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On spherulitic forms in an aromatic polyesteramide

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Abstract

A particular aromatic polyesteramide with flexible spacers has been shown to crystallize into a variety of spherulitic forms whose birefringence varies markedly with crystallization temperature. However, a temperature step crystallization technique allows the unambiguous recognition of the different forms in spite of the varying birefringence. Though their appearance under optical and electron microscopy is different, all observed crystalline forms show very similar X-ray diffraction patterns, which suggests that they share a common local molecular arrangement. Each form has a characteristic melting point which is almost invariant with crystallization temperature. From this it is suggested that the various forms comprise chainfolded crystals containing different integral lengths of the same rather long monomeric unit. No liquid crystalline phases were observed in this material. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyesteramide; Spherulites; Microscopy

1. Introduction

Polyesteramide PEA37 (formula shown in Scheme 1) is one of a family of materials with different numbers of methylene groups in the spacers between the ester (here 3) and amide (here 7) groups, many of which display interesting multi-phase behaviour.

In a previously published work from this laboratory [1], examples of different homologues of this series were shown. Some of these homologues had previously been synthesized by Aharoni [2–4] albeit by a different route. Aharoni had reported the observation of a series of solid phases in several of these, and in addition a liquid crystalline phase extending to higher temperatures. In contrast, the materials prepared here were seen (optically, by X-rays, and by thermal analysis) to pass directly from the highest melting solid form to the isotropic liquid at temperatures corresponding to Aharoni's reported solid to liquid-crystalline transition. In the present work, the morphologies of the observed solid forms in one of these materials, namely PEA37, have been investigated by optical and some electron microscopy and correlated with thermal analysis.

2. Experimental

2.1. Polymer preparation and fractionation

Details of synthesis of the polyesteramide PEA37 are given in a previous publication [1].

During preliminary studies on the polymer as synthesized, it became evident that it contained much low molecular weight material and perhaps some unreacted monomer. Such material was removed by:

dissolving the polymer in *N,N*-dimethylacetamide at 80–120°C;
pouring the solution into THF already cooled to near freezing;
allowing the solution to warm to room temperature;
slowly adding methanol sufficient to give visible precipitation.

The materials before and after this treatment will be referred to as the *fractionated* and *unfractionated* polymers.

2.2. Thermal analysis

Thermal analysis was performed in a Perkin–Elmer DSC-2C Differential Scanning Calorimeter. The scanning rate unless otherwise mentioned was 20 K min^{-1}.

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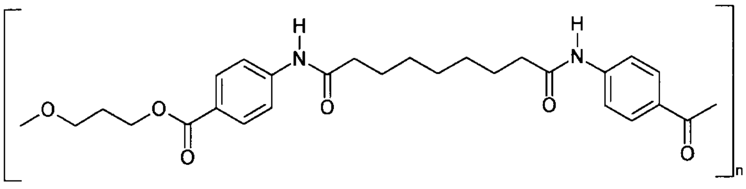

Scheme 1.

2.3. Optical microscopy

Film specimens on microscope slides were pre-melted on a Kofler hot bar and transferred to a Mettler hot stage pre-set at the chosen isothermal crystallization temperature, where their development was followed under a long working distance objective. The temperature was sometimes changed during the course of crystallization to give "temperature step" specimens. For example, a specimen would be grown for a time at 170°C, then the temperature raised to 180°C for a period before quenching.

After quenching, the specimens were transferred to a microscope with a higher resolution objective for photography. Specimens were studied between crossed polars, generally in conjunction with mica quarter-wave plates to give circularly polarized light. This shows the boundaries between different types of spherulites to best advantage, without confusion from the Maltese cross. Zernicke phase contrast was also used.

2.4. X-ray diffraction

Wide angle X-ray diffraction data was obtained at room temperature from isothermally crystallized samples which had been prepared by directly cooling from 300°C and holding at a temperature (T_c) of 185, 170, 155, and 140°C for about 16 h.

2.5. Electron microscopy

Films for electron microscopy were etched for 15 min in an 2% w/v solution of potassium hydroxide in *iso*-propanol. The reaction was stopped by washing in 20% aqueous acetic acid, followed by washing with distilled water, and drying. The etched surfaces were shadowed with tantalum/tungsten and coated with carbon. The polymer was extracted from areas (selected under the Nomarski reflection optical microscope) with an 8:5 mixture of trichloroacetic acid

