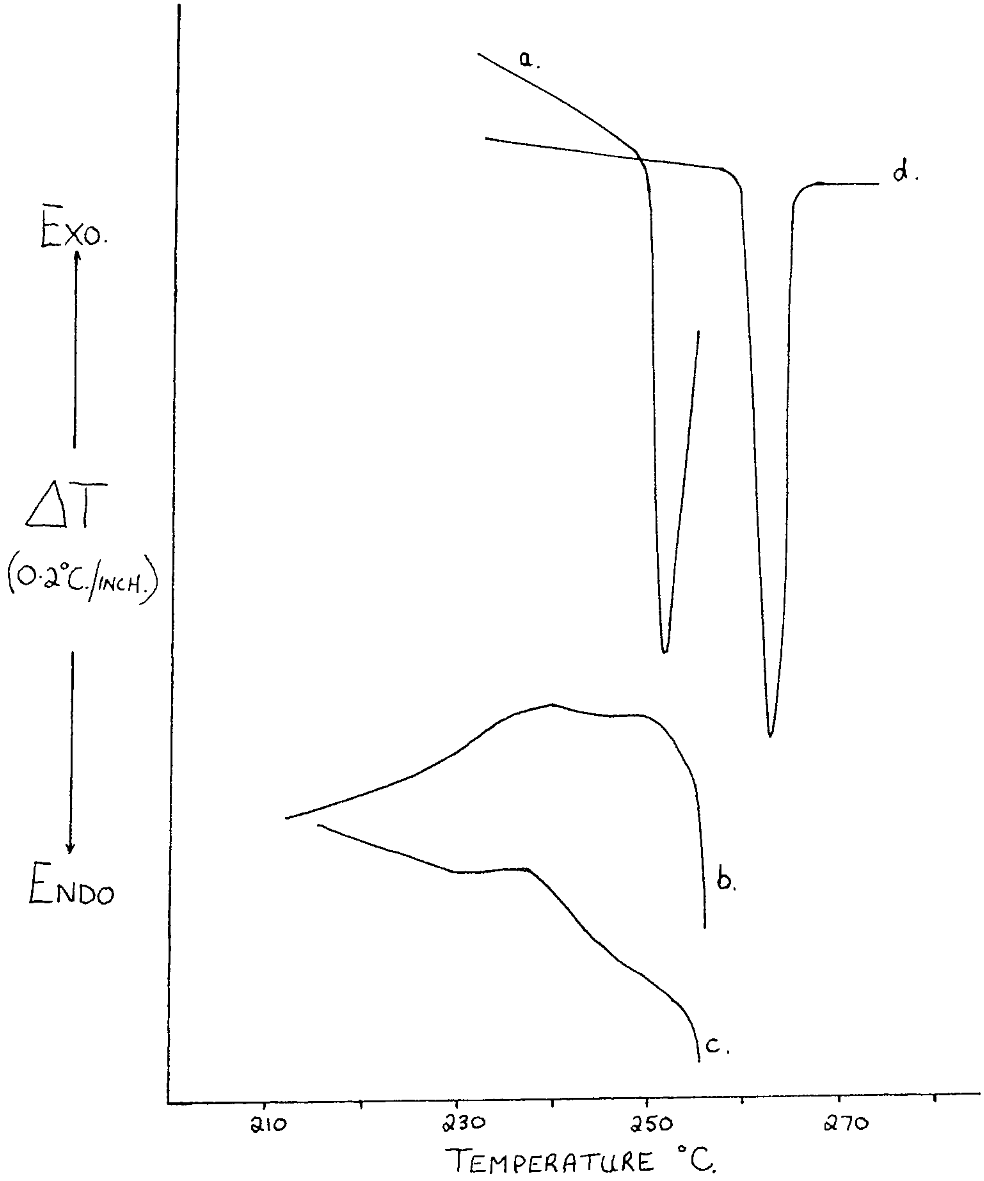


Diagram 33. Thermograms of annealed 66 Nylon chip (1 hr. at 242°C.),before being held for 30 and 60 mins.,respectively,at 254° C.(the temperature between the two endotherms),prior to cooling and remelting.

a),Initial thermogram of annealed chip up to 254° C.
b),Cooling after 30 mins. at 254°C.
c);Cooling after 60 mins. at 254° C.
d),Remelt after either c),or b).

precipitated 66 nylon. One sample had a single melting endotherm, the other, two.

The single endotherm sample had an equilibrium iodine sorption value of 0.021 g. of iodine/g. polymer, whereas the value for the double endotherm sample was 0.014 g. of iodine/g. polymer.

The results were significantly different, and much lower than that obtained normally for drawn 66 nylon monofilaments (0.08g. iodine/g. polymer), under similar sorption conditions. They indicate that the precipitated samples had higher crystallinity than drawn monofilament. The sample with two melting endotherms was more crystalline than that with only a single endotherm, as confirmed by the density and X-ray measurements carried out on similar samples. (See 5:3 and 5:10).

5:10 X-RAYS. RESULTS AND INTERPRETATION.

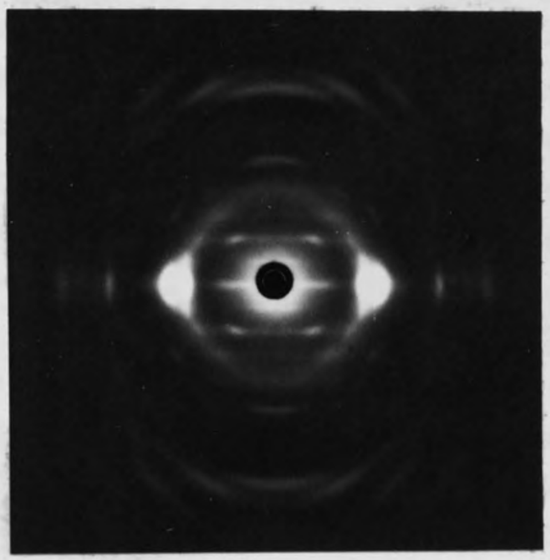
5:10:1 POWDER PHOTOGRAPHS.

The X-ray powder photographs of ground 66 nylon chip and the two different precipitated samples were compared visually by examining the negatives on a viewing screen. Since there appeared to be no differences in the major diffraction arcs, either in intensity, or diameter, it was assumed that there was no major change in the unit cell dimensions as a result of precipitation. Therefore, it was assumed that there was no significant change in the unit cell spacings between the samples. Hence, the difference in the D.T.A. thermograms of the precipitated samples was not caused by the presence of a different unit cell structure, formed during the precipitation process. This observation was also confirmed by the wide angle X-ray photographs of similar precipitated samples taken by I.C.I. Fibres Ltd. (5:10:3).

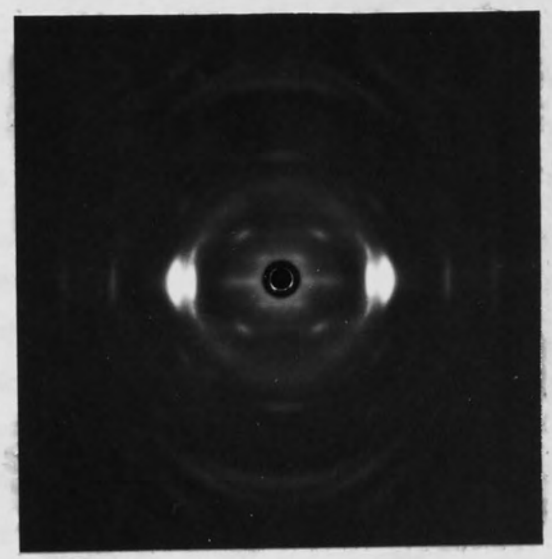
5:10:2 FIBRE DIAGRAMS.

Fibre diagrams were obtained for samples of 66 nylon bristle, after zero, 5 minutes and 2 hours annealing at 242°C. respectively. (Photographs page 122). They show the usual effect of increasing the annealing time (127) ie., an improvement in resolution and some loss of orientation. The improvement in resolution, indicated by a sharpening of the reflections, indicated an improvement in the quality of the lattice ordering, which was also revealed by the clearing up of the layer line streaks. The loss of orientation which always occurs when

X-RAY FIBRE DIAGRAMS OF DRAWN 66 NYLON BRISTLE. (FIBRE AXIS VERTICAL)



1). Untreated bristle.



2). Bristle annealed at 242°C. for 2 hours.

samples are heated in the absence of tension, was shown by the increased arc length and the way in which the weak 002 spots make a progressively increasing angle with respect to the layer line streak. (150)

The changes that these results show did not seem to be sufficient to explain the increase in the size of the first melting endotherm as the annealing time increased. The loss of orientation which has occurred, on White's theory for the origin of the first endotherm,(1) would be expected to result in a decrease, rather than an increase in the size of the first endotherm. The increase in lattice perfection would tend to sharpen the melting endotherms, but would be unlikely to cause a new one.

5:10:3 THE WIDE ANGLE PHOTOGRAPHS OF ANNEALED FILM.

The results of the X-ray photographs taken by I.C.I. Fibres Ltd., on annealed 66 nylon film are given in table 5:25 (page 124) and those of the precipitated polymer in table 5:26 (page 125).

The annealing decreased the orientation, until after 2 hours, the sample was unorientated. The width of the line was reduced as the annealing time was increased. This can be interpreted as an increase in the size of the crystalline regions or as an increase in the perfection of existing regions. (150) The diameter of the (100) diffraction rings remained effectively constant at 7.40 cms., whilst that of the (010) diffraction ring increased slightly from 8.85 cms. (zero annealing), to 8.94 cms., (18 hours annealing). This indicated a slight, but insignificant decrease in the spacing of the (010) planes which is a normal consequence of the annealing process. (151)

5:10:4 THE LOW ANGLE PHOTOGRAPHS OF THE ANNEALED FILM.

These show an increase in intensity of the diffraction pattern with the annealing time up to 2 hours. Then, it became reasonably constant. This behaviour is commonly observed in yarns (150) but has not yet been satisfactorily explained. The low angle ring was slightly elliptical indicating a larger spacing in one direction than the other.(151) Samples 1 and 2 (Table 5:25 page 124) show slightly larger orientation effects than the remainder. (150)

These results show that changes do occur in 66 nylon film and can be interpreted as being caused by an increase in perfection of

TABLE 5:25 THE RESULTS OF THE WIDE AND LOW ANGLE X-RAY PHOTOGRAPHS TAKEN OF 66 NYLON FILM ANNEALED AT 242°C. FOR VARYING TIMES.

Sample	Annealing time at 242°C. (hrs.)	Exposure time hrs.	Wide Angle	Low Angle
1	0	20.1	Good perfection; some orientation in extrusion direction	Oriented with meridional maxima
2	½	20.1	Improved perfection. Less oriented than 1	Still meridional maxima - increased intensity to 1
3	1	23.9	Perfection as 2, less orientation	More intense than 2. Elliptical pattern with major axis in extrusion direction
4	2	20.1	Perfection as sample 2 but no orientation	More intense than sample 3, still elliptical
5	4	20.1	As sample 4	As sample 4
6	18	20.1	---..---	---..---

TABLE 5:26 THE WIDE AND LOW ANGLE X-RAY RESULTS FOR 66 NYLON PRECIPITATED UNDER DIFFERENT CONDITIONS GIVING SINGLE OR DOUBLE D.T.A. MELTING ENDOTHERMS.

Sample	X-Ray Exposure Time (hrs.)	Wide Angle	Low Angle
1. MeOH/HCOOH System; 2 D.T.A. peaks (1.7mg. Sample.)	4.0	Powder Pattern - very good crystalline perfection	Appears to be two maxima
2. 50/50 MeOH/H_2O/HCOOH System; 1 D.T.A. peak (1.9mg. sample.)	4.0	Perfection as 1 above	Very weak intensity, one maximum
3. C_6H_5 CH_2OH System; 2 D.T.A. peaks (1.6mg. sample.)	3.8	Perfection as 1	Over exposed.
	0.75	----	More intense pattern. Similar to sample 1 weaker maxima, not as pronounced.
4. C_6H_5 CH_2OH System; 1 D.T.A. peak (1.4mg. sample.)	4.0	Perfection as 1 above	Much more intense pattern over exposed.
	0.75	----	Apparently only one maximum with diffuse outer background.

Sample 3 was prepared from a 2% benzyl alcohol solution of 66 nylon as follows. The solution was heated to 175°C. to dissolve the polymer initially. It was allowed to cool before being heated to 152°C. to redissolve the precipitated polymer and then held at that temperature for 1 hour before being finally cooled and isolated.

Sample 4 had exactly the same treatment until the final heating. It was then transferred to a silicone oil bath at 130°C. and held at that temperature for 3 hours before being finally cooled and isolated.

crystalline regions, either by development of new ones, or the improvement of existing crystallites. The increase in intensity of the low angle X-ray scattering has been observed previously. (39) It has been suggested that the formation of chain folds forming different sized crystalline lamellae caused this increase.

5:10:5 X-RAY PHOTOGRAPHS OF PRECIPITATED SAMPLES.

The wide angle photographs indicate that the precipitated samples are more highly crystalline or better ordered than the films (5:10:3) The spacing of the (100) diffraction ring is the same as for the film samples (7.40 cms.) whereas the (010) diffraction ring is now 9.18 cms. compared to 8.90 cms. (mean for the film samples). This indicated that the spacing of the (010) planes has been reduced slightly. (150) The overall perfection of all the samples was similar, however they were prepared.

It is noticeable however, that the precipitated samples having two D.T.A. melting endotherms, also show two diffraction maxima in the low angle photographs. Samples with only one D.T.A. endotherm have only one diffraction maximum. This was independent of the method of sample preparation.

The two diffraction maxima in these precipitated samples, having two D.T.A. melting endotherms, suggest that the cause of the two endotherms may be different, from that causing the effect in the annealed film samples. Alternatively, the effect may be more pronounced in precipitated samples and the elliptical pattern observed with the film samples might resolve itself into two separate maxima after a sufficiently long annealing treatment at the correct temperature. It is tempting to suggest, that the two diffraction maxima arose from there being two different long periods in the same sample, ie. two definite discrete chain fold lengths.

The samples prepared from benzyl alcohol solutions have more intense diffraction patterns than those prepared from MeOH/HCOOH systems.

5:11 OTHER POLYAMIDES.

The thermal behaviour of other polyamides was studied. This was to establish whether the melting, crystallization and annealing behaviour of 66 nylon was an exclusive property of that polymer, or whether it was a property of the polyamide polymers in general.

Details of the other polyamides studied are given in 4:2 to 4:5 inclusive. They fall into two groups, those of a more commercial importance, ie. 6, 610, and 11 nylon and those of more academic interest ie. 7, 7 6, 7 7 and 6.8 nylon.

5:11:1 MELTING, CRYSTALLIZATION AND REMELTING.

The thermograms of these other polyamides were obtained using the Du Pont standard D.T.A. cell as previously described. The various experiments were carried out under similar operating conditions to those used for 66 nylon so that direct comparison was possible. (See 5:1:2 for further details.) Tables 5:27 (page 128) and 5.28 (page 129) give the melting/remelting and the crystallization data respectively.

The crystallization thermogram was obtained after the sample had been heated for ten minutes above its melting point to destroy any previous thermal history. Column 3 of table 5:28 (page 129) gives the fusion temperature used. Samples were cooled to at least 30°C. below their crystallization exotherm, before remelting commenced.

A sample of ionically polymerized 6 nylon, made by B.A.S.F. was also examined.(Table 5:27 (page 128). The method of polymerization results in a polymer having the possibility of short branches which could affect its thermal behaviour. No annealing experiments as such were carried out on this polymer sample. However, 1 hour's melt crystallization at 187°C. was carried out, after its initial melting. The subsequent melting thermogram contained two endotherms at 208°C. and 212°C. the former being the larger of the two. A similar experiment, at 201°C. was carried out on a sample of "Celon" 6 nylon. The subsequent melting thermogram again contained two endotherms at 208°C. and 218°C. respectively. In this instance the endotherm at 208°C. was the smaller of the two.

The data given in tables 5:27 and 5:28 (pages 128 and 129) indicated that the thermal behaviour of 66 nylon was a common property of the polyamide system. This was further confirmed when annealing experiments were carried out (5:3:2 below.)

5:11:2 THE ANNEALING OF OTHER POLYAMIDES PRIOR TO MELTING.

These other polyamides were annealed under similar conditions to the original annealing experiments on 66 nylon. (see 5:1:6). This

TABLE 5:27 THE MELTING AND REMELTING DATA FOR VARIOUS POLYAMIDES.

Nylon Form	Source	Run +	Mpt. °C. Exo 1	Endo 2	Exo 3	Endo 4	Comments
6 Chip (bright)	I.C.I. Fibres Ltd.	I	–	–	–	219.8	
		R	–	210.8	–	217.8	2 ≃ 4
6 Chip	B.A.S.F. ionic polym.	I	–	–	–	212.2	
		R	–	204	–	212	Less well defined c.f. above.
6 Fibre (Drawn 1:3.9)	Celon	I	–	218	–	218	2 only inflexion
		R	–	211	–	217.5	
610 Chip	I.C.I. Fibres	I	–	–	–	221	
		R	–	–	–	220	
610 Bristle (Drawn)	I.C.I. Plastics	I	–	214	–	218	
		R	–	–	–	218	
11 Chip	I.C.I. Fibres	I	–	–	–	187.8	
		R	–	178.8	–	186.8	
7 Chip	I.C.I. Dyestuffs	I	–	–	–	230	
		R	–	–	–	225-229	Very broad
76 Chip	-"-	I	212	234	237	245	
		R	–	234	237	245	
77 Chip	-"-	I	–	–	–	202	
		R	–	–	–	202	
68 Chip	-"-	I	–	–	–	223	
		R	–	213	–	223	Slight inflexion.

