Invariance of lamellar thickness with crystallization temperature of polyesteramide 6NT6 crystals

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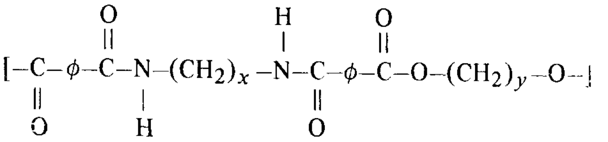
(Received 15 August 1978; revised 5 December 1978)

Polyesteramide of the type $[-CO-\phi-CO-NH-(CH_2)_6-NH-CO-\phi-CO-O-(CH_2)_6-O]_n$, conventionally referred to as PEA 6NT6, was crystallized from dilute solutions in benzyl alcohol at different temperatures. Single crystals were obtained in ellipsoidal and flat form, as revealed by electron microscopy. X-ray small- and wide-angle diffraction experiments were carried out on oriented mats of the lamellae. Invariance of long spacing with crystallization temperature in the range 72°–118°C was found. Annealing experiments revealed a quantized increase of the long spacing. The thermal behaviour of the single crystals was studied by differential scanning calorimetry and by i.r. spectroscopy. A chain-folding model based on tight folds and adjacent re-entry is proposed for this polymer.

INTRODUCTION

Chain-folding in polymer crystallization is still an open question, despite the large numbers of theoretical and experimental studies carried out by several polymer groups[1,2]. To explain the growth of polymer crystals two different theories have been developed: 'kinetic'[3] and 'thermodynamic'[4]. Equilibrium aspects of polymer crystals have also been considered, with particular respect to chain-folding, by means of potential energy calculations on folded macromolecules both isolated and in the crystals[5–10]. Experimentally, the most studied polymer has been polyethylene, because of its simple chemical structure. More recently attention has also been paid to chains of greater chemical complexity than polyethylene, such as polyamides[11–15], in which forces other than just the simple van der Waals play a role in stabilizing the crystal packing. The Keller and Dreyfuss studies on nylons lead to the conclusion that the lamellar spacing is greatly influenced by the hydrogen bonds present and by the length of the chemical repeat unit.

In recent years a new class of polymers of the type



$$[-\underset{\overset{\|}{O}}{C}-\phi-\overset{\overset{O}{\|}}{C}-\underset{\overset{|}{H}}{N}-(CH_2)_x-\overset{\overset{H}{|}}{N}-\underset{\overset{\|}{O}}{C}-\phi-\overset{\overset{O}{\|}}{C}-O-(CH_2)_y-O-]$$

with various x/y ratios, referred to as polyesteramide xNTy, has been synthesized in the Snamprogetti Laboratories of San Donato Milanese[16]. Because of their techological and scientific interest, a large number of studies have been carried out in order to characterize structural[17], thermodynamic, mechanical and rheological properties[18–20] of these polymers. On account of the presence in macromolecules of both the constituents of a polyamide and of a polyester, it seemed to us of particular relevance to undertake a morphological investigation of their single crystals as grown from dilute solutions, in order to establish correlations between chemical composition and morphology. The object of this paper is to report the results of the small-angle X-ray scattering (SAXS), calorimetric and i.r. studies on the polyesteramide 6NT6 (PEA 6NT6), as crystallized and annealed under different conditions.

EXPERIMENTAL

Materials and sample preparation

The polyesteramide 6NT6 used in this work was supplied to us by our laboratories in San Donato Milanese, the viscometric molecular weight being 3 x 10^4. As far as solution properties of this polymer are concerned reference is made to the paper of De Chirico[20]. The polymer was dissolved in benzyl alcohol (c = 0.1% w/v) at $T \simeq 170°C$ and then crystallized at different temperatures in thermostatically controlled oil baths. The upper temperature limit was chosen so as to obtain crystals in practicable time (maximum one week). Single crystals were filtered at the crystallization temperature (T_c) and the collected mats dried *in vacuo.*

Instrumentation

SAXS measurements were made on the dried crystal mats using an Elliott GX-6 rotating anode (CuKα radiation, λ = 1.54 Å) as X-ray generator and a Luzzatti–Baro small-angle camera. Dried crystal mat specimens were oriented with the mat plane parallel to the X-ray beam, the film–specimen distance being in the range 220–250 mm. The long spacing (L) of the lamellae was computed by applying the Bragg relationship. Wide-angle X-ray scattering (WAXS) measurements were carried out by means of a flat camera and a Philips powder diffractomer.