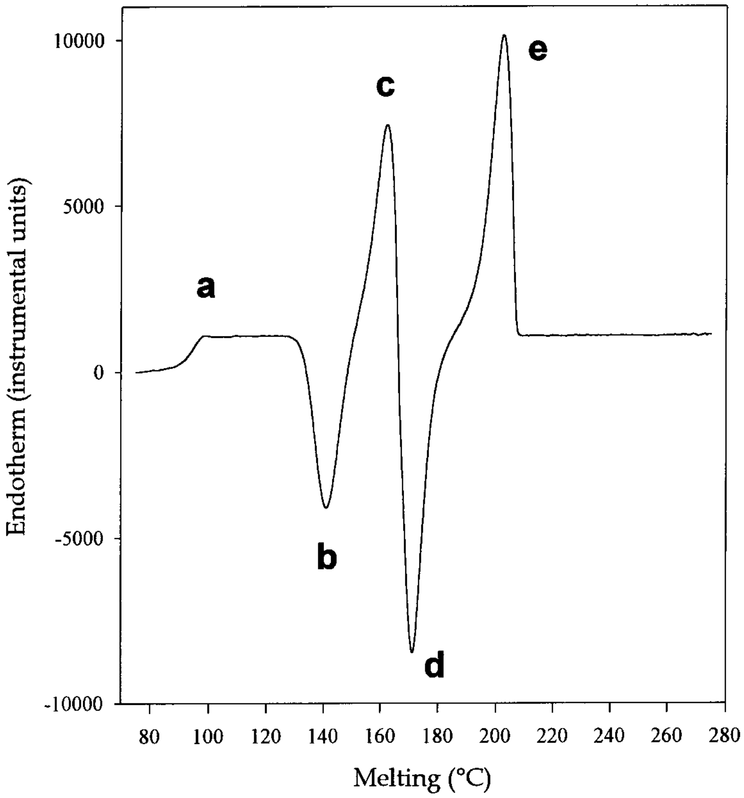

Fig. 1. Melting endotherm of PEA37, fractionated polymer, heated from the glassy state at 20 K min^{-1}.

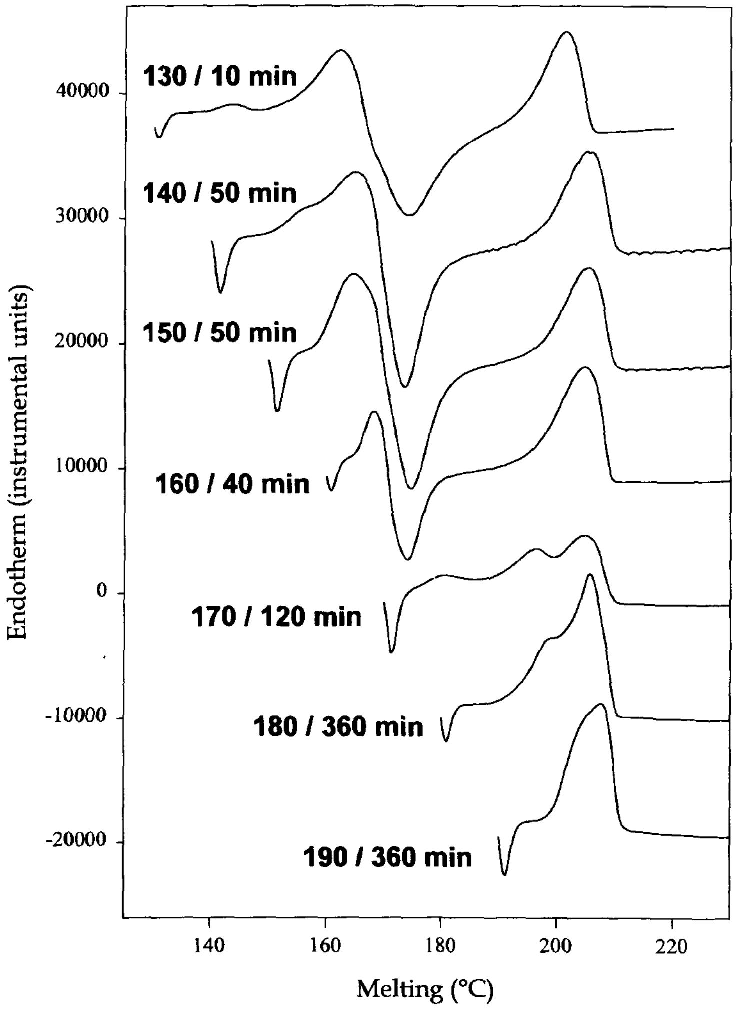

Fig. 2. Melting endotherms of fractionated PEA37 after isothermal crystallization at various temperatures.

and *meta*-cresol, leaving replicas, which were examined under TEM.