+ I = initial melting. R = remelting after crystallization.

TABLE 5:28 CRYSTALLIZATION DATA FOR VARIOUS POLYAMIDES.

(SOURCES OF POLYMERS AS TABLE 5:27 page 128).

Nylon	Form	10 mins. @ °C.	Peak temp. °C. a	Peak temp. °C. b
6	Chip (bright)	240	188	176 *
6	Chip (ionic)	237	-	179
6	Fibre	237	-	191
610	Chip	246	-	187 +
610	Bristle	240	-	190
11	Chip	203	-	164.8
7	-"-	248	-	204
76	-"-	270	-	214
77	-"-	227	177	167 *
68	-"-	240	-	202

* b was the major exotherm in both cases.

\+ This was a broad exotherm.

was to discover whether annealing these polyamides produced similar results to those observed with 66 nylon.

The data obtained on melting the samples, after they had been annealed at various temperatures is given in tables 5:29 and 5:30 (pages 131 and 132 respectively). After the annealing was completed, the sample was cooled to below its normal crystallization temperature (see table 5:28, page 129) before melting commenced. With all the samples, the sequence of melting, fusion for 10 minutes, followed by crystallization was carried out before the annealing process commenced.

Table 5:29 (page 131) shows that once the correct annealing temperature has been found, 6, 610 and 11 nylon samples show very similar annealing behaviour to 66 nylon. As the annealing time at a given temperature increased, both the area and the temperature of the first new melting endotherm increased.

Table 5:30 (page 132) also shows that the temperature at which the annealing takes place, will really determine whether a new melting endotherm was observed. It was assumed from the results in table 5:29 (page 131), that once the correct annealing temperature had been found, increasing the annealing time would increase the size of the first melting endotherm of the other polyamides also. Time did not permit a more detailed study to be carried out.

5:12 OTHER POLYMERS.

The thermal behaviour of other common thermoplastic polymers was studied, to discover whether under the correct annealing conditions, multiple melting endotherms could be obtained, similar to those observed with annealed 66 nylon. Details of the various polymers are given in 4:6 to 4:13.

Thermograms of the melting, crystallization and annealing have been recorded for each individual polymer in turn. They were obtained using similar operating conditions to those used for 66 nylon. (see 3:1:2).

Samples were always allowed to cool to well below their crystallization temperature prior to any reheating, after either a crystallization, or an annealing run. Crystallization data was obtained after the sample had been held for 10 minutes above its melting point (ie. + $15^{\circ} \rightarrow 20^{\circ}$C.) to destroy any previous thermal history. Annealing

TABLE 5:29 THE ANNEALING OF 6, 610, AND 11 NYLON FOR VARYING PERIODS OF TIME AT DIFFERENT TEMPERATURES PRIOR TO MELTING.

Polymer Source	Annealing Temp. (°C.)	Annealing Time. (hrs.)	Melting Temp. °C.		Comments ⊗
			T_1	T_2	
6 (I.C.I.)	207	¼	213	218	$A_1 > A_2$; A_2 was poorly resolved: tends to be a pronounced shoulder.
		½	213	218	
		¾	213	218	
		1	214	218	
610 (I.C.I.)	215	½	-	220	
	207	¼	211	220	$A_1 > A_2$; A_1 was always well resolved except after 1½ hrs., more of a shoulder. A_1 increases in area with time.
		½	211	220	
		1	212	220	
		1½	213	219	
	205	½	209	220	
11 (I.C.I.)	183	¾	-	188	Very sharp
	181	¼	-	186	
		½	-	186	
	177	¼	181	187	$A_1 \simeq A_2$ A_2 tends to a shoulder as time increases.
		½	182	187	$A_1 > A_2$
		¾	181	187	$A_1 \simeq A_2$
		1	182	187	$A_1 > A_2$
		1½	183	187	$A_1 > A_2$
	170	1	176/182	187	A_1 not well resolved.

⊗ In this column A_1 and A_2 refer to the relative sizes of the two melting endotherms T_1 and T_2 respectively.

TABLE 5:30 THE ANNEALING OF 7, 76, 77, AND 68 NYLON FOR 30 MINUTES AT VARIOUS TEMPERATURES PRIOR TO MELTING.

Polymer	Annealing Temp. °C.	Melting Temperature °C.				Comments
		T_1	Endo	Exo	T_2	
7	220	-			227	
	215	223			227	A_1 only a slight shoulder
	210	217			227	$A_1 < A_2$; definite peak
76	234-5	241			245	A_1 only a shoulder - not resolved
	227	226	234	237	245	A_1 change in baseline slope
	222	230	234	237	245	A_1 definite shoulder
	217	223	234	237	245	A_1 change in baseline slope
77	195	-			202	
	190	196			201	$A_1 < A_2$; not well defined 1st peak at all
	185	187			201	
68	217	220			227	Not really peaks just changes in baseline slope
	212	215			225	
	207	214			225	A_1 poorly resolved

A_1 and A_2 in "Comments" column refer to the melting endotherms, T_1 and T_2 respectively and their relationship to each other.

experiments were normally carried out on samples that had been previously melting and then recrystallized in the D.T.A. cell.

The results are given in the following tables.

1) Low Density Poly(ethylene). Table 5:31 (page 134).

2) High Density Poly(ethylene). Melting, Crystallization and Remelting. Table 5:32 (page 135).

Annealing. Table 5:33 (page 136).

3) Poly(propylene). Melting, Crystallization and Remelting of Various forms of Polymer. Table 5:34 (page 138).

Annealing. Table 5:35 (page 139).

4) Poly(4-methyl pentene-1). Table 5:36 (page 141).

5) Poly(formaldehyde). Table 5:37 (page 143).

6) Poly(ethylene oxide). Melting and Crystallization. Table 5:38 (page 143).

Annealing. Table 5:39 (page 144).

7) Isotactic Poly(propylene oxide). Table 5:40 (page 144).

8) Poly(ethylene terephthalate). Melting, Crystallization Remelting. Table 5:41 (page 145).

Annealing. Table 5:42 (page 145).

In all these tables, A_1, A_2, A_3 etc., in the "Comments" column, are used to refer to the various endotherms in the thermograms having melting temperatures of T_1, T_2, T_3 etc,. For example, "A_1 poorly resolved" means that the endotherm of melting temperature T_1 was not very well resolved in the thermogram. $A_1 > A_2$ means that the endotherm with the melting temperature T_1 was larger in size than the endotherm with melting point T_2, etc.

NOTE.

The data for the annealing of poly(ethylene oxide) table 5:39 (page 144) and isotactic poly(propylene oxide) table 5:40 (page 144) are given for a range of temperatures, rather than a single annealing temperature. This is because the Du Pont 900 D.T.A. Instrument fails to operate successfully isothermally below a minimum temperature. This temperature (50-60°C.), dependent on ambient conditions, represents the minimum current flowing through the cell heater to allow the programmer/controller to operate "isothermally".

TABLE 5:31 THE MELTING, CRYSTALLIZATION AND ANNEALING OF LOW DENSITY POLY(ETHYLENE).

Conditions	Annealing Temp. °C.	Annealing Time (hrs.)	Melting Temp. °C.		Comments
			T_1	T_2	
Melting	--	--	--	110	Broad peak
Crystn.	--	--	--	101	After 10 mins @ 140°C
Remelt	--	--	--	110	Sharper peak than melt.
Annealing	108 *	$\frac{1}{2}$	104	111	$A_1 < A_2$; A_1 broad, A_2 sharp
	105	$\frac{1}{2}$	107	110	$A_1 = A_2$ not too well resolved
	104	$\frac{1}{4}$	105	110	$A_1 < A_2$; resolution reasonable
	101	$\frac{1}{2}$	105	110	$A_1 < A_2$
	101 +	$\frac{1}{2}$	105	109	$A_1 \leq A_2$ resolution reasonable
	101	1	105	111	$A_1 < A_2$
	101	2	105	111	$A_1 < A_2$
	101	4	106	111	$A_1 < A_2$

* A small crystallization exotherm at $\simeq$ 98-100°C. was recorded when this sample was cooled after the completion of the annealing.

\+ This sample was annealed prior to melting.

TABLE 5:32 THE MELTING, CRYSTALLIZATION AND REMELTING OF HIGH DENSITY (POLY(ETHYLENE).

Sample	Conditions	Melt Temp. °C.	Comments
Rigidex Chip	melt	125	Fairly sharp.(Diagram 34a) (page 137)
	crystn.	115	After 10 mins. @ 160°C.
	remelt	126	Similar to melt
Courlene X3 Fibre from Rigidex. drawn 8:1	melt	123.8	Sharp
	crystn.	115	After 10 mins. @ 150°C.
	remelt	125.8	Smaller, broader than melt

TABLE 5:33 THE ANNEALING OF HIGH DENSITY POLY(ETHYLENE) AT VARIOUS TEMPERATURES.

Annealing Temp °C.	Time (hrs.)	Melting temp. °C T_1	T_2	T_3	Comments
120	18*	109	125	128	A_1 broad, ill defined $\ll A_2$
120	18+	109	125	128	Sharp; A_3 only inflexion
117	½	114	122	127	Diagram 34b, (page 137)
112	½		117	127	Diagram 34c, " "
105	½		115	127	Diagram 34d, " "
117	½		113	126	cf.Diagram 34d," "
117	1		125	128	$A_2 \simeq A_3$ poorly resolved
117	1	115	123	127	cf.Diagram 34b, (page 137); A_2
117	1½	115	123	127	here slightly better resolved
117	2		122	128	$A_2 < A_3$; A_2 only shoulder
113	½		118	127	cf.Diagram 34c, (page 137)
112	1		119	127	cf.Diagram 34c, " "
107	½	115	123	127	cf.Diagram 34b, " "

* Annealing in an air oven @ 120°C.

\+ Annealing in silicon oil in an air oven @ 120°C.

Diagram 34 (page 137) shows the effect of increasing the annealing time at 114°C. on the melting thermograms of annealed high density poly(ethylene.)

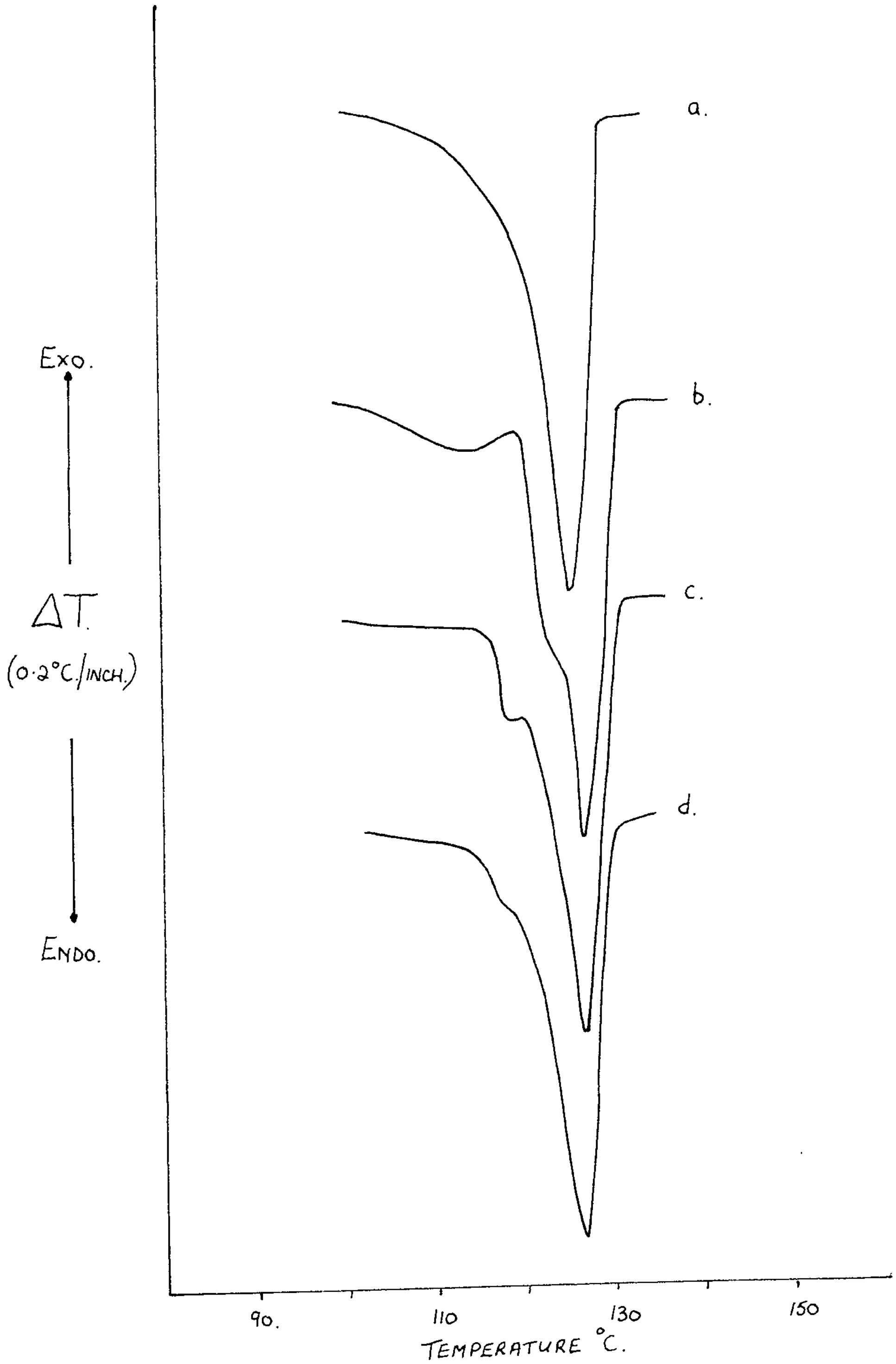


Diagram 34. The annealing of high density poly(ethylene).
a, initial melting,
b, after annealing for ½ hr. at 117°C.
c, --"-- --"-- 112°C.
d, --"-- --"-- 105°C.

TABLE 5:34 THE MELTING, CRYSTALLIZATION AND REMELTING OF VARIOUS SAMPLES OF POLY(PROPYLENE).

Sample	Conditions	Melting Temp. °C.				Comments
		T_1	T_2	T_3	T_4	
Chip (I.C.I.)	Melt				162	broad
	Crystn.				118	After 10 mins. @ 192°C.
	reheat	144	151	159	164	A_1, A_2, A_4 not well resolved
Drawn + Fibre (I.C.I.) Draw ratio unknown	Melt			164.8	170	Very sharp peaks $A_3 < A_4$
	Crystn.				118	After 10 mins. @ 192°C
	reheat	144	150	156.8	161	A_1, A_2 minor peaks A_4 only shoulder.
Undrawn + Fibre (I.C.I.)	melt				160	Broad
	Crystn.				118	
	reheat	143	150	157	161	A_1, A_2 minor peaks A_4 only shoulder.
Powder (unstabilised))Shell)	melt			147	159	147°C. peak very ill defined
	Crystn.					
	reheat				158	

\+ see diagram 35. (page 139).