Electron microscopy observations were made by using a Seemens Elmiskop 1A transmission electron microscope.

Apparent enthalpy of fusion (ΔH_{app}) and melting tempe-

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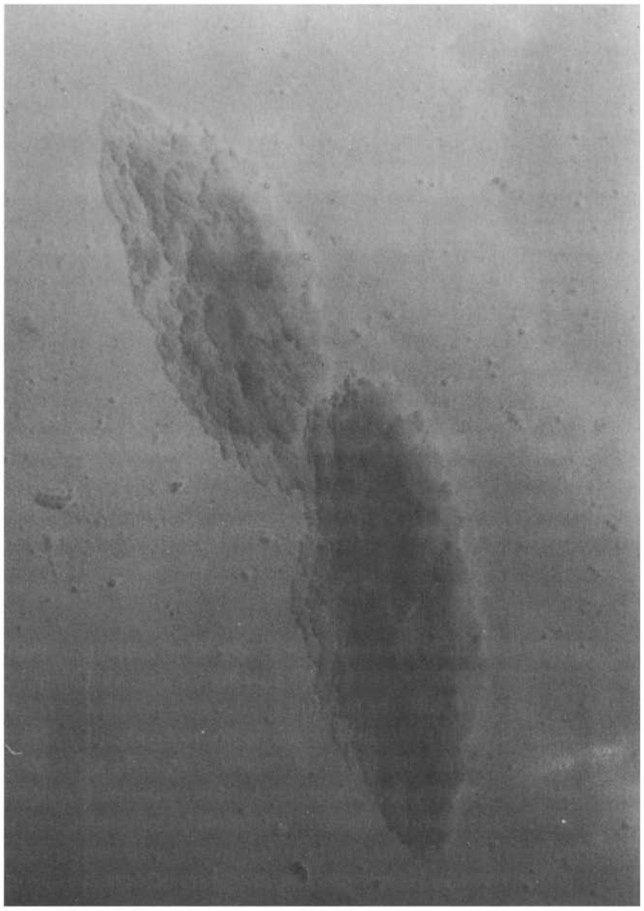

Figure 1 Electron micrograph of PEA 6NT6 single crystals grown at T_c = 50°C (C = 0.1% w/v). Magnification 50 000X

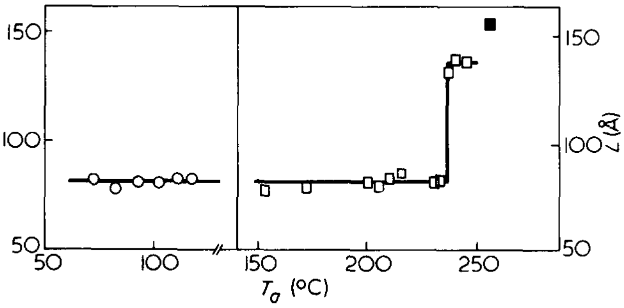

Figure 2 PEA 6NT6 single crystals long spacing as a function of T_c and T_a

ratures (T_m) of the dried crystals mats were measured by means of a Perkin–Elmer differential scanning calorimeter DSC 1B.

Perkin–Elmer 157 and 180 double-beam i.r. spectrophotometers were used to study spectroscopic characteristics of the single crystals of PEA at room and at elevated temperatures in a high temperature cell. The samples were prepared by dispersing the single crystals in KBr discs.

RESULTS AND DISCUSSION

The electron micrograph of PEA 6NT6 single crystals grown at T_c = 50°C is shown in *Figure 1*. As can be seen they appear in ellipsoidal and flat forms, mostly multilayer. The self-seeding technique[21] and lower concentrations could be used in order to obtain better crystals.

In *Figure 2* the long spacing is plotted *versus* crystallization temperature and annealing temperature (T_a). The lamellar thickness is constant over the entire range of T_c in which it was possible to grow the crystals, while in the annealing experiments a sudden increase of L is found at 240°C. The temperature region near the transition was carefully examined, so that it is possible to assess its quantized nature in the range of 1°C. The total thickness corresponds to ~3.5 monomeric units for the unannealed samples, ~ 6 units for the annealed and 6.5 for the melt-crystallized specimens. Similar behaviour was found by Dreyfuss and Keller[11] for polyamides. *Figures 3* and *4* show the melting temperature (T_m) and apparent enthalpy of fusion (ΔH_{app}) dependence on T_c. Two peaks appear on the thermograms. By increasing T_c the first peak (at lower temperature) is shifted to higher temperatures and becomes larger in area, while the second is constant with respect to both T_m and ΔH_{app}*. A possible explanation could be found in the recrystallization process after melting, as found for the ethylene–butadiene copolymers[22].