3. Results and discussion

The work presented here follows previous work [1], using the same four instrumental techniques but on a more detailed and precisely prepared series of specimens. Each of these techniques gave preliminary results which, if taken in isolation, point to simple interpretations, but when taken together reveal a more subtle and complicated picture. The first technique, differential scanning calorimetry (DSC), showed multiple peaks. Such results have to be analysed carefully in order to see whether they arise from a material with multiple phases, or from reorganization [5] or secondary crystallization [6], in both of which one crystal phase is found in the same basic structure, but with different levels of thermal stability, of which the more stable form is lamellar but the less stable one may be "bundle-like" [7]. With PEA37, the DSC results lent themselves initially to a two-phase interpretation. The X-ray diffraction patterns had been found initially [1] to alter with the thermal changes observed in the DSC, but even more refined results did not show changes which could definitely be assigned to crystallographically different phases, rather than minor modifications within one crystal phase. Infrared observations only demonstrated changes in hydrogen bonding, and showed no change which could be correlated with different crystal modifications. Detailed optical observations, however, showed at least four different spherulitic structures.

This leads to the question, can one basic crystal phase in a polymer give rise to different spherulitic structures? Although all techniques must be taken together, it is convenient to present results from the various techniques separately, then to weigh the evidence from all techniques together.

3.1. Thermal behaviour

The thermal behaviour of the fractionated and the unfractionated polymers is very similar. That of the fractionated

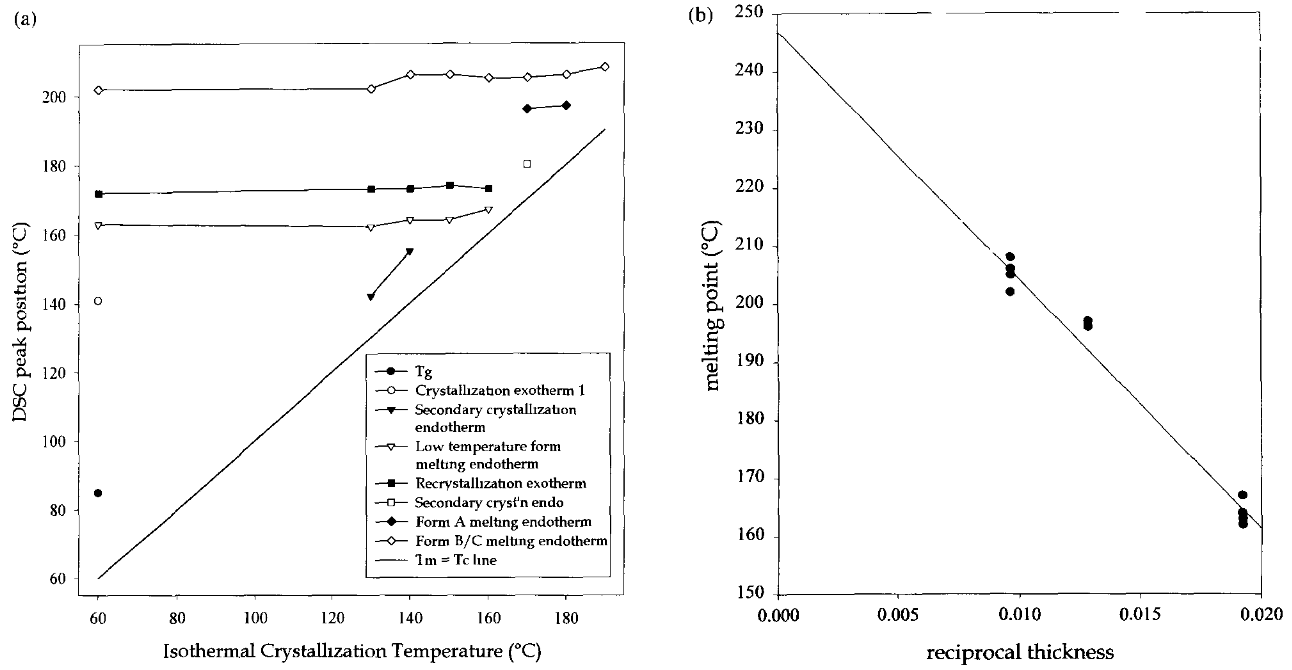

Fig. 3. (a) Peak temperatures observed in isothermally crystallized PEA37. (b) Melting peak plotted against 1/*l* (proposed).

polymer heated from the glass is shown in Fig. 1. This immediately suggests the existence of two kinds of crystal phase formed in the polymer, such as the α- and β-forms of polypropylene [8], or those of PEN [9] which not only have quite distinct crystalline lattices giving different wide-angle X-ray reflections, but which also have distinct "ideal" melting points T_m^0. On this basis, the features in the thermal trace would be explained as follows. After the glass transition (a) at 85°C, there follows an exothermic crystallization (b) at 142°C, forming a low-temperature solid phase. This melts (c) at 163°C, but recrystallization sets in (d) giving an exotherm at 172°C, and forming a high-temperature phase which finally melts (e) at 202°C. The formation of two or more types of spherulite in several members of this homologous series of polyesteramides predisposes towards the multi-phase interpretation.