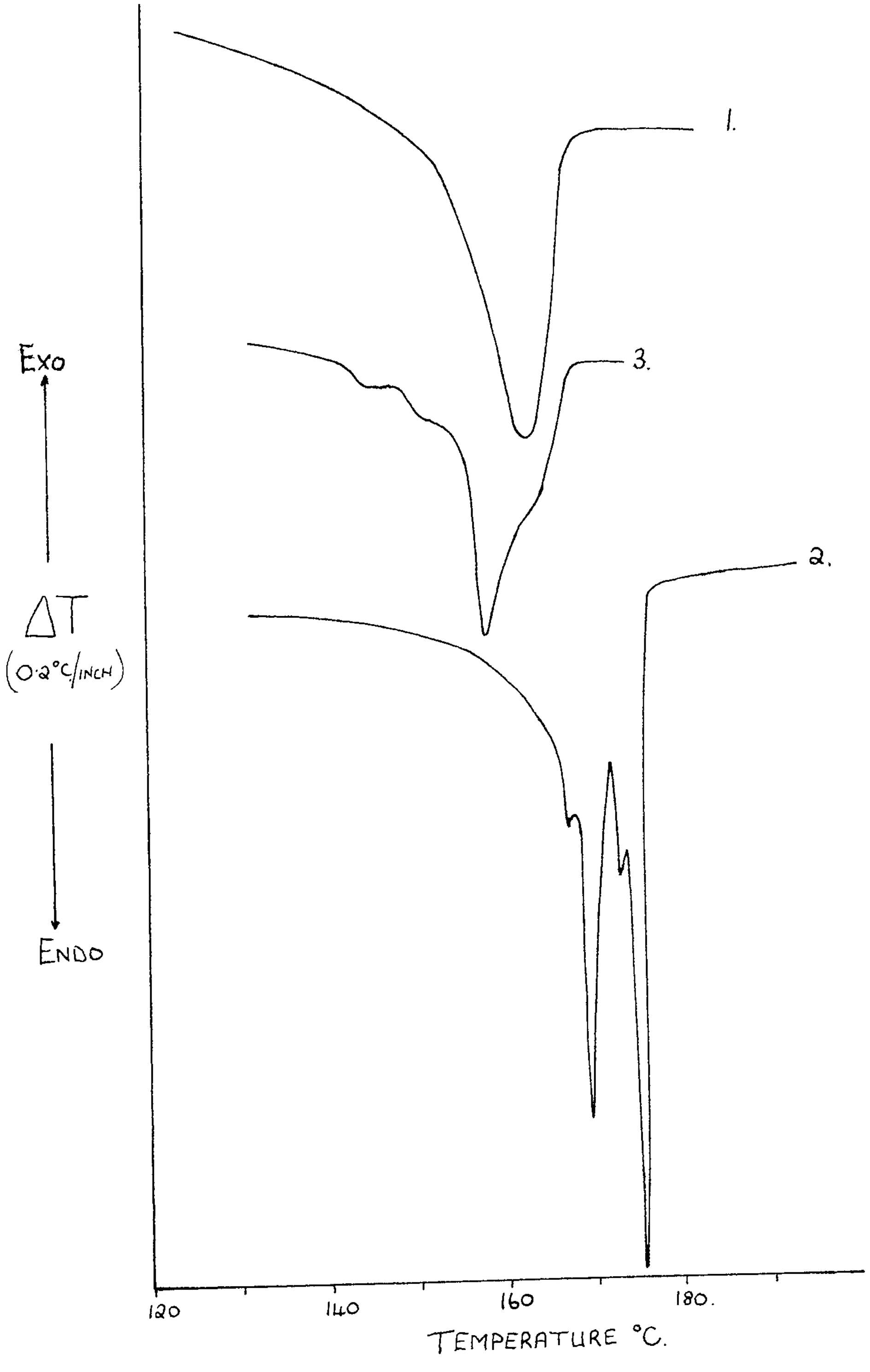


Diagram 35. The melting of different samples of poly(propylene).

1. chip or undrawn yarn.
2. drawn yarn.
3. remelt of 1. or 2.

TABLE 5:35 THE ANNEALING OF SAMPLES OF POLY(PROPYLENE) FOR VARYING TIMES AT VARIOUS TEMPERATURES.

No.	Annealing Temp. °C.	Annealing Time hrs.	Melting Temp. °C.			Comments
			T_1	T_2	T_3	
1	157	½			162	All fairly sharp peaks
2	152	¼			161	
3	152	½			162	
4	147	¼	152	158	160	A_1 appears more like a glass transition change than a peak A_2 is the start of the main melting peak A_3
5	147	½	153	158	160	
6	147	1	154	158	160	
7	143	½		157	161	
8	143	1	146	157	160	
9	141	¼	146	158	161	
10	141	½	146	160	164	A_1 well resolved A_3 inflexion
11	141 *	½	145	160	163	A_1 not very pronounced A_2 major peak
12	141	½	147	158	160	See nos. 4-9
13	141	¾	146	158	161	
14	141 *	1	147	152	161	A_1, A_2 not very pronounced A_3 main peak
15	141 *	2	147	153	161	
16	137	1	139	157	160	See nos. 4-9
17	132	½	146	160	164	A_2 main peak - others minor.

* Using Shell unstabilised poly(propylene) powder, all the others were carried out using I.C.I. poly(propylene) samples.

TABLE 5:36 THE MELTING, CRYSTALLIZATION, REMELTING AND ANNEALING OF SAMPLES OF POLY (4-METHYL PENTENE-1).

Conditions	Annealing Temp. °C.	Annealing Time hrs.	Melt Temp. °C.		Comments
			T_1	T_2	
Melt				227-229	Diagram 36 a (page 142)
Crystn. +			209	211	b
Reheat				228	Sharper than initial
Annealing	221	½	228	230	Diagram 36 c (page 142)
	221	1	225	229	d
	221	1½	225	229	e
	221	2	226	229	f
	221 *	2	227	229	$A_1 < A_2$
	216	½	222	228	$A_1 < A_2$ poor trace
	211	½		229	

+ After 10 minutes @ 270°C.

* This sample was not cooled down to room temperature and the two peaks were not well resolved. The previous run was cooled to room temperature resulting in two completely resolved peaks on remelting.

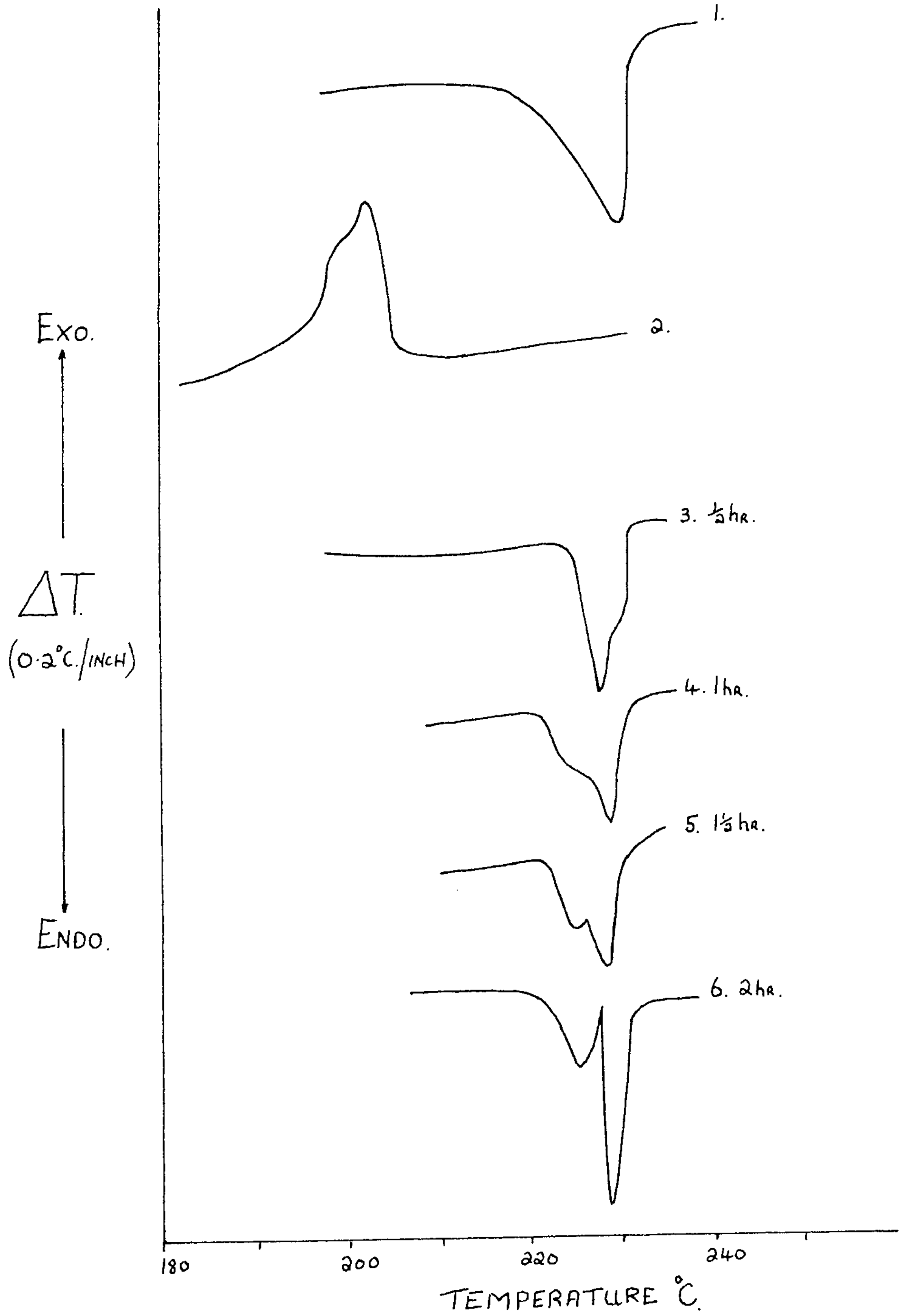


Diagram 36. Thermograms of poly(4-methyl-pentene-1). 1.,melting, 2.,recrystallization 3.--6.,after annealing at 221° C.

TABLE 5:37 THE MELTING, CRYSTALLIZATION, REMELTING AND ANNEALING OF POLY(FORMALDEHYDE).

Conditions	Annealing Temp. °C.	Time (hrs.)	Melt temp. °C. T_1	T_2	T_3	Comments
Melt					163	
Crystn.					139	Very sharp peak
Reheat					164	Sharper than melt
Annealing	157	$\frac{1}{2}$	153	160	165	(A_1 small broad, A_2 inflexion, start of main sharp peak T_3
	153	$\frac{1}{2}$	150	158	165	

TABLE 5:38 MELTING AND CRYSTALLIZATION DATA FOR POLY(ETHYLENE OXIDE).

Conditions	Melt temp. °C. T_1	T_2	T_3	Comments
Melt	48		59	A_1 small broad
			58	
Crystn.			46	Fairly sharp
			44	- " -
Reheat		55	58	A_2 definite shoulder
			56-57	56°, small shoulder near tip

TABLE 5:39 ANNEALING DATA FOR POLY(ETHYLENE OXIDE) (SEE PAGE 133).

Annealing Temp. °C.	Time (hrs.)	Melt Temp. °C. T_1	T_2	T_3	Comments
54-56	½	48	56	59	A_1 doubtful; $A_2 < A_3$ but well resolved; crystn. peak 48°C.
53-55	½	48	56	58-59	A_1 small broad; $A_1 < A_2$ as above; crystn. peak 47°C. very small
52-53	½	49		59	$A_1 < A_3$ broad small; crystn. peak not recorded.
49-51	½	46		58	A_1 small; crystn. peak not recorded.
49-51	½	48	57	59	A_1 small, ill defined shoulder; small crystn. peak 48°C.
54-56 *	1		55	58	A_2 shoulder; crystn.peak at 46°C. after melt crystn. ceased.

* Melt crystallization.

TABLE 5:40 MELTING, CRYSTALLIZATION AND ANNEALING DATA FOR ISOTACTIC POLY(PROPYLENE OXIDE.) (SEE PAGE 133).

Conditions	Annealing Temp. °C.	Time (hrs.)	Melt temp. °C. T_1	T_2	T_3	Comments
Melt				55	66	$A_2 < A_3$
Crystn.					47.5	broad low
Reheat				59.5	67	$A_2 < A_3$
Melt-crystn.	60	1		61.5	67.5	$A_2 \simeq A_3$; Crystn/peak at 47.5 very low and broad.
Anneal	52	1			66	Prior to melting sample
	53	3	56	63	66	$A_1 < A_2 > A_3$; A_1, A_3 shoulders
	43-57	1		64	67.5	broad peak, A_2 shoulder
	43-63	1.3			69	

TABLE 5:41 THE MELTING, CRYSTALLIZATION AND REMELTING OF VARIOUS FORMS OF POLY(ETHYLENE TEREPHTHALATE).

Sample	Conditions	Melt temp. °C.		Comments
		T_1	T_2	
Chip	Melt		253 +	
	Crystn.		200 x	Very broad, low peak
	Reheat	241.8	253 +	$A_2 > A_1$; not well resolved
Drawn	Melt		252-258	Broad tip - masked by recorder noise
Fibre	Crystn.		220	Sharp
	Reheat	247	252	$A_1 \simeq A_2$

\+ See diagram 37 (page 146)

x Varies between 197-205°C. for different samples.

TABLE 5:42 THE ANNEALING OF POLY(ETHYLENE TEREPHTHALATE) CHIP.

Annealing Temp. °C.	Time (hrs.)	Melt Temp. °C.			Comments
		T_1	T_2	T_3	
208.5 *	3	240.5	245	248-252	$A_1 \simeq A_2$; A_3 broad shoulder.
238	½		245	252	$A_1 > A_2$; A_1 very sharp
231	½		243	251	$A_1 > A_2$; A_1 very sharp
228	¼		239	253	see diagram 37, (page 146).
228	½		240	251	
228	1		245	253	
225	1			250	

* Melt crystallized chip.

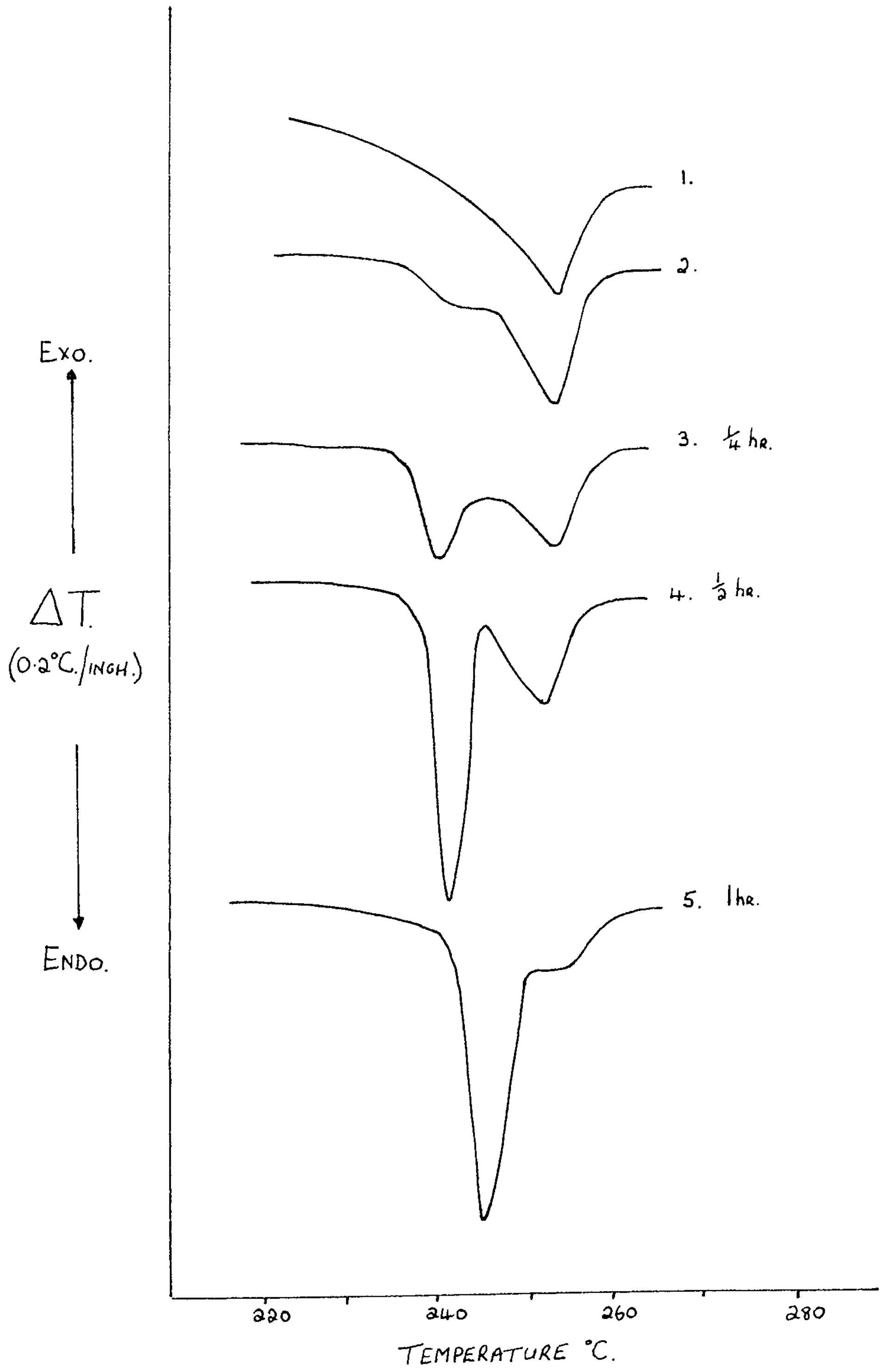


Diagram 37. Thermograms of poly(ethylene terephthalate).

1.,initial melting, 2.,remelt
3.,4.,5.,after annealing at 228°C.

The results given in these tables 5:31 to 5:42 (pages 134 to 145) are discussed in greater detail in 6:12 onwards.

In nearly every polymer examined, some degree of double melting endotherm formation was observed after annealing. Therefore, such thermal behaviour was not just a property of 66 nylon and the polyamides. The degree of resolution and the size of the new melting endotherm formed on annealing, varied from polymer to polymer. Only poly(ethylene terephthalate) seemed to show strictly comparable behaviour to 66 nylon. As the annealing time at a given temperature increased, so did the size and temperature of the first endotherm, whilst the final endotherm simultaneously decreased in size. (Diagram 37, page 146).

From these results, it was obvious that the temperature at which the annealing takes place was critical, if the most pronounced effects were to be obtained. Time only permitted a limited number of annealing temperatures to be studied for each polymer. It was quite possible that the optimum annealing temperature was not always found. A more detailed examination of these polymers could well result in thermal behaviour similar to that found for annealed 66 nylon being observed.