In *Figure 5* the NH stretching band (3320 cm^{-1}) absorbance, normalized to the CH bending band (745 cm^{-1}) absorbance, is plotted *versus* T_c. As it can be seen A_{3320}/

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* The total ΔH_{app} also remains constant (both peaks).

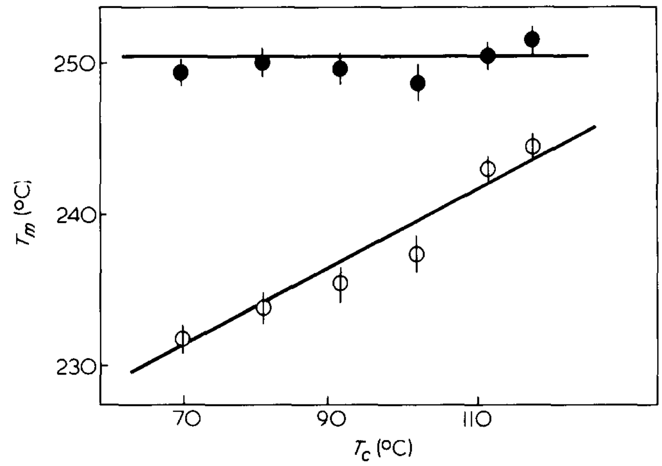

Figure 3 Dependence of the melting temperature of PEA 6NT6 single crystals upon T_c (○, first peak; ●, second peak)

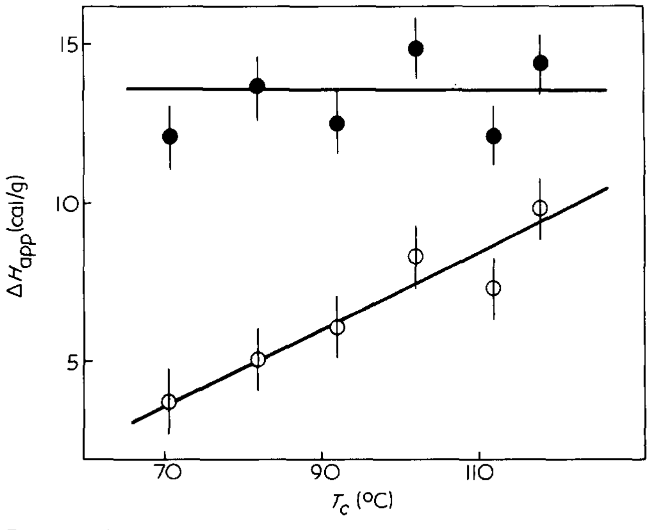

Figure 4 Dependence of the apparent enthalpy of fusion of PEA 6NT6 single crystals upon T_c (○, first peak; ●, first plus second peak)

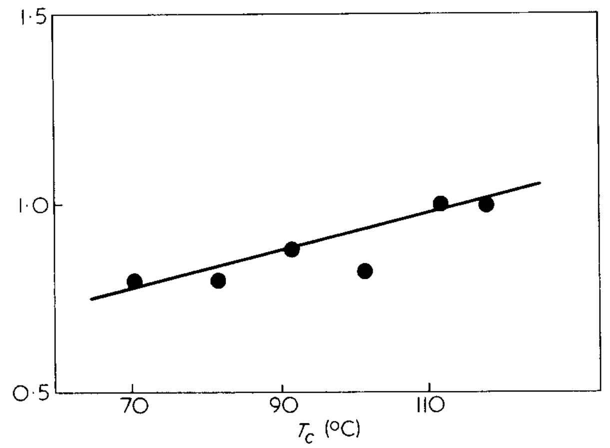

Figure 5 Dependence of the intensities ratio A_{3320}/A_{745} upon T_c for PEA 6NT6 single crystals

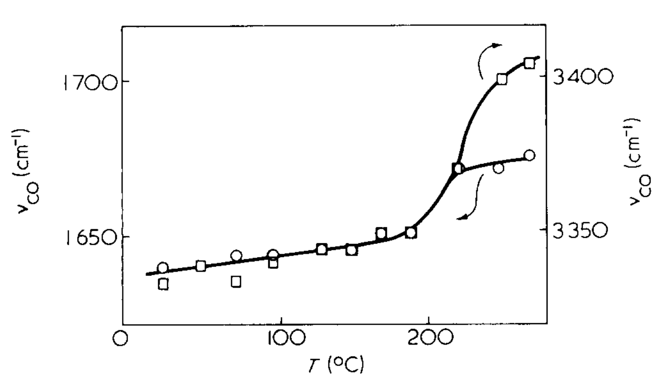

Figure 6 Absorption frequency dependence of ν_{CO} and ν_{NH} stretching vibrations upon temperature for PEA 6NT6 single crystals