Simply melting the polymer at different scan rates after cooling from the melt at 20 K min^{-1} showed nothing more than changes assigned to different instrumental resolution. Such invariance rules out an interpretation based on reorganization during the scan, such as occurs in isotactic polystyrene [5,10,11] or poly 4-methyl pentene-1 [12],

Table 1

Spherulitic form	T_m θ/°C	Birefringence as a function of T_c
Z-form	ca. 165	Faint, only up to 160°C
A-form	ca. 196	Bright from 160°C, increasingly faint up to 180°C
B-form	ca. 205	Medium from 160°C, becoming brighter up to 175°C, then fainter. Tight banding seen at 190°C
C-form		Dull, with banding visible from 165°C and band period increasing up to 185°C

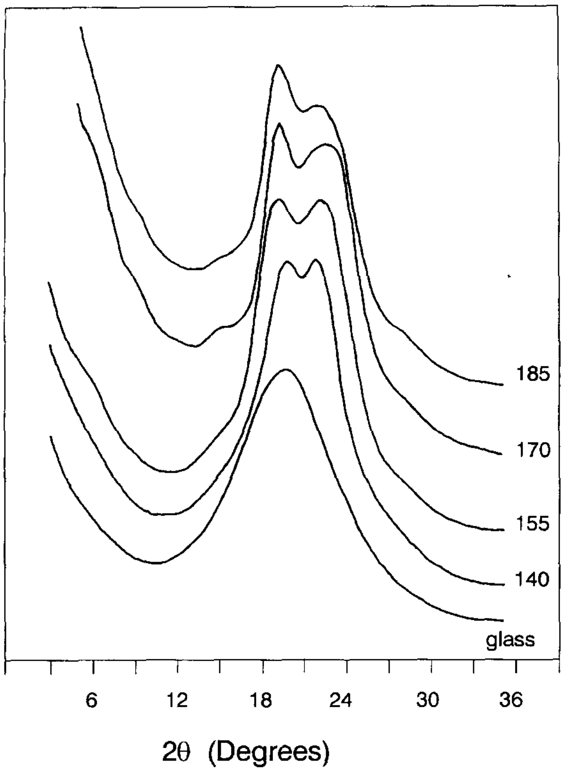

Fig. 4. Wide angle X-ray diffraction patterns of PEA37. Specimens prepared at T_c = (a) 185°C; (b) 170°C; (c) 155°C; (d) 140°C; and (e) quenched.