6. DISCUSSION OF EXPERIMENTAL RESULTS.

6:1 THE DETECTION OF MULTIPLE MELTING ENDOTHERMS BY D.T.A.

White's original observations (1) on the differential thermal analysis of 66 nylon fibres have been confirmed by using a Du Pont 900 Thermal Analyser. White obtained two melting endotherms for a drawn 66 nylon fibre in the temperature range 245-257°C. and 259-265°C. respectively and a broad single melting endotherm for undrawn polymer between 240° and 265°C. With the Du Pont instrument the two melting endotherms of the drawn fibre occurred at 250±1°C. and 258±1°C. whilst the single melting endotherm of the undrawn polymer occurred at 258±1°C. (See 5:1:2, diagram 15, page 64).

Other workers have also shown similar effects for both 6 and 66 nylon fibres, (66, 96-98) but thermograms of 66 nylon fibres have been published showing only a single endotherm. (66-67) It seems likely that this apparent anomaly results from the type of D.T.A. cell used by the different workers.

White's D.T.A. apparatus (2) had metal thermocouple pockets which fitted closely into metal sample and reference holders, fitting into holes in the D.T.A. cell block. He used fairly large samples (0.5 g.) to obtain a sufficiently large ΔT signal which could be recorded without further amplification, using a low heating rate. The fibre was wound as a thin layer around the outside of the metal thermocouple pocket. This cell design incorporated two major requirements of a D.T.A. cell able to resolve two neighbouring transitions. Firstly, because the fibre was wound as a thin layer, the thermal contact between the sample and sample thermocouple was high. Hence the heat change arising from any thermal transition in the fibre was rapidly transmitted to the sample thermocouple via the metal thermocouple pocket.

Secondly, the high thermal conductivity of the metal thermocouple pocket enabled the system to rapidly regain its dynamic thermal equilibrium after a transition had occurred. The metal assisted in increasing the rate of dissipation of the heat of the transition throughout the system. Hence the system's dynamic thermal equilibrium was regained in between the two transitions of the drawn fibre and two distinct endotherms were observed.

However, since D.T.A. is a dynamic technique, unless very slow heating rates are employed, true thermal re-equilibration can not occur in between two neighbouring transitions. As White's results (1) show, the complete resolution of the endotherms of the drawn yarn into two separate peaks was never quite achieved.

The modified Keavney and Eberlin D.T.A. cell, initially used in this work (3:1:1) lacked both of the essential properties of White's apparatus. The radial design resulted in a decreasing thermal gradient, (cell block → glass sample cell → sample → thermocouple) across the cell. There was only a limited thermal contact between the aluminium cell block and the loose fitting, low thermal conductivity, glass sample cells.

Since the sample size was again fairly large (up to 0.5 g.), to obtain a reasonable Δ T signal without further amplification for recording purposes, a thermal gradient could also exist within the sample. The outer edges of the sample would melt initially, and by the time the sample around the thermocouple melted, this molten material would be above its melting point. Since the temperature recording thermocouple was nearer the outer edge of the cell, the temperature of this molten material would be recorded as the temperature at which the transition occurred. Hence the high values for the melting point of benzoic acid and 66 nylon obtained with this cell. (Tables 5:1, 5:2, pages 60 and 61.)

The thermal gradients and the low thermal conductivity of the cell system effectively prevented the re-establishment of the cell's dynamic thermal equilibrium in between two melting endotherms. The resulting thermograms of drawn 66 nylon yarn therefore only showed a single broad melting endotherm at higher temperatures (260-280°C. Table 5:2, page 61) than those quoted by White. (1)

When silicone oil, which is chemically inert towards 66 nylon, thermally stable (above 260°C. it starts to "smoke"), and has a high thermal conductivity compared to nitrogen, was added to the sample and reference cells, much better results were obtained. The increase in the thermal conductivity, caused by the silicone oil, reduced the thermal gradients across the cell and so the transition temperatures decreased slightly (250°-270°C. for 66 nylon, see table 5:2 page 61). It also aided the re-establishment of the dynamic thermal equilibrium in the cell between the two melting endotherms of drawn 66 nylon. Thermograms with silicone oil present now showed two rather poorly resolved endotherms (table 5:2 page 61). When smaller samples were used (0.04 g.) although the peak area was reduced, the peak resolution was much better showing that the thermal equilibrium was restored more rapidly with the smaller sample. (Diagram 14, page 62).

The Du Pont standard "micro" cell (3:1:2), which was used for the majority of this work had similar properties to White's cell. The thermocouple was in direct contact with the sample. The same thermocouple also measured the temperature. The very small sample size (0.003 g.) in the small sample holders (2 mm. diameter) resulted in the rapid re-establishment of the cell's dynamic thermal equilibrium in between two neighbouring endotherms, without thermal gradients in the sample. It was possible, by choosing a very slow heating rate (1°C./minute) to resolve the two melting endotherms of a drawn 66 nylon fibre completely. (Diagram 8, page 36). Normally a heating rate of 5°C./minute was used. This gave sufficient resolution of the two endotherms within a reasonable period of time. A lower Δ T sensitivity setting could be used with the faster heating rate, thus reducing the "noise" level on the thermogram. (3:1:3).

The small sample size used and its rapid thermal equilibration led to much sharper endotherms than those described by White. It also probably accounts for the slight decrease in the temperatures of the endotherms recorded with the Du Pont instrument.

The importance of the rapid re-establishment of the cell's dynamic thermal equilibrium in resolving two neighbouring thermal transitions was emphasized when the Du Pont Calorimeter cell was used for quantitative determinations. In the Calorimeter cell (Diagram 10, page 39) the sample was placed in an aluminium liner in direct contact with the sample cup which was attached to the thermocouple. It was then completely isolated from the rest of the cell system. Hence after a thermal transition, re-establishment of the dynamic thermal equilibrium was slow and the endotherm resolution poor. Unless slower heating rates were used, the degree of endotherm resolution of the Calorimeter cell was much lower than the standard D.T.A. cell under comparable conditions.

6:2 WHITE'S OBSERVATIONS. - THE MELTING OF DRAWN 66 NYLON FIBRES AND BRISTLE.

White's observations, (1) on the melting of a drawn 66 nylon fibre have been confirmed. (3:1:2) Visual observation of the melting of the fibre, confirmed that it retained its physical form until almost the tip of the second melting endotherm (258°C.) was reached, as White suggested. (5:1:2).

White was not able to study the recrystallization and remelting of his samples very readily. His experiments were carried out in air, and once his samples had melted, degradation commenced, making the samples useless for further study. (2) However, he did describe an experiment in which a drawn 66 nylon fibre was heated to the temperature in between the two melting endotherms, cooled and then reheated. From observations made during this experiment, coupled with birefringence and X-ray examination of the fibre, he deduced that the first melting endotherm was caused by the loss of orientation produced by the original drawing process.

When drawn fibre or bristle was heated in an inert atmosphere in the Du Pont cell to the temperature between the two melting endotherms and allowed to cool, a crystallization exotherm was observed. This occurred at 242°C., instead of 238°-228°C., the normal crystallization temperature of molten 66 nylon. White did not report a crystallization exotherm when he carried out a similar experiment. (1)

This crystallization exotherm could have only arisen from the recrystallization of polymer molecules whose partial melting or disordering was represented by the first melting endotherm. The first melting endotherm could only result from a partial melting process, otherwise the physical form of the fibre would have been destroyed.

When the sample was reheated, melting did not appear to recommence until the temperature at which the first melting run ceased, was reached, then only a single melting endotherm was observed. Hence the structures represented by the first melting endotherm and the subsequent crystallization exotherm had been completely destroyed and the recrystallization must have occurred on residual nuclei, and not as a separate phase.

The drawn 66 nylon bristle had shrunk by as much as 16.9% by the time the first endotherm was complete, showing that loss of orientation has occurred. Presumably to allow this loss of orientation to occur some bonds in the structure of the fibre must have been broken and it was the recrystallization of these broken units that was represented by the crystallization endotherm. Then, on remelting, no further change would occur in the polymer until the final melting process commenced.

6:3 THE ANNEALING OF DRAWN 66 NYLON BRISTLE.

As the annealing time at 242°C. was increased, the first melting endotherm of unrestrained drawn 66 nylon bristle increased, whilst the second, simultaneously decreased. (5:1:6). The X-ray diffraction patterns of the annealed drawn bristle had sharper diffraction spots and arcs than the unannealed drawn bristle. (5:10). This showed that the crystalline perfection of the bristle had increased during the annealing period. Most of the increase in sharpness of the diffraction spots appeared to occur within a relatively short annealing time, cf. Fuller, et al., (127). Density measurements on the annealed bristle showed a similar trend, the density increased rapidly initially but levelled off as the annealing time increased (5:3, Diagram 29, page 94). This was further evidence that the crystalline perfection of the drawn bristle increased on annealing.

When the annealed bristle was heated to the temperature between the two endotherms, a crystallization exotherm was again observed on cooling. The total shrinkage of the annealed bristle was now only 8.0% compared to the 16.9% of the unannealed sample.

The annealing process would tend to relax the oriented structure of the drawn bristle. If White's original explanation of the two melting endotherms of a drawn fibre was correct, melting an annealed drawn bristle should have resulted in a smaller first melting endotherm, because there would be less oriented material to melt in the annealed sample. However, experimentally, the size of the first melting endotherm increased, rather than decreased after the drawn bristle had been annealed.

If the overall crystalline perfection increased, as indicated by the X-rays and density measurements, then the amount of heat required to finally disrupt the polymer and convert it from a solid to a liquid should be greater. However, the size of the final melting endotherm decreases.

It has been suggested that on the annealing of a drawn 66 nylon fibre, the extended polymer chains reform as a result of a partial melting process into folded polymer chains, with no change in crystal orientation. (8) In poly(ethylene), Wunderlich and Arakawa have shown that poly(ethylene) crystallized in the form of extended chains, melts at a higher temperature than the polymer in the folded chain form. (78)

If this was occurring in the annealed drawn 66 nylon bristle, then the increase in size of the first melting endotherm, and also the decrease in the shrinkage observed, could be due to the reduction in the number of extended chains.

This could also explain the recrystallization exotherm observed when a drawn annealed bristle was heated to the temperature between the two endotherms. The crystallization peak would represent the random crystallization of the folded chain units that had melted, causing the first melting endotherm. Because their recrystallization was random, on remelting, they would melt with the remainder of the relaxed molecules in the polymer. However, what caused the recrystallization exotherm observed when a non annealed bristle was heated to the temperature between the endotherms and allow to cool?. In this case, there should be no folded chains to melt, as all the polymer chains were thought to be in an extended chain form in the drawn polymer.

6:4 THE MELTING OF ANNEALED 66 NYLON CHIP AND FILM.

66 nylon chip or film, as received from the manufacturers, only showed a single melting endotherm. If the chip or film was annealed prior to melting, two melting endotherms were observed. As the time of annealing at a given temperature increased, the size of the first endotherm increased, whilst simultaneously the second decreased.

No melting of the polymer should have occurred at the temperature at which the annealing experiments were carried out (220-254°C.) as shown by experiments using the Du Pont visual D.T.A. cell. (5:1:2) However, the onset of segmental chain rotation in 66 nylon has been shown to occur at much lower temperatures ($\simeq$ 160°C.) when the crystalline unit cell changed from triclinic to psuedo-haxagonal. (29) Therefore, during an annealing process, the molecules could undergo some rearrangement without any melting occurring.

By analogy with other bulk polymers, it was assumed that the basic morphology of bulk 66 nylon was based on some form of folded chain unit. On annealing, some change occurred which altered these original folded chain units and caused them to melt at a lower temperature than before. The experimental evidence from other annealed polymers suggested that on annealing, the size of the folded chain units should increase, because the fold length increased. (39) These longer folded chain units should then melt at a higher temperature, since they more nearly approach an extended chain configuration. The longer the annealing period, the higher the percentage of molecules in the equilibrium chain fold length at that temperature and therefore the narrower the melting range.

In this work however, the new melting endotherm has always appeared at a lower temperature than the original final melting endotherm. This has also been observed with other polymers. This was contrary to the previously reported facts, (39) and suggested that smaller folded chain units were being formed on annealing. These then melted at a lower temperature than the original folded chain units. The longer a sample was held at a given temperature, the greater the number of these new folded chain units formed, resulting in the increase in size, sharpness and melting temperature of the first endotherm.

Normally, the higher the annealing temperature, the greater the fold thickness and the higher the final melting point. This did not apply to 66 nylon, firstly since at annealing temperatures above 248°C., the first endotherm was not observed, unless the sample was allowed to cool, indicating the thermal instability of the cause of the first endotherm. Secondly, the final melting did not increase with higher annealing temperatures.

The partial melting of these smaller chain fold units would explain the crystallization exotherm observed when an annealed 66 nylon sample was heated to the temperature between the two endotherms and allowed to cool. However, it is difficult to see why fresh chain folds could not develop during cooling to give a small first endotherm on remelting as observed on cooling a truly molten sample (see 6:5). On remelting an annealed sample which had been heated to the temperature between the endotherms and allowed to cool, melting recommenced at the temperature at which the previous melting run ceased.

Density measurements on annealed 66 nylon film, showed that the density of the film initially increased rapidly, but soon became more constant. (Diagram 28, page 94). This indicated that there had been an increase in crystallinity during the annealing.

The wide angle X-ray results on the annealed film showed that after a fairly short annealing time, the crystalline perfection had become effectively constant in a similar manner to the density changes (5;10). A similar result was obtained by Fuller, et.al. (127) when they examined the effect of heat treatment on the crystallinity of 66 and 610 nylons. Initially on annealing, there was an increase in crystalline perfection, as shown by the sharpening of the X-ray reflections. This increase rapidly ceased (after 5 minutes at 200°C. for 66 nylon)and no further increase was observed even after longer annealing periods.

The small angle X-ray scattering photographs also showed that changes occurred in the film on annealing. These changes (5:10) can be interpreted as either a change in the crystalline fold length, or an increase in the overall crystalline perfection of the sample.

The quantative data on the annealing of 66 nylon polymer chip indicated that the crystallinity of the sample increased as the annealing time increased. After a sufficiently long annealing time, only a single melting endotherm was observed and the percentage crystallinity had reached its highest level. (5:4:2b).

It must therefore be assumed that if new smaller chain folded units were being formed from the original chain folded units, these smaller units had a higher crystalline perfection than the original ones.

6:5 THE MELTING OF SAMPLES OF 66 NYLON WHICH HAVE BEEN MAINTAINED IN THE MOLTEN STATE FOR SOME TIME BEFORE CRYSTALLIZATION.

White was unable to study the remelting of 66 nylon for reasons already discussed. (6:2). When remelting was examined using the Du Pont 900 Thermal Analyser, the same form of thermogram was always observed, providing the sample whatever its original physical form or thermal history, was kept molten for ten minutes and then cooled naturally to 200°C. before remelting. This thermogram contained two endotherms. The first, the minor, occurred between 242° and 249°C., the second, the major, between 254° and 259°C.

Initially a melt temperature of 270°C. was chosen purely arbitarily, and the results of many remelting traces were very similar. However, it was suggested that 270°C. was not a high enough temperature to ensure that a sample's previous thermal history and structure were destroyed. The melt temperature was increased to 290°C. for several experiments, but no major differences were noted in the subsequent remelting endotherms.

Further experiments using different melt temperatures between 260° and 290°C. on the same 66 nylon sample indicated that both the crystallization exotherm and the remelting endotherms decreased in temperature as the melt temperature increased. (5:1:3).

This behaviour can be regarded as the result of two concurrent effects. Firstly, as the melt temperature increased, the number of residual nuclei which still probably remained undestroyed after a low temperature melt (262°C.) allowed recrystallization to occur at a fairly high temperature. Since the rate of crystallization on these existing nuclei would be comparatively slow, a low broad crystallization exotherm would be expected, as observed experimentally. As the melt temperature increased, the number of residual nuclei would decrease. Recrystallization would then begin at the temperature at which nuclei reformed. These nuclei would grow more rapidly than the older ones and so crystallization would be fairly rapid. Thus, it would occur over a shorter time and give rise to a much sharper crystallization exotherm. (5:1:3).

Evidence for this behaviour was shown when a thin film of 66 nylon, containing large spherulites was melted on the hot stage microscope. The optical birefringence disappeared at 271°C., and then the heating was stopped. As the hot stage cooled, the birefringence reappeared in exactly the same spherulites that existed before the birefringence disappeared. (5:1:4b). This showed that the original spherulites had not been completely destroyed at the temperature at which the birefringence disappeared. Eventually a melt temperature would have been reached above which all the nuclei would have been completely destroyed and all subsequent recrystallizations would have occurred at effectively the same rate. However, simultaneously, as the melt temperature increased, the possibility of sample degradation also increased. Any degradation products would tend to reduce the overall crystallinity of the sample and prevent crystallization from occurring until lower temperatures were reached. Being impurities, they would tend to lower the melting point of the sample. The amount of degradation would be dependent on the melt temperature, and the time the sample remained in the molten state.

