ENGINEERING POLYMERS AND COMPOSITES

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The Society of Plastics Engineers

SEPTEMBER 23 & 24, 1987

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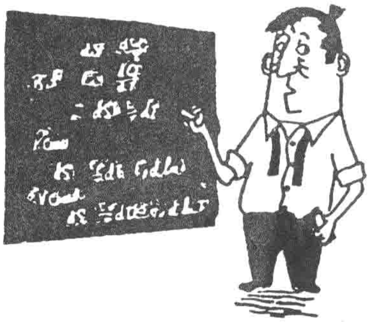

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Morphology and Crystallization Mechanisms in Liquid Crystalline (Thermotropic) Polymers

BY

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Background

Since the patent disclosure (1) in the early Seventies by DuPont on the processing and unusual properties of liquid crystalline polymers, research in this area grew at a phenomenal rate. Kevlar (poly phenylene terephthalamide), the first commercial product marketed by DuPont (in form of fibers), displayed almost five times the modulus of any other organic fiber known before (2,3). this fiber was wet spun from a concentrated solution of H_2SO_4 (4,5). The most important consideration during fiber spinning were to achieve high concentrations of the polymer in the spinning dope, to employ solutions which exhibit anisotropic or liquid crystalline properties, and to use air gap in spinning. A review of the conditions required to form an anistropic phase is given elsewhere (6).

One can immediately forsee a problem in forming three dimensional objects from these liquid crystalline (lyotropic) solutions. During spinning, the solvent has to be removed from the precipitating polymer, thus imposing severe mass transport considerations for forming thick objects and problems in attaining high orientation, A way to avoid this problem was to synthesize polymers that could exhibit a liquid crystalline state above their melting point (thermotropic). Research in this area was initiated by Jackson and Kuhfuss (7,8) working in the laboratories of Tennesse Eastman. They made a copolymer of PET (poly ethylene terephthalate) and p-hydroxy benzoic acid. Soon DuPont , Celanese, Carborundum and Teijin (Japan) entered into the race, swelling the patent literature (e.g., 9-12). However, the commercial growth in this area has been slow, due to the high cost of the monomers required. The properties obtained by thermotropic polymers are inferior to that of Kevlar , because to make these polymers processable, asymmetric or flexible groups are added to the backbone, which impose a constraint on the maximum achievable orientation. Reviews on the nature and formation of small molecule (13) and polymeric liquid crystals (14) have been published. Microstructure and the phase transformation characteristics of these polymers have yet to be explored in detail, and the present research work was undertaken to study some of the basic properties of a class of thermotropic co-polyesters.

Materials and Objectives

The objectives were to study the morphology and explore possible correlations between the liquid crystallinity and the crystallization kinetics. A polyester system containing hydroxy-naphthalic acid (HNA)-42 mole % and hydroxy benzioc acid (HBA)-58 mole % was chosen (Fig. 1a). This polymer exhibited a nematic structure above its melting point and cooled to a crystalline solid . The material was supplied in the form of extruded, chopped pellets by Celanese Co.

Results & Discussion

This system was examined by transmission electron microscopy (TEM), scanning electron microscopy (SEM), wide angle X-ray diffraction (WAXD) and optical microscopy. Thermal characterization was carried out with a differential scanning calorimeter (DSC) and an optical microscope with a hot stage.

Fig. 1b shows an optical micrograph under crossed polarizers. The dark lines indicate the local direction of the molecules such that the polarization of light is cancelled by the analyzer (15,16). This was confirmed by looking at some of these lines by rotating the analyzer and the polarizer. When this polyester was polished and etched for two hours by propyl-amine, it revealed domains of about one micron in width, which were well defined (Fig. 2). Fig. 3 shows a section that was microtomed. It shows extremely well defined rods packed in the direction of extrusion. When these are viewed under TEM, nonuniform density features 500-1000 A in size were observed (Fig. 4). Similar structures have been observed earlier by TEM for a thermotropic polymer made out of Polyoxybenzoate/polyethyleneterepthalate POB/PET (17). The WAXD patterns are shown in Fig. 5. The solid sample was mounted parallel to the extrusion direction. The three reflections on the equatorial line corresponds to 1.62, 2.33 and 3.66 A spacings as calculated by the Bragg's law. Since the basic features are similar in both cases, this suggests that some orientational order is retained even if the initially oriented polymer is heated through its melting point.

Blackwell et al (18) have shown that the meridional reflections do not arise from any blockiness of the HBA/HNA which may be distributed unevenly along a chain, but from a complete random arrangement. When these materials are drawn and crystallized, the equitorial reflections get very sharp and a few others appear, this indicates that there is a perfection and a change in the crystal structure.

Although an orientational order exists in the liquid crystalline state, but it is far from a crystallographic (long range) order i.e. the position of the chains with respect to each other is not well defined. This has been confirmed by looking at the X-ray pattern of a liquid crystalline polymer in the isotropic (disordered), nematic (liq. crystalline) and solid (crystalline) states (19). The change in X-ray pattern on transformation from isotropic to nematic is small. Both states exhibit amorphous like halos; but on lowering the temperature below the crystallization temperature, there is a considerable sharpening of the diffracted beam.