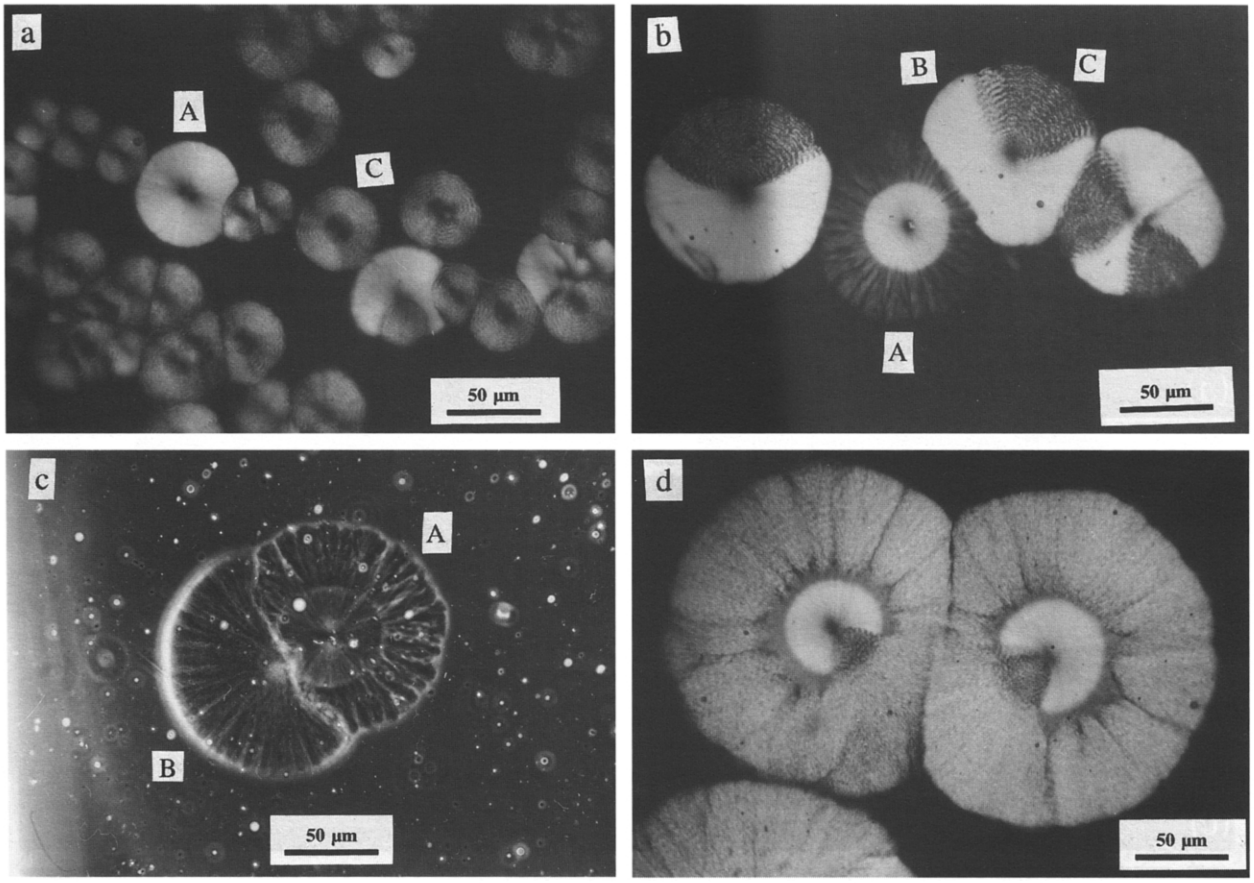

Fig. 5. Optical micrographs demonstrating the use of the temperature step technique, unfractionated polymer: (a) 160–170°C; (b, c) 170–180°C; (d) 180–190°C. (a), (b) and (d) are in circularly polarized light; (c) is in phase contrast.

where multiple melting peaks arise by melting and recrystallization of one phase. So with the greater than the expected number of spherulitic forms, it is necessary to correlate these more precisely with the thermal behaviour. As with PEEK [13], more information is gained by isothermal crystallization carried out at different temperatures. Samples of fractionated PEA37 were grown isothermally at a series of temperatures, 130–190°C by 10° steps. They were immediately reheated from T_c to observe their melting endotherms, to avoid any confusion from material which might crystallize if they were cooled in between. These endotherms are displayed in Fig. 2, and the peak temperatures are plotted graphically in Fig. 3(a) (the assignments are related to the optical work below).

Specimens isothermally crystallized (Fig. 2) below 160°C, show a first melting endotherm and the subsequent recrystallization exotherm which are clearly separated. This further emphasizes the distinction from polymers that reorganize during the scan, in which the resulting peaks are found in close conjunction. In some cases, peaks which can be readily assigned to secondary crystallization are seen, especially the small peaks just above T_c for 130 and 170°C. In PEEK, the two endotherms have been shown to arise from distinct locations in the morphology of one crystal phase, the higher melting peak from primary lamellae which form the main architecture of the spherulites, and the lower melting from intervening crystallites which formed during secondary crystallization [13]. PEA37 heated from a glassy state shows as in Fig. 1 a typical rise in specific heat following the glass transition, but in pre-crystallized specimens this is absent. This behaviour is common in low-crystallinity polymers such as PEEK and PET and is explained by Cheng [14] in terms of a rigid amorphous phase which does not "unlock" immediately on heating above T_g.

It is to be noted from Fig. 3(a) that the position of the melting peaks do not vary much with crystallization temperature. There are many examples reported in the literature where the observed relationship of crystallization and melting temperatures follows the equation

$$T_m^0 - T_m = M(T_m^0 - T_c),$$

where it might be expected [15] that M would be 0.5 for a lamellar crystal (as is generally observed in practice) and be 0 as here only for an extended chain crystal, which (as subsequent electron microscopy shows) these are not. The monomer unit is quite long, however, and this suggests the possibility that these apparent phases are, instead, one crystal form with lamellae folded in quantized lengths.