The fact that changes occurred when samples were maintained in the molten state for considerable periods of time was shown by the quantitative studies on the annealing of 66 nylon (Table 5:16, page 105). If the area of the crystallization peak was plotted against the total time the samples had been in the molten state (285°C.), a gradual decrease in the peak area with increasing time was observed. (Diagram 38, page 158). The changes that occurred were shown to be due to degradation effects since when the sample was finally removed from the calorimeter cell, it failed to completely dissolve in 98% formic acid. This result may be a slight over simplification, since no account has been taken of the fact that the sample had been maintained at 242°C. for considerable periods in between the actual melting and recrystallization experiments. However at 242°C., when the polymer was still in the solid state, degradation would not take place so rapidly as in the molten state.

Hence, the melt temperature could affect the sample's subsequent thermal properties, by affecting the temperatures at which endotherms occurred. It appeared that 270°C., the original melt temperature was sufficiently high to destroy most of the sample's previous history without causing too much degradation. However, it did not explain why these particular melting endotherms were always observed.

A possible explanation was that the small first endotherm was caused by the remelting of polymer that had recrystallized or rearranged itself into a smaller folded chain configuration as suggested previously (6:4). The rate of cooling in the D.T.A. cell was such that the sample might remain long enough at the temperatures at which the

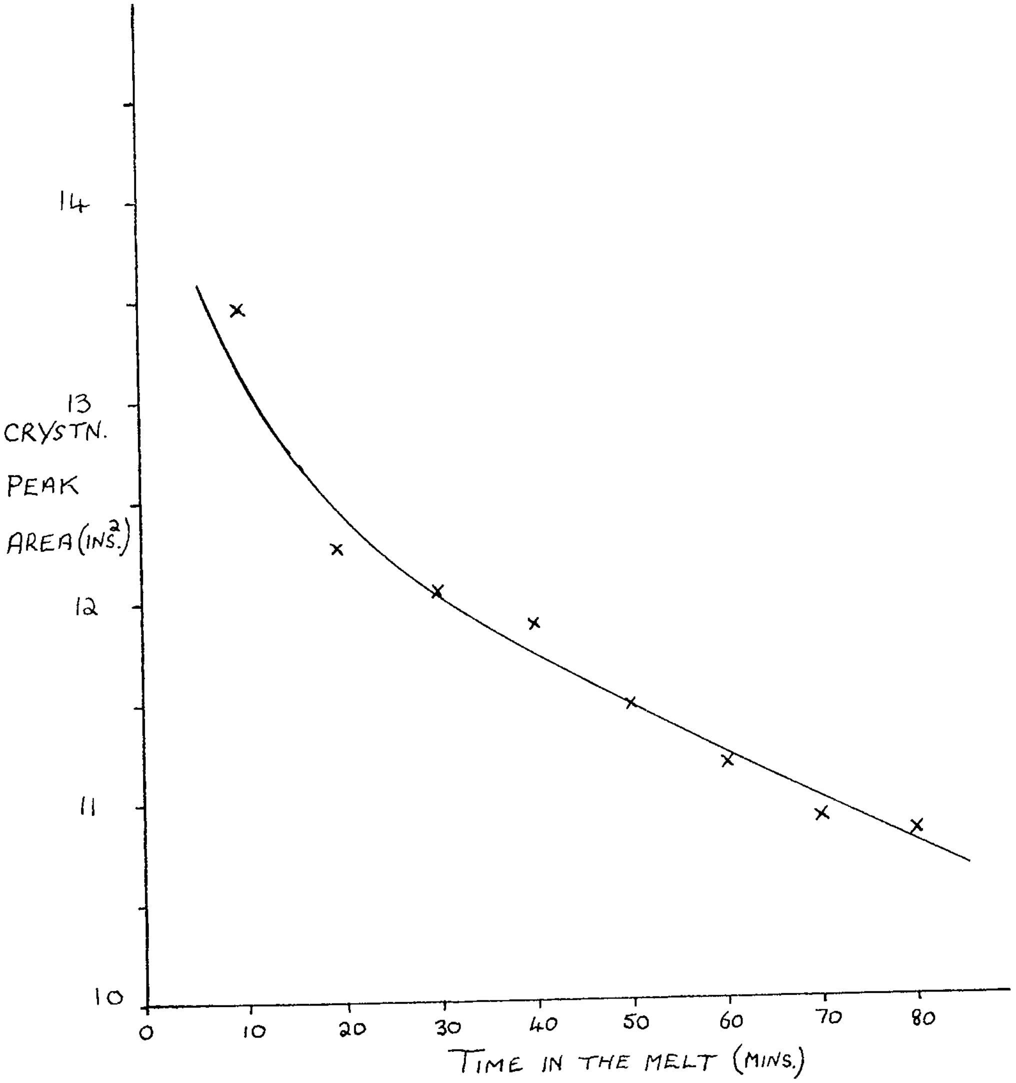


Diagram 38. The effect on the crystallization exotherm area of a single 66 Nylon sample as the time in the melt (285°C.) was increased. (Data taken from Table 5:16)

new smaller chain folds could form. Since the time at these temperatures would be fairly limited, only a small number of the new chain folds would form, hence the small size of the first endotherm. These folds must have been formed either before, or during the actual crystallization, since the effect was observed if the sample was reheated directly after the crystallization exotherm was complete, and no further cooling took place.

When 66 nylon polymer chip was manufactured, it was extruded and rapidly cooled. The rate of extrusion and cooling were sufficiently rapid to prevent any of the smaller folded chain units from being formed. So, on the initial melting of the polymer chip, only a single melting endotherm was observed. This was confirmed, when a 66 nylon film was heated for ten minutes at 270°C. on a hot plate and then allowed to cool rapidly in air. A subsequent thermogram of the sample only contained a single melting endotherm, thus showing the more rapid cooling prevented any smaller chain folds from being formed.

It was possible that the shape of the sample tube in the D.T.A. cell block was influencing the results obtained. However when 66 nylon samples were annealed in a silicone oil bath, (3:2) exactly similar effects were observed to those obtained when the samples were annealed in the D.T.A. cell. Therefore, the shape of the D.T.A. cell was not affecting the thermograms.

6:6 THE EFFECT OF CONTROLLED MELT CRYSTALLIZATION ON THE SUBSEQUENT REMELTING THERMOGRAMS OF 66 NYLON.

It has been suggested (6:5) that the rate of cooling from the melt influenced the subsequent D.T.A. melting thermograms. Isothermal crystallization of a molten sample would alter its cooling rate and therefore should have some effect on a subsequent thermogram.

Isothermal melt crystallizations were carried out for various periods of time at different temperatures between 238° and 255°C. (5:1:5) As the crystallization time at a given temperature increased, so did the size of the first melting endotherm, whilst simultaneously, the second decreased. The lower the crystallization temperature, below 242°C., the longer the time required to obtain an equivalent increase in the size of the first endotherm.

At melt crystallization temperatures of 245°C. and above, the change was much less marked than at lower temperatures. This was to be partly expected since now the melt crystallization was taking place at temperatures approximately the same, or above that, at which the first melting endotherm occurred. Unless the sample was allowed to cool before reheating, the first melting endotherm was not observed. This suggested that above a certain temperature the phenomenon which caused the first melting endotherm was thermally unstable. (6:4) The cause of the first endotherm, on remelting after cooling from 248°C. and above, must therefore have developed during the cooling.

When samples, which were crystallized at 242°C. or below, were reheated directly from the melt crystallization temperature without cooling, much better resolution of the two endotherms was obtained, than when the sample was allowed to cool to 200°C. before reheating commenced. (Compare Diagrams 20 and 21, pages 74 and 76). Except after the very short melt crystallization times no significant crystallization exotherms were observed.

This suggested, firstly, that if the crystallization was complete, then the poorer resolution of the melting endotherm of samples which were cooled before remelting, could not be attributed to polymer which had crystallized out during the cooling process. Secondly, since the first melting endotherm continued to increase in size with increasing melt crystallization time, although crystallization was complete, the cause of the increase in size of the first endotherm was not the primary crystallization. The disappearance of the crystallization exotherm within 10 minutes at 242°C., ie. the primary crystallization was complete, agreed with Magill's work on the crystallization of 66 nylon at various temperatures.(145)

As a result, the annealing experiments discussed in 6:4 were carried out, confirming that the first melting endotherm was the result of annealing rather than the primary crystallization.

The lack of resolution observed after a sample had been cooled from the melt crystallization temperature rather than remelted directly, must be the result of further changes that occurred in the sample after the annealing process ceased. If during the cooling, further chain folding occurred, obviously to a much lesser extent than before, this would increase the size distribution of the chain folded units. This would cause melting to occur over a wider temperature range and so reduce the overall peak resolution. Since this involved no heat changes, no crystallization exotherms were observed.

6:7 THE EFFECT OF MOLECULAR WEIGHT ON THE MELTING THERMOGRAMS.

66 nylon is a condensation polymer, made from hexamethylene diamine and adipic acid.

$$NH_2(CH_2)_6NH_2 + HOOC(CH_2)_4COOH$$

$$\rightleftharpoons$$

$$HN/CH_2)_6NHOC(CH_2)_4CO + H_2O \qquad \text{———eqn.6:1.}$$

Further polymerisation on heating is possible, when two polymer molecules can further react with the elimination of water.

$$P_2NH_2 \; + \; P_2COOH \; \rightleftharpoons \; P_1NHOCP_2 \; + \; H_2O. \text{———eqn.6:2.}$$

(where P = polymer molecule.)

This type of reaction has been shown to occur at fairly low temperatures (up to 130°C.) in the solid state, in a stream of nitrogen.(152) Conditions in the Du Pont D.T.A. cell during the annealing process were similar to those described, but the temperatures involved were much higher. Therefore, kinetically the forward reaction would be even more favoured, both during an annealing process and in the melt, and changes in the sample's molecular weight might be expected to occur.

Because of the small sample size and the design of the D.T.A. cell, it was difficult to recover and examine samples for possible changes in molecular weight caused by a particular experiment. The alternative procedure of examining the melting, recrystallization and annealing of commercial samples of increasing molecular weight, was adopted.

Experiments showed (5:1:2 and 5:1:6) that no changes in the melting, recrystallization or annealing behaviour were observed that could be attributed to an increase in the molecular weight.

This was not surprising, when the melt, recrystallization, remelt sequence was considered. If any molecular weight change did occur, it did not affect the remelting thermograms to any great extent as shown by their reproducibility.

6:8 THE MELTING AND ANNEALING OF 66 NYLON CONTAINING NEGATIVE SPHERULITES.

66 nylon has been shown to exist in at least three different

spherulitic forms. (35,36) The positive spherulites which melt at 258°C. were the most common. Negative and also larger fibrous birefringent spherulites which both melt at 265°C., were prepared under more rigid crystallization conditions.

Samples of 66 nylon containing either positive or negative spherulites were prepared on a hot stage microscope. (5:1:4). The subsequent thermograms of these samples showed either a single melting endotherm at 258°C. for the positive spherulites or a low broad endotherm at 256°C. followed by a much sharper one at 265°C. for the negative spherulites. The broad peak at 256°C. was almost certainly due to the melting of polymer in the sample which had not been crystallized as negative spherulites.

Therefore, the two melting endotherms that have been observed could not be the result of the co-existence of positive and negative spherulites in the same sample.

When samples containing either positive or negative spherulites were annealed at 242°C. on the hot stage microscope, no visual changes occurred in the spherulites, as photographs taken throughout the annealing period showed. (5:1:7).

However, the subsequent thermograms of these annealed samples showed that changes had occurred. After annealing, the sample containing positive spherulites had two melting endotherms instead of the original single one. (5:1:7). This was identical with the effect observed when bulk 66 nylon chip was annealed. (5:1:6). In the sample containing negative spherulites, the original broad first melting endotherm had developed into two endotherms at 247°C. and 257°C. respectively on annealing, whilst the second original endotherm (265°C.) remained unaltered. (5:1:7). Similar changes were observed when samples were annealed in the D.T.A. apparatus rather than on the hot stage microscope. (5:1:7).

The following conclusions can be drawn from these experiments. Firstly, the changes responsible for the formation of the first melting endotherm on annealing were of such a nature that they could not be detected by the optical methods used here. Therefore the changes must occur within the polymer on such a scale so as not to disrupt the spherulitic morphology.

Secondly, it appeared from their thermograms, that the negative spherulites were relatively unaffected by the annealing process. Therefore, the effect must occur in the regions of the sample containing either non spherulitic polymer or else positive spherulites.

6:9 THE PRECIPITATION OF 66 NYLON FROM SOLUTION.

When 66 nylon was precipitated from solution, the subsequent melting thermograms were related to the method used.

6:9:1 THE SOLVENT/NON SOLVENT METHOD OF PRECIPITATION.

When this method was used, the factor that influenced the melting thermogram most, was the rate at which precipitation took place.

Instantaneous precipitation from a formic acid solution into excess methanol yielded samples with only a single melting endotherm. Slower precipitation, by adding methanol to the formic acid solution, yielded samples with double melting endotherms. (5:2:3).

Badami & Harris, (135) using a slow rate of precipitation, similar to the second method described above, were able to isolate lamella structures in the precipitate. These they identified as being single crystals. They found the slow evaporation of a solution of 66 nylon in formic acid also produced what they described as single crystals.

Their experiments were repeated, and the subsequent thermograms both contained two melting endotherms. (5:1:4A).

It was assumed that the structures described by Badami & Harris were present in the samples prepared by their techniques. Attempts to show that they were using an electron microscope (by the kind permission of the Metallurgy Dept.) were unsuccessful. This was most probably due to the lack of technique in preparing the samples for the electron microscope, rather than disintegration of the polymer sample when exposed to the electron beam, as observed by Keller. (133)

It has been proposed that polymer single crystals are formed by the polymer molecules regularly folding back on themselves. (2:1) If 66 nylon single crystals could be made by precipitation methods, and these samples have double, rather than single melting endotherms, it seems reasonable that the new lower temperature endotherm was associated with the single crystal formation.

Unlike instantaneous precipitation, the slower method will allow folded chain units to form more readily. Density measurements on precipitated samples having single or double melting endotherms were consistent with this idea. The density of precipitated polymer having two melting endotherms was greater than that of polymer with only one. (1.780 g./ml. compared to 1.1500 g./ml.)

The regular folded chain single crystals would be expected to have a greater packing density than the more random folded bulk polymer. Therefore the voids content would be less and the density of the sample containing more regular chain folded units would be higher.

This difference was further confirmed by the iodine sorption values of the two precipitated samples. (5:9). The double melting endotherm sample absorbed 0.007 g.I_2/g. polymer less than the single melting endotherm sample. This indicated that the sample with two endotherms had a higher structural order than that with a single endotherm.

The X-ray diffraction data showed similar differences. The wide angle diffraction patterns of precipitated polymer samples having either a single or double melting endotherm were identical. Thus the crystalline perfection of the two samples must have been identical.

However, there were marked differences in the small angle X-ray scattering patterns. Such differences are usually interpreted as either a change in the fold length of the folded chain units, or a decrease in voids content, thus supporting the suggestions proposed above. (5:10).

During a slow precipitation process, some fractionation of the polymer into different molecular weights might be expected to occur. The effect of molecular weight changes on the thermograms has already been discussed. (6:7). Except in one instance, (5:2:3) no further polymer was recovered after the initial precipitation had taken place and it was assumed that if any fractionation had occurred during precipitation, it did not affect the subsequent thermogram.

6:9:2 PRECIPITATION FROM HOT BENZYL ALCOHOL SOLUTION.

The results from samples precipitated by this method were not clearly defined. (5:2:4)

Cooling is a slower process than instantaneous precipitation.

Therefore, if the rate of precipitation was a controlling factor, then cooling a hot benzyl alcohol solution should result in samples with some double endotherm character. Double melting endotherms were observed when precipitation was carried out by this method. (Table 5:9a, page 89) Controlling the precipitation rate still further, gave results which depended to a certain extent on whether the sample had been precipitated once or twice from the hot solution.

If the sample had only been precipitated once, the subsequent thermograms showed two melting endotherms, independent of the precipitation conditions used. (Table 5:9a, page 89). At the highest precipitation temperature though, (130°C.) the first melting endotherm was not very well resolved.

When the sample had been precipitated once, redissolved and then finally reprecipitated, using similar conditions to the previous experiments, only a single melting endotherm was observed at the highest precipitation temperature (130°C.). At lower precipitation temperatures, two melting endotherms were still observed, but their overall resolution was considerably reduced. The effect of precipitation at 130°C. on the thermograms was independent of the temperature to which the original precipitated sample was reheated to obtain a homogeneous solution, and the time the sample remained at 130°C. (5:2:4).

It was possible that the first melting endotherm was being caused by annealing occurring even at these low temperatures during the precipitation period, the benzyl alcohol acting as a plasticizer to enable the annealing to occur. When a sample of 66 nylon was annealed without having been dissolved in benzyl alcohol at 100°C., no difference could be detected between its melting thermogram and that of a similar sample annealed in silicone oil under identical conditions. Therefore, the presence of benzyl alcohol did not aid any annealing processes to occur at these temperatures.

If any annealing did occur, then it would be expected to take place more rapidly at the higher precipitation temperatures. No changes were observed in the melting thermograms of the precipitated samples, that were similar to those observed when true annealing experiments were carried out.

The temperature of the final melting endotherm of these samples remained effectively constant whether the sample had been reheated or not. The poor resolution of the endotherms after the initial precipitations at 130°C., and after the solutions had been reheated before being finally precipitated, suggested that some changes had occurred. However these changes only appeared to have affected the first melting endotherm.