A_{745} increases in materials crystallized at higher temperatures; the explanation for this cannot be found in an increase of the number of H-bonds related to the lamellar spacing, which does not vary, but in a better crystal morphology achieved for smaller ΔT of supercooling. Moreover the A_{3320}/A_{745} *versus* T_c trend is in agreement with those shown in *Figures 3* and *4* by the T_m and ΔH_{app} of the first peak of the thermograms.

The i.r. characteristics of a sample of PEA 6NT6, crystallized at T_c = 72°C were studied as a function of the heating temperature of single crystals dispersed in a KBr disc In *Figure 6* the absorption bands shifts of ν_{CO} (1640 cm^{-1}) and ν_{NH} (3320 cm^{-1}) are plotted against T. It can be seen that both Figures reveal a transition, centred at ~220°–230°C, which corresponds to the melting temperature of the first peak of the thermogram. The gradual shift before the transition could be explained in terms of thermal expansion in the crystals involving weakening of H-bonds; this is in agreement with the dilatometric evidence[18].

Wide-angle X-ray scattering (WAXS) patterns obtained from sedimented mats of PEA 6NT6 single crystals grown at different temperatures do not reveal changes with T_c in lattice spacings or (qualitatively) in the relative intensity of the reflections, suggesting the absence of variation in the crystalline phase.

In agreement with the above-mentioned i.r. and d.s.c. results is the evidence that a small increase in volume crystallinity is present, increasing T_c. The density values vary from 1.291 ± 0.001 g/cm^3 for the samples crystallized at T_c = 82°C, to 1.295 ± 0.001 for those obtained at T_c = 112°C. The presence of defects inside both the crystalline and the fold regions, accounting for a looser crystal packing, could explain this small variation without implying any particular confinement of the imperfections in the fold region.

A comment is needed at this point about the fold structure of PEA 6NT6 lamellae. The presence of hydrogen bonds in the (110) planes, as revealed by the crystal structure[17] and the energetic implications connected with it favour the hypothesis that chain-folding preferentially occurs along these planes. By inspection of space filling models of PEA 6NT6 folded-chains (see *Figures 7* and *8*) two possible situations can be realized for tight folding, in the (010) and (110) crystallographic planes, respectively. In the first case both the amide and ester group can be found on the lamellar surface, while in the second, because of the presence of H-bonds, the ejection of the ester groups would be preferred. In this case the first amide group below the folding surface in the two neighbouring chain segments could interact to give H-bonds. A tight fold could also explain the experimental data regarding the long spacing of the PEA 6NT6 lamellae *versus* the crystallization and the annealing temperature. The constancy and the quantized increase of L, corresponding to multiples of half of the monomeric unit, which may be justified by the similarity of the ester and amide groups, in fact are better justified