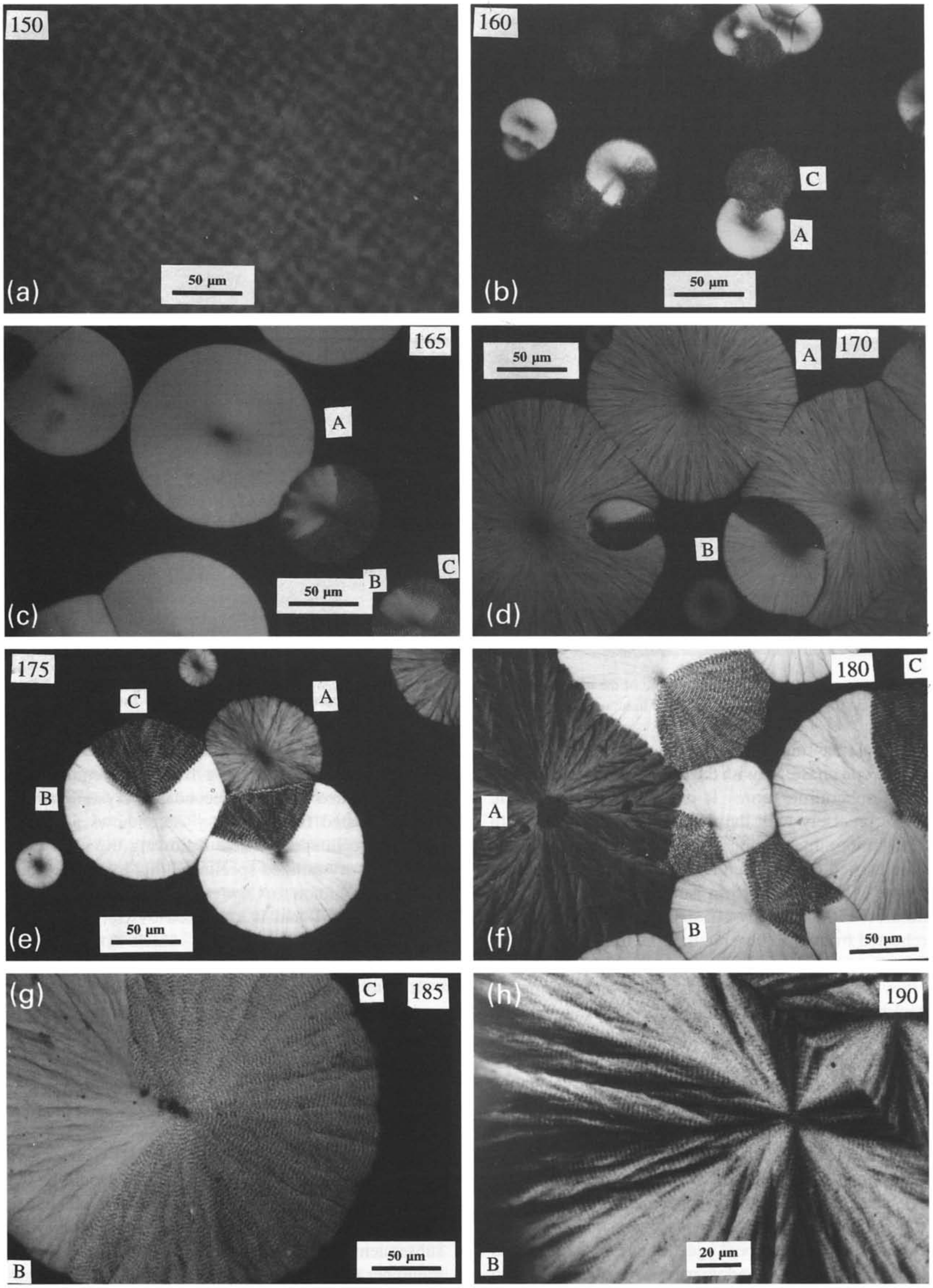

Fig. 6. Optical micrographs of the unfractionated polymer crystallized isothermally at the temperature indicated on each picture: (a) 150°C; (b) 160°C; (c) 165°C; (d) 170°C; (e) 175°C; (f) 180°C; (g) 185°Cl; (h) 190°C; all in circularly polarized light, except (h) which is in linearly polarized light.