It was possible that some of the acid end groups of the 66 nylon molecules had been esterified with benzyl alcohol during the time the solutions were at 130°C. and above. The polymer molecules would therefore be terminated with sterically bulky "benzyl" groups. These would not affect the hydrogen bonds between the polymer molecules (see later), and would be unlikely to affect the final melting point. However, because of their bulk they would hinder the formation of new chain folded units, since the bulky groups would tend to disrupt the uniform folding of the molecules. The presence of the more imperfect chain folded units would therefore give rise to a less well defined first melting endotherm as observed. (5:2:4).

It must however be assumed that some esterification occurred during the precipitation time at 130°C., even with a freshly prepared solution, to affect the subsequent thermograms. On reheating a previously precipitated solution, in which the polymer was already in a finely divided state, the chance of esterification would be increased and could have even taken place at temperatures below 130°C. Such behaviour would explain the reduced resolution of the melting endotherms of samples which had been cooled and reheated before they were finally precipitated.

The wide angle X-ray diffraction patterns of samples precipitated from benzyl alcohol solutions, and having either single or double melting endotherms, showed that both samples were highly crystalline. (5:10). Therefore the benzyl alcohol had not seriously affected the hydrogen bonding, otherwise a decrease in crystallinity would have occurred. The small angle X-ray scattering patterns showed similar changes to those observed with polymer precipitated by another method. (6:9:1). These indicated that the sample with two melting endotherms has less voids, or alternatively, changes in fold length, than the sample with only a single endotherm. This was consistant with the possibility of esterification with benzyl alcohol. The bulky end group hindered the formation of chain folds and increased the voids content, thus giving rise to samples which had poorly resolved double melting endotherms.

6:9:3 THE HEATING OF SAMPLES OF PRECIPITATED 66 NYLON TO THE TEMPERATURE IN BETWEEN THE TWO MELTING ENDOTHERMS.

Samples of precipitated 66 nylon having two melting endotherms which had been prepared by the solvent/non solvent method (6:9:1) were heated up to the temperature between the endotherms. They were then cooled before they were remelted. No crystallization exotherms were observed on cooling, unlike those obtained when similar experiments were carried out on drawn or annealed samples. (6:2 and 6:4). On reheating, only a single melting endotherm was observed, commencing at the temperature at which the initial heating run had ceased. (5:5).

With drawn or annealed samples, the crystallization exotherm was attributed to the recrystallization of polymer where partial melting caused the first endotherm. (6:2, and 6:4). With the precipitated samples, either a different effect caused the first endotherm, or else something prevented the recrystallization of the partially melted material. It seems unlikely that the precipitation, which would probably produce the more perfect chain folded units, would be likely to alter the melting process very much. Its most likely effect would be to increase the final melting temperature rather than cause two melting endotherms.

If partial melting caused the first endotherm of the precipitated samples, then recrystallization must have occurred simultaneously with the melting process. Otherwise, a crystallization exotherm would have been observed on cooling. Since an endotherm was recorded, the rate of melting must have been slightly faster than the rate of recrystallization. Therefore when the melting had ceased, there must have been some partially molten material present. This molten material would probably have had time to recrystallize in the short time between the end of the heating run and the start of the cooling run. This recrystallization would not have been recorded, since in the process of changing from a heating to a cooling run, the recorder pen was lifted off the chart paper.

6:10 DILATOMETRY.

The dilatometric experiments gave no further information about the melting, crystallization or annealing of 66 nylon (5:6).

6:11 QUANTITATIVE MEASUREMENTS ON THE ANNEALING AND MELTING OF 66 NYLON.

These experiments were performed to obtain some quantitative information about the changes that occurred in the thermograms of 66 nylon as a result of various thermal treatments, as observed by normal D.T.A. techniques. From them, it was hoped that the changes in the sample's crystallinity during a melt, crystallize, remelt, experiment could be determined. They would also show whether a sample's total crystallinity changed in the course of an annealing experiment and if there was any relationship between the annealing time and the measured crystallinity of the sample.

6:11:1 USING THE DU PONT CALORIMETER CELL.

A description of the cell and its method of use is given in section 3:1:4. The results obtained are given in 5:4 and fall into two separate sections, a) calibration and b) results on 66 nylon.

6:11:2 CALIBRATION OF THE DU PONT CALORIMETER CELL.

The calibration of the cell obtained the values of the heat transfer coefficient between the sample cup and the remainder of the cell, at different temperatures.

The initial attempts at calibration with pure metals, using the Du Pont X-Y recorder gave "E" values (calculated from eqn. 5:4:1 page 96) with large percentage errors. (Table 5:11, page 97). These errors increased as the temperatures of the melting transition increased.

Pure metals have a very narrow melting range and therefore very sharp D.T.A. melting endotherms. As the melting temperature increased, it was necessary to reduce the X axis ($T^oC.$) sensitivity, to be able to record the endotherms. So the actual peak recorded became even sharper. Measuring the areas of these small sharp peaks with a planimeter gave inconsistent results.

Although the peaks were sharp and well defined, the base line before and after the transition was not quite identical. It was possible to draw more than one baseline to a peak, thus giving rise to further errors.

To try to reduce the errors a time based recorder was used. This spread a transition out over a greater area of chart paper and thus reduced the effect of errors in the planimeter measurements.

Experiments were carried out, with a suitable time based recorder (5:4:2) to determine the reproducibility of the "E" value for the same calibration standard under various operating conditions (Tables 5:13, page 100 and 5:14, page 101). As these results show, no major changes were caused by using different heating rates (Table 5:13, page 100). Changing the ΔT sensitivity from 0.2 to 0.5°C./inch did not produce an exactly proportional increase in the total peak areas as the equation 5:4:2 (page 98) suggested. To minimise errors caused by this, experiments were carried out at the same ΔT setting whenever possible.

In all the calibration experiments carried out, the overall experimental reproducibility was approximately ± 5.0%. It was not possible to pin point the causes of the errors exactly, but some of the possible causes are discussed below.

The samples were weighed to ± 0.0001g. ie, to approximately ± 1.0% for a 11.0 mg. sample. The heating rates were carefully checked in some experiments, by measuring the rate of temperature increase in a given time. (see Table 5:13, page 100). Variations of up to ± 2.0% were recorded for any nominal setting of the heating rate. These variations would ultimately affect the value of the calibration factor since the heating rate is involved directly in eqn. 5:4:1 (page 96), or indirectly through the relationship with the recorder chart speed in eqn. 5:4:2 (page 98).

The errors in measuring the areas of the thermogram peaks by planimeter were small. A more major source of error was in the drawing of the base line for the various transitions. The peaks tended to have "tails" and not to return exactly to the identical base line before the onset of the peak. It is difficult to assess the actual percentage error for this, since it varied from each determination, even with consecutive ones on the same sample.

Variations in the cell atmosphere, and the degree of thermal contact between the sample, the sample liner and sample cup could also occur. These would have small but finite effects on the peak areas and hence on the calculations. They were kept to a minimum by trying to use identical operating conditions for each experiment.

The cumulative effect of such errors would account for the observed experimental error of ± 5.0% in the calibration experiments. This error meant that any calculations involving the derived "E" values also had an initial ± 5.0% error.

With polymer samples, the sources of error increase. With 66 nylon, there was the finite possibility of a weight change occurring during the course of an experiment due to the loss of equilibrium moisture or further condensation.

66 nylon melts over a relatively wide temperature range and its endotherms are not so well defined. The errors in measuring the correct peak areas will therefore increase. Therefore it was reasonable to expect somewhat larger percentage errors in the 66 nylon experiments than those obtained calibrating the Calorimeter Cell.

6:11:3 QUANTITATIVE DATA FOR 66 NYLON.

The results of the quantitative experiments on 66 nylon are given in 5:4:2B. They will be discussed in terms of their implications rather than in absolute terms. The heats of fusion (ΔH_f) were obtained by using equation 5:4:2 (page 98) and were then used to obtain the percentage crystallinity of the various samples. The percentage crystallinity was obtained by expressing the experimentally calculated heat of fusion as a percentage of the heat of fusion of 100% crystalline polymer. (5:4:2B).

The average crystallinity of the 66 nylon chip when it was first melted was 30.5 ± 6.7%. On recrystallization after being held for ten minutes at 285°C. the average crystallinity was 29.4 ± 7.2%.

These results indicated, as expected, that on crystallization after the initial melting, almost all the original crystallinity is regained. Normally, on reheating the samples after this crystallization, two melting endotherms appear. It has been proposed that the first melting endotherm observed on reheating was due to the melting of smaller folded chain units formed during the cooling from the melt. These new smaller folded chain units would only increase the overall percentage crystallinity slightly by increasing the packing together of the crystalline units (ie, by reducing the voids). However, any degradation which had taken place in the melt would help to offset this increase in crystallinity.

When 66 nylon chip was annealed in nitrogen, double endotherms formed as in the qualitative experiments (5:1:6) and the percentage crystallinity increased with the increasing annealing time, whether the experiments were carried out on the same sample or a fresh one each time. (Tables 5:15, page 104, and 5:17, page 106). The percentage crystallinity developed on crystallization from the melt following an annealing experiment, in general, decreased as the annealing time increased. (Table 5:16, page 105, 5:18, page 107 and 5:20, page 111). The implications of this decrease have already been considered. (6:5)

6:11:4 QUANTITATIVE DATA FOR 66 NYLON OBTAINED WITH WATER PRESENT DURING THE EXPERIMENTS.

Similar experiments to those described in 6:11:3 were carried out with water present in the calorimeter cell. (see 3:1:5 for further experimental details.)

Comparison of the results carried out in nitrogen alone or with water present would indicate whether the presence of water affected the experimental results.

With water present in the cell, the increase in the crystallinity after 14 hours annealing at 242°C. was 46%. (Table 5:19, page 110). The increase was only 27% when a similar experiment was carried out in nitrogen alone. (Table 5:17, page 106). The data obtained on crystallization from the melt with water present showed a similar trend.

These results show that the presence of water in the calorimeter cell during the quantitative experiments on the melting, crystallization and annealing of 66 nylon resulted in higher crystallinities. The reasons for this behaviour are not entirely clear. As suggested with drawn fibres, (147) water may be necessary to obtain highly crystalline samples. Other possibilities are that the water would prevent further condensation reactions from occurring. It would also help to reduce the amount of degradation taking place, thus allowing higher percentage crystallinities to be achieved.

It is difficult to decide which of these effects was responsible for the increased crystallinity observed when water was present in the cell. The effect can be emphasized by expressing the difference between the melting endotherm areas (as a percentage of the original endotherm's area), before and after an annealing experiment. For strict comparison purposes the experiments carried out before and after the actual annealing experiment were similar in nature, ie, 15 minutes annealing before and after the actual long annealing period. These results are given in Table 6:1 (page 173).

These results show that the presence of water in the calorimeter cell reduced the percentage decrease by 40% compared to a similar experiment carried out in nitrogen alone. They also show that as the annealing time increased in a nitrogen atmosphere, the percentage decrease in peak area also increased. This was probably indicative of the increasing amount of degradation taking place as the annealing time increased.

6:11:5 GENERAL OBSERVATIONS ON THE QUANTITATIVE DATA.

The calorimeter cell, under the operating conditions used, did not completely resolve the two melting endotherms obtained after a sample had been annealed. In practice the peaks were resolved visually and then their individual areas measured with a planimeter as before.

Table 6:2 (page 174) shows the average contribution of the two melting endotherms to the total peak area. It also shows the average percentage crystallinities of these samples.

These results contain large errors since the areas of the two peaks were obtained by extrapolation. However they indicate that the contribution of the first melting peak on annealing to the total area of the melting endotherm increased as the annealing time increased. The value of the average total percentage crystallinity only increased by about a third over the same period of time. Therefore the first melting endotherm did not completely result from just an increase in crystallinity.

This behaviour was consistent with the formation of smaller folded units, since although they would improve the crystalline perfection of the sample, the effect on the total percentage crystallinity would not be very marked. The inherent rigidness of the hydrogen bonded 66 nylon

TABLE 6:1 THE % DECREASE IN PEAK AREA AFTER THE ANNEALING OF IDENTICAL WEIGHT 66 NYLON SAMPLES FOR VARIOUS PERIODS OF TIME IN NITROGEN AND NITROGEN/WATER ATMOSPHERES.

Cell Atmosphere	Annealing Time hrs.	Peak Area Before ins.^{2}	Peak Area After ins.^{2}	% Decrease
N_2	1	10.92	10.46	4.2
N_2	2	12.25	10.29	16.0
N_2	14	11.80	9.22	21.8
H_2O/N_2	14	11.52	10.54	8.5

Data abstracted from Tables 5:17 (page 106) and 5:19 (page 110).

would restrict a great improvement in the total crystallinity of the sample.

However, by forming new chain folds, there is the possibility of the formation of intra molecular hydrogen bonding. A minimum of 5 backbone carbon atoms have been suggested as being necessary to form a fold in polyethylene.(6) Therefore folding could only occur in a hexa-methylene diamine residue rather than in an adipic acid remnant. Such folding is just feasible without destroying the overall hydrogen bonded structure of 66 nylon. These new intra molecular hydrogen bonds would tend to increase the samples perfection without seriously affecting the overall total crystallinity.

6:12 MULTIPLE MELTING ENDOTHERMS IN OTHER POLYMERS.

The melting and annealing of other common polymers, including polyamides, hydrocarbon polymers and polyesters were examined to discover how widely the effects observed in 66 nylon applied to other polymers. If the effect was more general, then further study of one of the lower melting polymers, such as poly(ethylene), could be carried out and be used as a model to further study the causes of multiple

TABLE 6:2 THE CONTRIBUTION OF THE TWO MELTING ENDOTHERMS OF SAMPLES OF 66 NYLON ANNEALED AT 242°C. FOR VARIOUS PERIODS OF TIME, AS THE ANNEALING TIME INCREASED.

Annealing Time(hrs)	Average % Contribution of the 2 endotherms to the total area		Average % Crystallinity of samples
	1st peak	2nd peak	
Nil	-	100	30.5
0.25	28.8	70.2	29.7
0.5	28.7	71.1	29.3
1	35.5	63.2	37.1
2	47.7	52.3	38.5
4	67.5	31.7	38.7
14	100	-	41.7

(Data abstracted from Tables 5:15, 5:17, 5:19, (pages 104, 106, 110).

melting endotherms.

6:12:1 OTHER POLYAMIDES.

The experiments with other polyamides were carried out under similar operating conditions to those used for 66 nylon, using the Du Pont 900 Thermal Analyser. The results are given in 5:11. The polymers fall into two groups, a, those of commercial importance ie, 6, 610, 11 nylon and b, those of a more theoretical academic interest, ie, 7, 76, 77 and 68 nylons.

The drawn samples of 6 nylon fibre and 610 nylon bristle showed two melting endotherms on their initial melting, similar to those observed for drawn 66 nylon fibres. The first melting endotherm for the drawn sample of 6 nylon was not really a separate peak but only a slight inflexion on the low temperature side of the main melting endotherm, unlike the resolved peaks reported by Japanese workers. (97,98)

All the "chip" samples of these various polyamides had initial melting thermograms with only a single endotherm, except 76 nylon. The melting points of the samples agreed fairly well ($\simeq \pm$ 2.5%) with those quoted in the literature. (84,96,130) The variations were probably due to the different methods of manufacture of the various samples.

Ke and Sisko (96) in their examination of the melting of polyamides show similar thermograms for the same polymers studied here. Their thermogram of 76 nylon, although containing multiple melting endotherms, had a less pronounced first melting endotherm and no obvious exotherm between the two endotherms. The behaviour of the sample examined here suggested that at 212°C., some slight crystallization took place. Then at 234°C., melting occurred and this molten material recrystallized at 237°C. before the polymer finally melted at 245°C. (Table 5:27, page 128).

On reheating the samples, after they had been maintained in the molten state for ten minutes and then recrystallized, only 6, 68 and 11 nylon showed similar behaviour to that of 66 nylon under similar conditions, ie, the presence of a new small melting endotherm before the final endotherm. The effect was not very marked in the 68 nylon sample. This suggested that the conditions used in most instances did not result in the same effect as observed with 66 nylon.

On annealing, these other polyamides behaved like 66 nylon. In all instances, providing the correct annealing temperature had been found, a new lower temperature melting endotherm had developed after 30 minutes annealing. In a similar manner to 66 nylon, the temperature of annealing controlled the appearance and rate of development of the new endotherm.

A slightly more detailed study of 6, 610, and 11 nylon showed that the new endotherm also increased in size as the annealing time increased. (5:3:2). However, the effects were not so pronounced as with 66 nylon. Similar behaviour has been reported by Japanese workers for 6 nylon. (97,98)

Although a similar effect occurred with the 7, 76, 77, and 68 nylon samples, it was much more ill-defined compared to 66 nylon.

It can be said that the behaviour observed with 66 nylon when it was annealed, also applied to other members of the polyamide group of polymers. However, in most instances, the characteristic sequence of the melt, recrystallization, remelt thermograms was not comparable with that of 66 nylon under similar conditions.

A sample of 6 nylon made by ionic polymerisation was examined. Because of its method of manufacture, the polymer would be expected to contain some side chains and branches. These would then tend to disrupt the uniform packing of the polymer and could affect the melting point of the polymer.