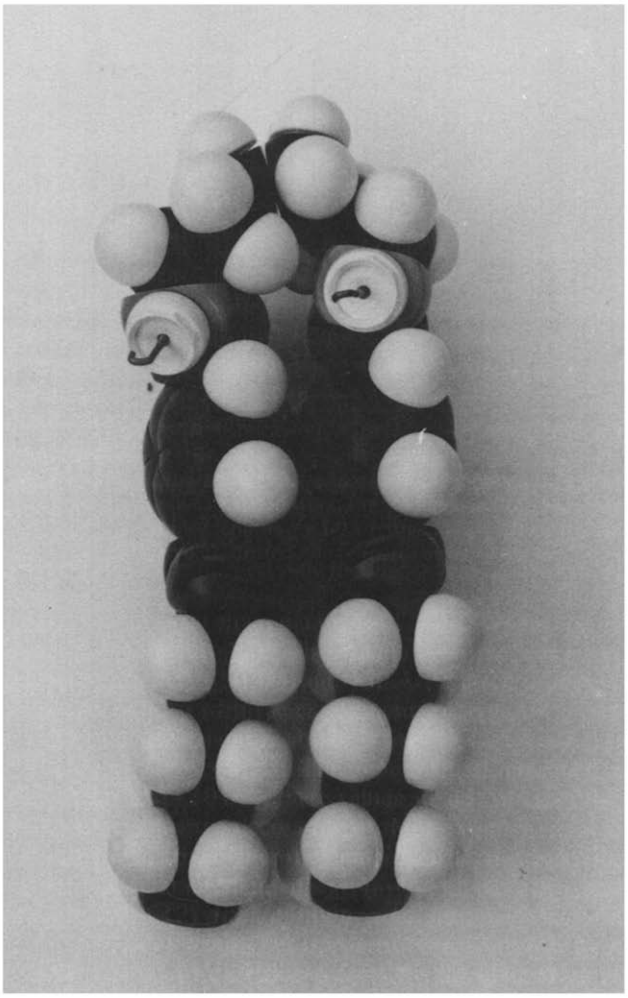

Figure 7 Space filling model of PEA 6NT6 molecule folded in the (010) crystallographic plane. The atoms with hooks and slits are hydrogen and oxygen atoms respectively, which could be involved in hydrogen bonding

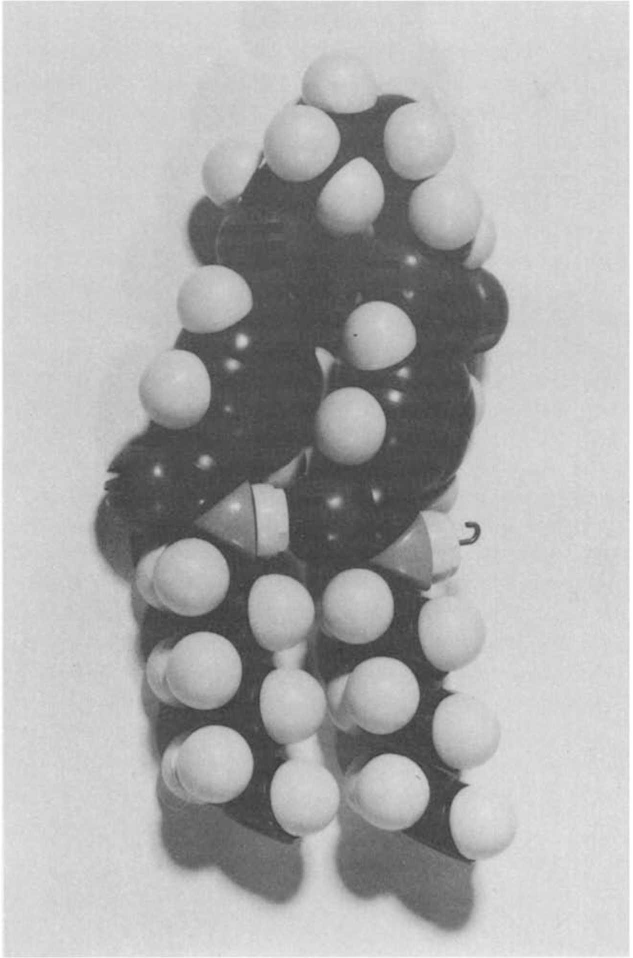

Figure 8 Space filling model of PEA 6NT6 molecule folded in the (110) crystallographic plane. The atoms with hooks and slits are hydrogen and oxygen atoms respectively, which could be involved in hydrogen bonding

by a sharp rather than a loose fold, owing to the higher activation energy needed to rearrange chains already coupled by hydrogen bonds than to adjust loose folds and free cilia, mainly governed by dispersion forces.

In conclusion, from the experimental evidence it appears that, as in the case of nylons, the stereochemical complexity of the monomer unit plays an important role in determining the morphological characteristics of the lamella and of its fold surface for PEA 6NT6, on which a series of tight folds, with adjacent re-entry would occur. However, it must be kept in mind that this characteristic is not unique, if we consider that in the case of short polymers, such as iodine-terminated paraffins[23], with particular sharpness in the molecular weight distribution, it is possible to find the same nature of the fold surface, at least for given molecular length and crystallization conditions. Poly(decamethylene oxide)[24] offers further evidence in favour of the idea of regularly folded surfaces in polymer single crystals, which, however, does not necessarily mean that this situation would always be achieved, on account of the many experimental results obtained in the study of this still open problem.

ACKNOWLEDGEMENTS

Thanks are due to Dr A. De Chirico and Dr G. della Fortuna for supplying us with the samples, to Dr A. Melis for the electron microscopy, and to Professor E. Giglio for the many helpful discussions.

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