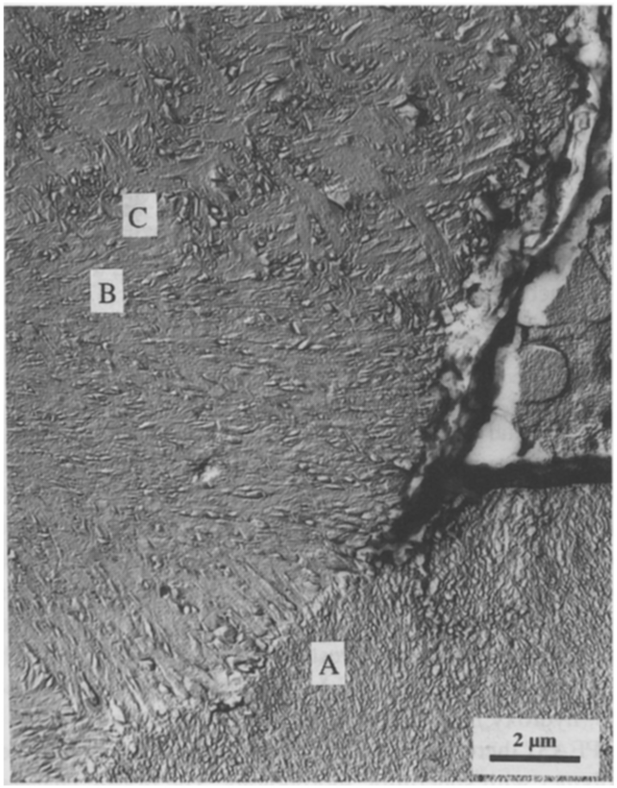

Fig. 7. Electron micrograph of etched specimen grown at 175°C, showing A-, B- and C-form spherulites.

The best characterized family of polymers which form crystals with a small but definite integral number of monomer units in each stem traversing a chainfolded lamella are the polyamides [16–18]. While in PEA37 methylene sequences are found in both ester and amide units, folds would be much more likely in the longer sequence in the amide unit, located so that the amide groups would be able to hydrogen bond to each other in layers, as occurs with nylons [18]. In that case the different melting species in PEA37 could consist of basically one crystal phase folding with a small defined number of the long (27.3 Å) repeat units in each chain. The melting behaviour of PEA37 crystallized between 130 and 160°C is very similar to that of the poly(aryl ether ketone) PK99 crystallized over the range 230–260°C, where the lengths of stem in the lamella are rather strictly defined by the number of *meta*-phenyl groups in the stem [19]. PK99 shows half-integral folding: however, the methylene sequence in the ester unit of PEA37 is rather short, and so integral folding based only on the amide sequences is much more likely. A simple molecular model of PEA37 gives a length of 27.3 Å for each esteramide unit, with a tendency for each to be inclined at 144° to its neighbour. If these were packed in a lamellar crystal, then there would be a chain inclination of 18° to the lamellar normal, which would then give a crystal thickness of $l = 26n$ Å, where n is the number of units. If the melting point of the three identifiable forms (listed in Table 1) are plotted against $1/l$ as in Fig. 3(b), then a reasonable straight line graph is obtained. Unfortunately heat of fusion data are not available, but the slope is such that a value of the ratio of surface free energy to heat of fusion is not out of line with what is generally observed in semicrystalline polymers.

3.2. X-ray evidence

Even within the minor variations in the X-ray diffraction (Fig. 4), several features can been seen. Firstly, at $T_c = 140$°C, where the low temperature form is expected, the two peaks appear close together and show only a small difference in d-spacing. The peaks are distinctly further apart at $T_c = 155$°C and above. At even higher T_c (170 and 185°C) additional peaks become apparent which suggests a greater extent of perfection of ordering at the higher temperature. Finally, the relative intensity of the two strong peaks is seen to change systematically with T_c, albeit to a small extent. These X-ray results, taken by themselves, would hardly suggest anything more than one phase with systematic changes with T_c in molecular packing. Taken with DSC, they indicate strongly that even if several different crystal phases exist in PEA37, these display only minor differences in molecular packing. Then accounting for the double peaks in DSC and the four different spherulite types become more difficult. From further infrared experiments more, not less, hydrogen bonding is found in the specimen crystallized at 185°C, and much more free –NH– is found in the other specimens (i.e. $T_c = 170$, 155°C, and the quench specimens), according to band assignments in the previous paper [1]. Comparing with the previous results, it implies that different hydrogen bonding exists in the specimen crystallized at $T_c = 185$°C and the molecules are packed into a more ordered structure. Taken together, infrared and X-ray diffraction indicate a systematic increase in crystal ordering with T_c, with longer range reflections appearing at 170°C and hydrogen bonding (presumably within the crystal lattice) at 185°C.

3.3. Optical microscopy

Two series of specimens, of fractionated and unfractionated polymer, were crystallized on microscope slides isothermally at temperatures 150, 155, 160,…,190°C. An initially bewildering variety of birefringence patterns was observed, suggesting even six different forms of spherulite. This arose chiefly because the birefringence or banding of spherulites displayed by any one form changed markedly over even a 10° step. The number was eventually reduced to four by the use of the temperature step crystallization technique, which allowed a particular form to be followed through its changes without ambiguity, even those where the birefringence first increased with T_c, then decreased. The use of this technique is shown in Fig. 5, which is a selection from a larger number of specimens. The possibility of mutation between different forms over a temperature step has been ruled out by electron microscopy (below), which shows that the distinct lamellar morphologies are maintained over all observed steps.