The recorded melting point was 212°C., some 8°C. lower than the other samples of 6 nylon. Although no annealing experiments were carried out, on melt crystallization at 187°C., two melting endotherms were recorded at 208°C. and 212°C. So, even if the presence of side chains lowered the final melting temperature, they did not stop or hinder very much the process during the melt crystallization/annealing period that produced the double endotherms. At the melt crystallization temperature used, the crystallization would have been completed before the experiment was complete and therefore the sample would have been annealed as well.

6:12:2 POLY(ETHYLENE).

Both low density and high density poly(ethylene) were studied (see 4:6/4:7 for details of polymers). The low density material contains more side chains and these affect its melting and crystallization behaviour. The experiments were carried out under similar operating conditions to those used for 66 nylon and the results are given in tables 5:31; 5:32; 5:33. (Pages 134, 135, 136.)

The melting temperatures of 110°C. and 126°C. for the low density (L.D.) and the high density (H.D.) poly(ethylene) chip were comparable with the literature values. (130) Neither polymer showed any sign of a second melting endotherm after the sequence, melt, recrystallize, remelt, as 66 nylon did.

Highly drawn fibres of the H.D. poly(ethylene), (draw ratio 8:1) did not show any evidence for a second melting endotherm, suggesting that orientation did not affect the melting behaviour of this polymer.

When the L.D. poly(ethylene) was annealed at various temperatures between its D.T.A. melting and crystallization temperatures, two melting endotherms at approximately 105° and 110°C. were observed, whatever the annealing temperature. The new endotherm always appeared at a lower temperature than the original melting endotherm, similar to 66 nylon, and was always the minor of the two endotherms in size. Its degree of resolution varied and usually was not so well resolved as the first endotherm of annealed 66 nylon. It seemed to reach its maximum size after a fairly short annealing time and did not increase further after longer annealing times.

The annealing of H.D. poly(ethylene) followed a similar pattern to that of the L.D. material. Diagram 34, (page 137) shows the effect observed after a sample had been annealed for 30 minutes at various temperatures. The higher the annealing temperature, the larger the effect in a given time. Simultaneously the temperature of the new endotherm peak tended to decrease (Table 5:33, page 136). Again, no significant increase in the area of the first endotherm occurred, as the time of annealing increased.

The results of 18 hours annealing at 120°C. are more confused. The main melting endotherm occurred at 125°C., almost the same temperature at which the polymer originally melted. Since there was an inflexion at 128°C., (the final melting temperature of the previously annealed samples) it seems likely that the 125°C. endotherm rather than the 128°C. one was the new one. Its increase in melting temperature from 122° to 125°C. is consistent with the increase in the annealing temperature from 117° to 120°C., if the trend of the earlier annealing experiments was continued. The overall effect can then be compared with that observed during the annealing of 66 nylon.

From these results, it seems that similar effects occur in poly(ethylene) as in 66 nylon. However the important temperature/time dependence did not occur during the short annealing periods, and so the effects could not be strictly compared.

Poly(ethylene) has been one of the most intensely studied polymers. Annealing experiments have been carried out using D.T.A. techniques, (70,82,83) and results similar to those described above have been reported. Holden (70) has suggested that the two peaks resulted from the melting of different forms of crystalline units formed by slightly different modes of crystallization. Gray and Casey (82) proposed that they arose as the result of the formation of a discontinuous crystalline size distribution produced by the annealing process. The various sized crystallites then melted at different temperatures. Hoashi and Mochizuki (83) have proposed that the initially stable crystalline units tend to melt on annealing and reform as smaller crystalline units which subsequently melt at a lower temperature when the sample was remelted. They have also recently reported similar observations when poly(ethylene) was crystallized isothermally at 126°C. (153)

Although the ways in which these workers proposed that the different sized crystalline units were formed are different, they all concluded that it was the melting of these units that caused the multiple endotherms.

Four melting endotherms have been observed with poly(ethylene) crystallized under high pressures. (79) The major two of these have been shown to correspond to the melting of two different types of lamellae. (78) The melting of folded chain lamellae caused the lower temperature endotherm. It was tentatively proposed that the smaller endotherms preceeding these two were caused by the onset of segmental motion within the lamellae crystals.

Mandelkern and Allou (42) have shown that the two endotherms observed in the melting of poly(ethylene) single crystals can be further resolved to reveal an extra exothermic peak. This was suggested to be consistent with partial melting followed by recrystallization before the final melting. Peterlin and Meinel (154) reported that a double endotherm occurred with poly(ethylene) single crystals after short periods of annealing, and this could be explained in terms of the thickening of the crystals on annealing. Bair et al. (155) have also observed double melting endotherms for annealed poly(ethylene) single crystals. They also showed that they were related to the rate of lamellae reorganization that took place during annealing.

Peterlin and Meinel (86) have also observed double melting endotherms for nitric acid treated drawn poly(ethylene) film. They showed by careful fractionation, that the endotherms resulted from the melting of two different molecular weight fractions, which corresponded to two crystal types of different thickness.

Experiments on the annealing of bulk poly(ethylene) have shown.

that the lamella thickness increased as the annealing time increased at a given temperature. (39) These changes have been attributed to changes in the fold length of the polymer molecules. They take place without apparently affecting the visual morphology of the sample.

The changes observed in the melting thermograms after the polymer had been annealed could therefore be related to changes in the polymer's fold length. Such changes would lead to different sized crystalline units and therefore probably multiple melting endotherms.

6:12:3 POLY(PROPYLENE).

The melting behaviour of various samples of poly(propylene) is given in table 5:34, (page 138). The melting point obtained agreed with that given by Schotland (88) but was lower than that quoted by Geil. (130) Geil's sample was probably purer than the commercial samples used here and by Schotland and would have a higher melting point.

The drawn fibre had a very distinct sharp double melting endotherm at 164.8° and 170°C. The undrawn fibre only had a single melting endotherm at 160°C. (Diagram 35, page 139) Similar observations have been reported by Schwenker et al. (67) The two endotherms in their published thermogram were not so well resolved as those obtained with the Du Pont apparatus.

They found that the D.T.A. thermal behaviour of drawn poly(propylene) fibre was very similar to that reported by White (1) for drawn 66 nylon. For instance, the initial double melting endotherm of the drawn fibre reverted to a single one when the sample was remelted. They suggested that drawn poly(propylene) had two melting endotherms for the same reasons as drawn 66 nylon.

The lower melting point of the Shell poly(propylene) sample was probably due to the sample being unstabilised. As a result, some degradation of the sample would have occurred during its exposure to the atmosphere (it was an oldish sample) and this would have tended to lower its melting point.

The remelting endotherms of the stabilised polymer all contained multiple endotherms. (Diagram 35, page 139). In no instance were the endotherms fully resolved; they were a series of inflexions forming the main endotherm. They were characteristic of the polymer and occurred with most of the samples on remelting. What caused them is unknown. Whether they represented the melting of different types of spherulite formed during the crystallization from the melt was open to conjecture. At least four optically different types of poly(propylene) spherulite have been described, some of which melt at different temperatures.(156) A more detailed thermal study of the polymer should reveal whether this was a feasible explanation or not.

The results of the various annealing experiments on poly(propylene) are given in table 5:35 (page 140). Like 66 nylon there appeared to be a maximum annealing temperature (≃ 150°C.) above which multiple endotherms were no longer observed. Presumably the phenomenom causing the multiple endotherms was thermally unstable above 150°C.

At annealing temperatures below 150°C., multiple endotherms were observed after the majority of experiments. The endotherms were very poorly resolved compared to those of annealed 66 nylon. These thermograms appeared very similar to the remelting thermogram. (Diagram 34, page 137).

In none of the annealing experiments performed, was there any evidence of a systematic increase in the temperature or size of the new endotherm as the annealing time at a given temperature increased. It appeared, therefore, that under the conditions used, the annealing of poly(propylene) did not yield similar results to those of 66 nylon.

The annealing of poly(propylene) by D.T.A. techniques has been reported by Schotland.(88) His published thermograms indicated that the maximum changes in the melting endotherms occurred within a limited annealing temperature range 120° - 150°C. This was confirmed by the results obtained in this work. He also showed that after 1 hour's annealing at various increasing annealing temperatures, that the size and temperature of the lower temperature melting endotherm increased. This observation was not confirmed in this work. However, much shorter annealing times were used in this work, and so the effect may not have developed to the same extent.

Schotland suggested that the endotherms resulted from the melting of two crystallites of differing perfection. These were formed during crystallization from the melt, due to different nucleation processes. Heterogeneous nucleation took place at lower temperatures, producing less perfect crystallites, with lower melting points. The subsequent annealing process improved the perfection of the poorer crystallites, giving rise to the thermograms he observed.

6:12:4 POLY (4-METHYL PENTENE-1).

The results of the melting and annealing experiments on poly(4-methyl pentene-1) are given in table 5:36 (page141). The observed melting point, 227-229°C. was 7°C. lower than that quoted by Geil. (130) A double crystallization exotherm at 209° and 211°C. always occurred when samples were crystallized from the melt. The two exotherms were not fully resolved and suggest that two different crystallization processes may have taken place. Such a process had no obvious effect on subsequent remelting experiments, when only a single endotherm (228°C., sharper than the original) was observed.

Only a limited number of annealing experiments were performed. At temperatures above 211°C., two melting endotherms were always observed after 30 minutes annealing. When annealing was carried out at 221°C., the resolution of the two endotherms increased with increasing annealing time, similar to annealed 66 nylon. (Diagram 36, page 142). However the temperature of the first melting endotherm did not increase with increasing annealing time as occurred with 66 nylon. The results were sufficient to show that multiple endotherms could also be produced in poly (4-methyl pentene-1) by an annealing process.

Other workers have reported their studies on the melting and annealing of poly (4-methyl pentene-1) single crystals. (157) Their samples were produced by crystallizing a 0.024% toluene solution for either 48 hours at 72°C.(A) or 72 hours at 79°C.(B). The thermogram of sample (A) contained two distinct melting endotherms at 236° and 249°C., whilst sample (B) had only a single endotherm at 249°C. They were able to show by electron microscopy that sample (A) contained two distinct morphological types of crystals which they believed caused the two endotherms. They believed that the smaller ones had the lower melting point. Sample (B) only contained one type of crystal, similar in size to the smaller ones of sample (A). Therefore, they suggested that the crystalline perfection of the crystals was the deciding factor in controlling the subsequent melting behaviour.

These two samples were also annealed for 2 hours at various temperatures. After annealing at 230°C., the initial lamella thickness of all the crystals had increased by at least 100Å. Simultaneously holes had developed in the single crystals.

Single crystals are a selected type of polymer morphology. It is believed that all polymers, even in bulk are probably composed of some form of lamellae. In the experiments carried out on the annealing of bulk poly(4-methyl pentene-1), at much higher temperatures, it seemed reasonable to assume that a similar effect to that observed with the single crystals was occurring. After relatively short annealing times, the two different crystalline morphologies would not have developed sufficiently to give two distinct separate endotherms. They would be present in a matrix of polymer, containing a spectrum of all the variations of the two final crystalline morphologies. The thermogram of this sample would therefore be expected to contain two poorly resolved melting endotherms.

As the annealing time increased, the quantity and perfection of the two crystalline morphologies would also increase. A thermogram of a well annealed sample would therefore be expected to contain two reasonably well resolved melting endotherms. The results obtained on annealing poly (4-methyl pentene-1) were consistent with this type of behaviour.

6:12:5 POLY(FORMALDEHYDE).

The results of the experiments carried out on this polymer are given in table 5:37 (page 143). The experiments listed were performed as an initial "scouting" exercise and the results are included for completeness.

The two annealing experiments indicated that there was the possibility of producing multiple melting endotherms as a result of annealing.

6:12:6 POLY(ETHYLENE OXIDE).

The melting and crystallization data obtained for this polymer are given in table 5:38 (page 143). The melting points obtained, 58-59°C. are again lower than those quoted by Geil.(130) The reason for this was not known. It could have resulted from the different methods of measuring the melting point and also on the molecular weight distribution of the samples used. On remelting after crystallization, there was some evidence of a second melting endotherm appearing.

The results of the annealing experiments carried out on this polymer are given in table 5:39 (page 144). It proved difficult to maintain a stable annealing temperature. This was because the annealing temperature fell just below the minimum isothermal operating temperature of the Du Pont instrument. (see 5:12).

When the samples were annealed for 30 minutes at temperatures between 49° and 56°C. multiple melting endotherms were observed. However on the cooling from the annealing temperature prior to remelting, a small crystallization exotherm was observed. This suggested that some melting had taken place during the annealing. It was probably lower molecular weight polymer which had melted at the upper end of the annealing temperature range.

The results only indicate that under suitable annealing conditions multiple melting endotherms could be produced. A more detailed series of experiments would be necessary to establish whether the polymer followed similar trends to those observed with annealed 66 nylon.

6:12:7 ISOTACTIC POLY(PROPYLENE OXIDE).

Table 5:40 (page 144) gives the results of the various experiments carried out on this polymer. The melting point obtained agreed with that quoted by Geil (130) and also with the results obtained by Cooper, et al. (95)

For similar reasons to those given previously in 6:12:6, stable annealing temperatures were difficult to achieve. However, the results obtained indicated that annealing isotactic poly(propylene oxide) under the correct conditions also resulted in multiple melting endotherms.

The melting behaviour and the influence of the crystallization conditions on the melting point of isotactic poly(propylene oxide) have been investigated in detail. (95) Thermograms, with multiple melting endotherms were obtained under certain conditions. A premelting exotherm was observed in many instances. It was suggested that the melting endotherms were caused by different morphological forms of the same crystal structure or by crystals of differing perfection. The differing morphologies or crystals arose from multiple independent nucleation processes as suggested by Holden (70) for poly(ethylene).

Annealing the polymer would favour the improvement of the perfection of the different forms present. Therefore, they would be likely to melt at different temperatures and so give rise to the multiple melting endotherms observed experimentally.

6:12:8 POLY(ETHYLENE TEREPHTHALATE).

The melting and crystallization data for this polymer are given in table 5:41 (page 145). The observed melting point 252-253°C. fell within the range quoted by Schwenker et al. (67) but was lower than the normally accepted value 265°C. (130) On remelting after crystallization, two melting endotherms were observed. These were similar to those observed on the remelting of 66 nylon.

It was assumed that the sample of fibre examined had been drawn (see 4:12:1). Its melting thermogram only contained a single endotherm similar to those published for both drawn and undrawn fibre samples.(67)

Double melting endotherms have been observed with drawn poly(ethylene terephthalate) fibres. (104,158) Yubayashi et al. (104) describe them as being similar to those observed by White (1) for drawn 66 nylon fibres. Their explanation of the effect was slightly different. The first melting endotherm they attributed to the melting of "bundle-like" crystals formed during the hot drawing process. The second endotherm resulted from the melting of lamella crystals formed during the actual D.T.A. heating process. They claimed the temperature at which the first endotherms occurred was dependent on the size of the crystals present. The area of this endotherm also corresponds to the degree of crystallinity of the sample as estimated from density measurements.

Under the correct annealing conditions, poly(ethylene terephthalate) also developed multiple melting endotherms. (Table 5:42, page 145). As the annealing time at 228°C. increased, both the area and the melting temperature of the first endotherm also increased. (see table 5:42 page 145 and diagram 37, page 146). These observations were comparable with those obtained after annealing 66 nylon at 242°C.

Kanetsuna and Maeda (103) have reported similar observations on the annealing of undrawn poly(ethylene terephthalate). From their published thermograms it appeared that the development of the first melting endotherm was dependent on the annealing temperature. Also, at a given annealing temperature,(220°C.) the size and temperature of the first endotherm increased as the annealing time increased. Their results were similar to those reported here. They suggest that the first endotherm was caused by the melting of a metastable state produced by the annealing process.

7. A GENERAL DISCUSSION OF MULTIPLE MELTING ENDOTHERMS.

Double melting endotherms have been observed with drawn, annealed or precipitated 66 nylon. The annealing of other common crystalline polymers has also produced double melting endotherms. (5:12). Similar observations have been reported for drawn and annealed polymers (6:12). No other D.T.A. observations specifically on precipitated polymers have been reported.

One significant observation, was that independent of the method used, drawing, annealing or precipitation, the new endotherm always appeared at a lower temperature than the final melting endotherm of the untreated polymer. This may have been fortuitous, but its reproducibility implied that this was not so. Experiments have shown that it was not connected with the D.T.A. apparatus used. Therefore, whatever theory is proposed to explain the double endotherms, it should perhaps be applicable to any of the processes that result in double melting endotherms. Hence it should involve changes in a property common to all crystalline polymers, such as chain folding, rather than a specific property of an individual polymer.

7:1 DRAWN POLYMERS.

The first endotherm of drawn 66 nylon resulted from a partial melting process. This was shown by the exotherm on cooling after the first endotherm was complete. At this temperature the fibre still retained its physical form. It did not melt until well into the final endotherm. On remelting, melting recommenced at the temperature at which the first run ceased, thus showing that the cause of the first endotherm had been destroyed.

By the time the first endotherm was complete, a drawn sample had shrunk by up to 17% of its original length. Repeating this experiment on a drawn sample that had been annealed prior to melting, only produced a shrinkage of 8.0%, whilst the size of the first endotherm had increased. Therefore, loss of orientation was not the complete cause of the first endotherm.