The step from 170–180°C is particularly informative. Fig. 5(b) shows in the middle a very bright 170° **A**-spherulite centre giving way to much less birefringent 180° material; whereas at the left one sees a moderately bright 170° **B**-centre giving way to even brighter 180° material (this has been printed darker, because otherwise the range of greyscales is too great for normal photographic paper). Electron microscopy shows such transitions to take place smoothly, without any drastic jump in lamellar texture. In contrast, the 180–190° specimen (Fig. 5(d)) shows a 180° **B** and **C** mixed centre giving way to the corresponding 190° material, but at several points in the newly formed halo of the 190° material, the **B**-form mutates to the **C**-form; this, being much faster growing at higher temperature, rapidly engulfs the rest of the **B**-form [8]. Another interesting growth rate effect is seen in Fig. 5(c). Here, the boundary between the coarse 180° **A**-spherulite and the finer textured **B**-spherulite curves first towards, and then away from, the **B**-nucleus. This implies that the **B**-form is faster growing at 180°C than the **A**-form. Under isothermal conditions, it would also imply that the **B**-form had nucleated later, but here it seems to have been induced by the two-stage treatment.

The four types of spherulite thus identified are as follows: the **Z** form arising at low temperatures, and the three types which grow at higher temperatures, **A**, **B**, and **C**. Their appearance at different T_c is presented in Fig. 6, and the trends are listed in Table 1. Circularly polarized light has been used in most cases, since the boundary shapes and relative birefringences of neighbouring spherulites are shown clearly, without interference from the Maltese cross. However, for 190°C, simple crossed polars are used, since the banding is so weak it only appears prominently in the arms of the Maltese cross. Under the hot stage microscope, the **A**-form is seen to melt between 187 and 196°C (depending on T_c) and the **B**- and **C**-forms between 201 and 212°C.

Under the optical microscope, the **A**-form spherulites have a feathery appearance. It has intense birefringence at lower temperature that becomes progressively weaker as crystallization temperature is increased. This kind of spherulite grows faster than the others at the temperature range of ~160–170°C. The **B**- and **C**-forms grow together, but the nucleation of one appears slightly offset from the other. The **C** form spherulite is found mainly in the unfractionated polymer: in the fractionated polymer, it is only occasionally seen at the edge of the specimen (where low molecular weight residues would concentrate). Temperature step crystallization of specimens showed that **B** and **C** are definitely two different kinds of spherulite though **C** has not been found separate from **B**. A similar situation has been reported [20] in the DuPont Polyamide J-1; this displays six different spherulitic forms with distinct electron diffraction patterns, but two forms which grow in close association have closely matching *b* and *c* lattice parameters.

3.4. Electron microscopy

Electron microscopy of etched specimens as in Fig. 7 showed that the lamellae of the **A**-form are finer in texture than those of the **B**- and **C**-forms: these two forms have very similar lamellae, except that the spherulites of the latter are banded. Electron microscopy of temperature step specimens shows that the distinct lamellar morphologies are maintained over all observed steps, only becoming coarser as T_c is increased.

3.5. Overview

The initial work on this polymer was undertaken as part of a programme on liquid crystal polymers. However all phases observed, other than the isotropic glass or melt, have shown nothing different from classical semicrystalline polymer morphology, both optically and (as to be published) under the electron microscope. What is seen is quite unlike the non-periodic layer crystallites observed in the liquid crystalline polyesteramide Vectra B900, which moreover displays thermal behaviour like hydroxy benzoate–hydroxy naphthoate liquid crystal polymers [21,22].

PEA37 therefore appears to be a classical semicrystalline polymer with spherulitic morphology. The drastic changes in birefringence with crystallization temperature are not unique, and in Nylon-66 the predominant spherulitic form is observed to change from positively to negatively birefringent with crystallization temperature [23]. The particular feature of PEA37 is that the different observed spherulitic forms appear to arise from quantized fold lengths related to the great length of the repeat unit. The different forms show very little by X-rays or infrared that could be related to different crystalline packings; indeed the association of **B**- and **C**-spherulites suggests that these two forms especially are very similar indeed in crystal structure. So it is a matter of crystal size and surface free energy, rather than differences in crystal structure, which lead to such gross differences in morphology and thermal stability.

4. Conclusions

1. The polyesteramide PEA37 displays at least four kinds of spherulites, mutually distinguishable under the optical microscope by their birefringence pattern.
2. The birefringence pattern of a given spherulitic type is not constant, but varies systematically over a range of crystallization temperatures.
3. Three different melting temperatures have been found whose values suggest quantized folding and relate to the distinct spherulitic types.
4. The **C**-form spherulites appear in conjunction with the **B**-form, and would seem to be associated with low molecular mass material in the polymer.

5. No liquid crystalline forms have been observed with this polymer.

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