However, loss or orientation produced by the drawing process must contribute to the first melting endotherm as has been shown by shrinkage and X-ray diffraction measurements. (1) The highly al~~l~~igned molecules in the fibre would prefer to relax to a more thermodynamically stable folded chain configuration. However in view of the annealing results, it would seem likely that the heat generated in the drawing process also contributes to the first endotherm.

On drawing, heat is generated at the point of draw. It is very localized and is generated very rapidly. Under the drawing conditions, this heat could result in a very localised, almost instantaneous, annealing process. This would tend to relax the oriented molecules slightly. Besides this, it could affect the unoriented regions of the polymer molecules. This would contribute to the loss of orientation on remelting. Thus it would help to give rise to the large and relatively sharp endotherm observed with drawn fibres. The higher the degree of drawing, the greater the orientation/annealing effect, hence the larger, the first endotherm.

With any polymer sample, particularly a drawn fibre there was the possibility that the actual D.T.A. heating process would be sufficient to affect the sample's structure. This type of behaviour has been suggested to explain the double endotherms of drawn poly(ethylene terephthalate).(104) In that instance, the first endotherm resulted from the drawing process, whilst the second arose from the melting of lamella crystals formed during the D.T.A. process. This is feasible, but under the conditions used here, it seemed unlikely that sufficient recrystallization could have taken place during the heating up process.

Annealing a drawn 66 nylon fibre has been shown to produce chain folded structures from the extended chains of the fibres.(8) If some chain folds were formed from the extended chains during the heating up process, then the first endotherm of the drawn fibre could represent the loss of orientation and also the energy required to form the more normal folded chain lamellae. These would then melt at a higher temperature. Alternatively, since they would be relatively small chain folded units, they would melt at a lower temperature and contribute to the first endotherm.

There is no specific evidence for this type of behaviour until the process of drawing polymers has been finally elucidated, except from the results of annealing. These indicate that loss of orientation may not be the sole cause of the first endotherm of a drawn polymer fibre.

7:2 ANNEALING.

Considerably more information is available about the annealing process. The following forms a summary of the major experimental observations from the annealing of 66 nylon.

A) The first endotherm resulted from an annealing process and not from the primary crystallization.

B) The first endotherm always occurred at a lower temperature than the final melting endotherm of the unannealed polymer. This also applied to the annealing of other crystalline polymers.

C) Annealing did not visually change the morphology of a spherulitic sample. Simultaneously, however changes occurred in the thermograms.

D) Once the correct annealing conditions had been found, the D.T.A. results were completely reproducible.

E) There was an upper temperature limit ($\simeq 250^{\circ}$C. for 66 nylon) for the annealing process. Above this temperature, the first endotherm did not occur after annealing.

F) The higher, the annealing temperature up to 250°C., the faster the development of the first endotherm in a given time.

G) At a given annealing temperature, the size of the first endotherm increased at the expense of the second endotherm, as the time of annealing increased. Eventually only a single lower temperature endotherm remained. This behaviour was further confirmed by the quantitative annealing experiments.

H) On annealing, at a given temperature, the temperature of the first endotherm increased slightly as the annealing time increased.

J) Quantitatively, the heat of fusion and the percentage crystallinity increased as the annealing time at 242°C. increased.

K) Although no visual melting occurred, on cooling after the first endotherm was complete an exotherm was observed. On remelting, melting recommenced at the temperature the previous run ceased. Thus the cause of the first endotherm was destroyed by heating and was not reproduced by just cooling. This indicated that the first melting endotherm resulted from at least a partial melting process rather than any other process.

L) Changes in the molecular weight distribution of the 66 nylon samples did not appear to affect the annealing process. Annealing experiments on other polymers of different molecular weights produced similar results. Therefore it was unlikely that some form of fractionation during the annealing process caused the first endotherm.

M) There was a slight increase in the density of both annealed 66 nylon film and drawn bristle with increasing annealing time at a given temperature. The density increase tended rapidly to an equilibrium value, long before the maximum effects of annealing had been observed. This suggested that there was a large initial increase in the sample's crystallinity which tended to rapidly fall off. Similar but not so rapid trends were shown by the quantitative results (J).

N) The wide angle X-ray diffraction patterns showed a sharpening of the diffraction rings, characteristic of annealing (39) but otherwise no changes were observed on annealing. This indicates that there was no change in the unit cell dimensions, such as the α / β 66 nylon polymorphism , that could explain the first endotherm.

P) Changes were detectable in the small angle X-ray scattering patterns as the annealing time increased. Similar changes have been reported with other polymers on annealing (see 2:2). They are normally interpreted as changes occurring in the long period, ie the chain folding, as a result of annealing.

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Some of these observations were consistent with the previously published observations on the annealing of polymers (see 2:2). Others, however, were not.

Annealing a polymer has been shown to improve its crystallinity and structural perfection, change the fold length of the molecules etc., without necessarily altering its basic "macro-morphology". It has been shown that there was a minimum annealing temperature below which changes in the long period on annealing did not take place. (See 2:2).

Similar behaviour has been observed with the annealing experiments on 66 nylon. The increase in density (M), the increase in the percentage crystallinity (J), no change in visual morphology (C), the X-ray diffraction results (N and P), and the dependence of the rate of formation of the double endotherms on the annealing temperature, all fit the previous ideas about annealing. The increase in the temperature of the first endotherm once formed, with increasing annealing time at a given temperature was also characteristic of annealing.

The main observation not fitting the current ideas on annealing was that the new endotherm always occurred at a lower temperature than the final melting endotherm of the unannealed polymer (B). This was not fortutious, it was reproducible, not a function of the apparatus used and was observed with other crystalline polymers on annealing.

The previously expected behaviour of a polymer after annealing, was an increase in its final melting point. This was because the annealing process, allowed the structure to improve by removing imperfections and relieving stresses. In this work the final melting point did not increase as expected. With increasing annealing time, it effectively decreased (G) until only a single lower temperature endotherm remained. However the temperature of this endotherm had increased slightly during the annealing process (H). The quantitative experiments on annealing further confirmed this (J). The heat of fusion and percentage crystallinity increased as the size of the first endotherm increased.

The effect was not caused by two different morphologies present in the sample simultaneously, unless they have not been previously observed. It was not related to different modes of crystallization nucleation as suggested by Holden, (70) or Cooper et al. (95), otherwise some form of double endotherm should have been detectable in the original samples before annealing took place. Besides, on melt crystallization the double endotherms continued to develop long after crystallization was complete. (A).

However, two different nucleation processes would explain the formation of the double remelting endotherms observed when a sample of 66 nylon was crystallized from the melt, and then remelted. In this instance the rate of crystallization might have been sufficient to allow a second nucleation process to take place and compete with the more usual rapid form of crystallization nucleation.

Whatever caused the effect was very temperature sensitive. There was obviously a maximum temperature at which the rate of formation of the first endotherm was a maximum (F). This was very close to the temperature at which the first endotherm was no longer thermally stable (E). These suggest that a certain amount of thermal motion was necessary to allow these changes to take place. Up to a point, the higher the energy, the greater the change.

Different molecular weight fractions do not seem to be the cause of the two endotherms (L). Changing the molecular weight distribution did not apparently affect the annealing of 66 nylon. Other polymer samples of different molecular weights also showed two endotherms on annealing. (5:12). A double endotherm obtained after annealing single crystals of poly(ethylene) has been shown to correspond to two different molecular weight fractions.(86) However since after a sufficiently long annealing time, the whole 66 nylon sample reverted to a single endotherm this explanation is unlikely. If it were, simultaneous depolymerization and polymerization would be necessary to yield a sample containing only a single very narrow molecular weight fraction giving rise to the single melting endotherm.

The annealing experiments in the calorimeter cell, quantitatively confirmed the earlier D.T.A. qualitative results (J). After 14 hours annealing, when only a single low temperature melting endotherm remained, the sample's percentage crystallinity was about 40%, compared to the original, unannealed 30%. Most of the increase took place during the initial part of the annealing period, as the first endotherm developed. This indicated that the first endotherm did not result from just an increase in crystallinity, but the crystallinity had increased as a result of the annealing.

After 14 hours annealing with water present in the calorimeter cell, the percentage crystallinity had reached 45%. Since only a single determination was carried out, this may have been fortuitous. If not, then it showed that the water aided the development of the increased crystallinity in some manner. It could have either reduced degradation effects or even increased the rate at which the changes, causing the increased crystallinity were taking place.

One explanation for the cause of the two melting endotherms which can explain almost all the observed facts is the formation of smaller crystalline units on annealing. They would have to have an increase in crystalline perfection to satisfy observations (J,M,). Being smaller they would melt at a lower temperature (B). They could be formed during a crystallization in very small numbers which would normally be undectectable (A), but would form nuclei from which more could form on annealing (G) at the expense of the final melting endotherm. Their presence would cause changes in the small angle scattering (P). They would not be affected by molecular weight effects (L), and their melting would not be likely to disrupt the visual morphology of the samples. (C). Since they would melt at a given temperature, an exotherm would be observed on cooling from that temperature (K), and as they were not formed in sufficient numbers on crystallization, they would not be detected on remelting. Once formed, further annealing would improve their perfection and increase their melting point. (H). All the listed observations, bar (G), can be satisfactorily explained by the formation of smaller crystalline units.

To explain (G) it is necessary to discover why on annealing smaller crystalline units should be formed. Normally the long period increases due to an increase in fold length on annealing (see 2:2). Voids develop and although the crystals get thicker, their surface area tends to decrease. This also fits the concept of smaller crystalline units, whose perfection has increased. However, normally, annealing results in an increase in the melting temperature. Extended chains melt at higher temperatures than folded chains.(78) The larger the chain fold length the higher the melting point of the sample. In this case the melting point of the first endotherm was lower than the final endotherm although it did increase slightly during the course of annealing.

At least two other workers have suggested that the first endotherm resulting from annealing was caused by the melting of two different sized crystallites.(83,157) In the work on poly (4-methyl pentene-1) the smaller crystals were actually observed in electron micrographs.(157) It was suggested that it was a combination of smaller size and degree of crystalline perfection that caused them to melt at a lower temperature.

More recently, some observations on the thermal analysis of unorientated isotactic poly(propylene) film have been published by two Japanese workers.(159) On annealing, they found double melting endotherms not only with the film but also with solution grown crystals. To quote from the English summary of their work, "The appearance of the small peak is independent of the annealing method, heating media, duration of heat treatment, molecular weight and its distribution. The peak temperature is several degrees higher than the annealing temperature. It is experimentally shown that the appearance of the small peak can not be ascribed to the melting of a portion of lower degree of microtacticity, partial melting of the β-form, transition of the smectic form to a monoclinic one, degradation, disorientation of crystallites before melting and that the small peak may be due to the melting of thermally unstable crystallites having a monoclinic form of highly isotactic chains, which are formed during heat treatment."

These observations were similar to those made here on 66 nylon, bar the fact that the size of the first endotherm was not affected by the time of the annealing process. Observations on the annealing of poly(propylene) have indicated that the endotherm was affected by the time of annealing.(88)

These published results, coupled with the observations made in this work suggest that the cause of the first melting endotherm produced on annealing was the melting of small crystallites produced during the annealing. Such crystallites could form in any crystalline polymer under suitable annealing conditions, and would therefore be consistent with the results obtained on annealing other crystalline polymers.

To prove or disprove such a proposal, an electron microscope study of the annealed polymers, coupled with D.T.A. examination would be necessary. The results might even explain why high percentage crystallinities have never been achieved with polyamides, as with poly(ethylene) and other polymers on annealing. They could also throw more light on the changes in the structure of bulk polymers that take place during the commercial processing of these thermoplastic materials.

7:3 PRECIPITATED SAMPLES.

Only precipitated samples of 66 nylon were prepared and examined. The following list summarizes the major experimental observations made on these samples.

A) Slow precipitation favoured the formation of two D.T.A. melting endotherms. This indicated that a finite time was required for the changes to take place in the sample to cause the new endotherm.

B) The new endotherm was always observed at a lower temperature than the original first melting of the unprecipitated polymer. The two endotherms were approximately equal in size in most instances.

C) No exotherm was observed on cooling after the first endotherm was complete. On remelting, melting recommenced at the temperature at which the first melting run had ceased. The cause of the first endotherm had therefore been destroyed by heating. The absence of an exotherm on cooling suggested that the first endotherm had not been caused by a melting process.

D) The density of the precipitated sample with two endotherms was higher than that with only one. This was taken to indicate that the double endotherm sample had the higher crystalline perfection.

E) The iodine sorption of the sample with two endotherms was lower than that with one. This also indicated that the double endotherm sample had the higher crystalline perfection.

F) The wide angle X-ray diffraction patterns of both the double and single endotherm precipitated samples were almost identical. Both indicated that the samples were highly crystalline. They also indicated that the unit cell dimensions of the two samples were the same.

G) The small angle X-ray scattering of the double endotherm sample contained two maxima, whereas that with a single endotherm only had a single maxima. This also indicated that there were differences between the two precipitated samples.

H) When precipitated polymer with two melting endotherms was annealed at 242°C., similar changes occurred in the melting endotherms as described in 7:2 (G) and (H).

No previous D.T.A. observations have been published on precipitated 66 nylon. However, slow precipitation methods as used here, have been shown to produce single crystals.[135]

Single crystals usually have a high degree of crystalline perfection. This arises from the chain folding necessary to form the single crystals. The X-ray diffraction results (F), the density and iodine sorption values (D and E) of the precipitated sample with two endotherms were all consistent with the possibility of single crystals being present. Unfortunately attempts to show the presence of single crystals were unsuccessful.

The observations on the precipitated samples of 66 nylon with two endotherms differ from those of drawn fibres or annealed polymer in two ways. Firstly, no exotherm was observed on cooling after the first endotherm was complete (C). Secondly there were distinct differences in the small angle X-ray scattering patterns of the two different precipitated samples. (G).

The cause of the first endotherm was therefore not necessarily the same as in the two previous instances. Slow precipitation would favour the formation of relatively large perfect crystals. These would be expected to melt at a higher temperature. In actual fact, the new endotherm again occurred at a lower temperature. (B). The rate of precipitation could have been such that the crystals formed were very perfect but relatively small since their time of formation was still relatively short. The melting of these smaller crystals could therefore have caused the first endotherm. Contradicting this hypothesis, is the fact that no crystallization exotherm was observed on cooling after the first endotherm was complete. (C). If melting had taken place there should have been some evidence of an exotherm on cooling. However, the results of the small angle X-ray scattering experiments indicated that some changes had taken place. They could indicate the presence of two different causes of scattering in the double endotherm sample. Such an effect could be caused by two different chain fold lengths, giving rise to different sized crystallites. Further, more detailed study would be necessary to prove or disprove this suggestion.

As before, the experimental results proved to be contradictory. With the information available at present, it was not possible to arrive at a conclusive reason for the formation of the first melting endotherm. In considering the results obtained from precipitation from hot benzyl alcohol solution, it was not possible to discover why the experimental conditions gave the results that were obtained. (6:9:2) It seems however that the most likely explanation lies in some change taking place in the original chain folded structure of the polymer as a result of precipitation.

8. CONCLUSIONS.

Multiple melting endotherms occur more widely in crystalline polymers than was originally thought. They have been observed with drawn, annealed and precipitated 66 nylon. They have also been observed with the following polymers after annealing:- 6; 11; 610; 7; 76; 77; and 68 nylon; poly(ethylene); poly(propylene); poly(4-methyl pentene-1); poly(ethylene oxide); isotactic poly(propylene oxide) and poly(ethylene terephthalate). The new endotherms always occur at a lower temperature than the original final melting endotherm of the untreated polymer. On annealing, the development of the new endotherm was dependent on the temperature of annealing. For 66 nylon and poly(ethylene terephthalate) it was also related to the time of annealing.

With 66 nylon, the area of the new endotherm increased at the expense of the final melting one, as the annealing time at a given temperature increased. Simultaneously, there was a slight increase in the sample's percentage crystallinity. This increase was not the cause of the changes in the thermograms. Nor were they apparently caused by changes in the crystalline unit cell, the molecular weight distribution, or the visual spherulitic morphology of the samples.

The rate of precipitation of 66 nylon from solution affected its subsequent thermograms. Samples with two endotherms were more crystalline than those with only one.

The cause of the multiple melting endotherms has not been established, however a reasonable explanation of the experimental results is that they arose from changes in the size, fold length, and perfection of the polymer's crystalline units.

9. RECOMMENDATIONS FOR FURTHER STUDY.

A). Further study of the morphological changes that occur when polymers develop multiple melting endotherms, ie. on annealing, using the techniques of electron microscopy, electron diffraction, small angle X-ray scattering and micro-X-ray diffraction especially, to discover the relationship between the morphological changes and the polymer's thermogram.

B). The effects of careful molecular weight fractionation of a polymer on its thermograms before and after annealing.

C). An investigation into the precipitation of other crystalline polymers from solution. What is the effect of the rate and temperature of precipitation on the thermograms?.

D). A further study of the relationship between the morphology of polymer single crystals, prepared by different methods, and their thermograms.

E). A study of the more mechanical properties of polymers, such as tensile strength, which are affected by thermal treatments like annealing, in relationship to their morphology and thermograms.

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