Typical DSC traces of 58/42 (HBA/HNA) are shown in Fig. 6. The first run always contained more than one peak at the melting point. However, it was only the second peak (at 246 °C) that could be reproduced on subsequent heating. To investigate the nature of the first peak, different samples were heated and then annealed at 150, 167, 187 °C for several hours and also at room temperature for ten days, but the first peak could not be reproduced (the T_g of these samples is about 100 °C). A sample was extruded through a melt indexer (with zero tension), but again it failed to show the first peak. It has been observed with PET/POB copolymers, that extra thermal transitions are induced when the material is crystallized in the stretched state (17), therefore the first peak may have been induced by the extrusion process. As mentioned earlier the X-ray data by Blackwell (18) indicates that after crystallization in the stretched state, the patterns get sharper and many spots appear which were not visible earlier. This may be taken as an indication of a second crystalline phase introduced by orientation. Wunderlich (20) has raised the possibility of conformationally distorted (condis) crystals in these materials. This indicates that the orientation may have induced a second phase that consisted of chains in conformations which are not allowed when crystallization occured under quiescent conditions. This is consistent with the fact that crystals produced by orientation melt at lower temperatures (See the low temperature peaks in the first scan, Fig. 6).

In this work no importance was attached to the extra peak observed in the first run because crystallization was studied under quiescent conditions. Table 1 shows the melting point (T_m) and enthalpy associated with the melting transformation as measured by DSC. The enthalpy of phase change during cooling is a more reliable measure as compared to that during heating because of the problems associated with the base line determination (see Fig. 6 for cooling and heating curves of this sample). These samples were heated to 335 °C for short periods , and no thermal degradation was observed.

A Sample was heated above T_m and cooled rapidly to a temperature below T_m. The sample was held isothermally at this temperature and the change in exotherm was monitored. The areas under the exotherm is related to the enthalpy of crystallization. If the exotherm is divided in a number of slices (along the time axis), the area of each of these slices indicates the amount of crystallization occurring during that time interval (21). The cumulative amount of crystallization (W_t) at any time can them be expressed as a ratio to the total crystallization (W_∞) that can take place at that temperature. Plots of W_t/W_∞ vs. time are shown in Fig. 7. These curves can be expressed by an Avrami equation (22,23) given below.

$$W_t/W_\infty = 1 - \exp(-Zt^n)$$

Z is the rate constant, and the index 'n' is related to the mode of crystallization. Table 2 shows the interpretation of various values of 'n'. However, non integral values for 'n' are reported when the nucleation mechanism changes during transformation, or when secondary crystallization intervenes or when the growth is diffusion controlled (22, 23, 25).

A plot of double logarithm of W_t/W_∞ vs. logarithm of t would then yield straight lines of slope 'n'. Fig. 9 shows the Avrami plots for this sample. Table 3 shows the total enthalpy of crystallization at these temperatures. The Avrami plots in Fig. 9 exclude the curves at 215 and 217 degrees °C, as they yielded curved plots, with initial slopes greater than 4. At 218.5 °C, the value of 'n' is high. These kind of discrepancies occur when the crystallization rate is high at the temperature of observation. It took two minutes after the material was quenched (from the melt to the isotherm) before the DSC could respond resulting in a loss of information on the kinetics during this period. This explains the low values of enthalpy of crystallization (Table 3) at 215 and 217 °C. It can be seen from Figure 8 that 50 % of the crystallization at these temperatures was complete in 3.9 and 4.3 minutes respectively. It has been shown (26) by error analysis that a 4 % error in the estimation of crystallization time may change this exponent from 4 to 4.3.

In the optical microscope, at this transition only a slight intensity change is observed without any reorganization. Since the value of 'n' lies between 3 and 4, it can be inferred from Table 4 that the growth of the crystals is not diffusion controlled and it is three dimensional, but the nucleation mechanism is not clear. It seems that the rod like structures seen under SEM (Fig. 3 or 4) were not formed during crystallization but were also present in the nematic state. This is being suggested as no change was observed in the optical microscope (on the micron level) as the material is cooled through the solidification temperature . The change in entropy ($\triangle S_m = \triangle H_m/T_m$) at melting for this sample can be calculated from the data in Table 1. The molecular weight of the repeat unit can be taken as 350.5 gms/mole. This yields a $\triangle S_m$ of 0.9 J/mole degrees K as compared to 43.5 in polyethylene-terephthalate and 16.8 for high density polyethylene(see Table 4). This shows that the change in entropy or the rearrangement of the molecules due to the melting of this liquid crystalline polymer is small. If one were to assume that these rod like structures seeded the crystal centers (heterogenous nucleation), then the Avrami exponent 'n' would exceed 3 only if a non linear three dimensional growth occurred (i.e., the area of the growing crystal expanded faster than the rate of change in volume).

Concluding Discussion

The transformation energies for polymers containing only rigid moieties in the backbone are small (less than 0.4 cal/gm). These materials do crystallize in an ordered manner because the X-ray diffraction pattern for these change from an amorphous halo to a sharp crystalline pattern at the nematic-crystal transition (26,29) although the tranformation energies are small . When these are cooled rapidly, their X-ray patterns are not as sharp as those obtained from slow cooling.

Blundell (30) observed that although the effect of cooling through T_m was considerable on X-ray patterns but this occurred with a little change in the melting endotherm . He suggested that this may happen due to a small surface energy (γ) of these crystals, i.e.,

$$\triangle H = \triangle H_\infty - A\ \gamma/V$$

where $\triangle H$ and $\triangle H_\infty$ are the melting enthalpies for crystal of volume V and of an infinite size. On this basis, when we crystallized these materials, no significant surface energy was involved, e.g., as in surfaces formed by chain folding in conventional polymers. This would be consistent with the fact that the crystallization may have proceeded from nuclei in a three dimensional growth pattern as suggested by Avrami analysis, but without any large reorganization of the domains (as seen by optical microscopy). Therefore, it can be concluded that these extruded materials, which had been melt stretched, consist in the solid state, of elongated entities (200-500 A in diameter) in the flow direction (Fig. 4), which further agglomerate to form structures of similar shape, but which are about one micron in diameter (Fig. 3). The boundaries between these are distinct; and thus needle-like voids will be present in the materials. The crystallization kinetics suggests that the micron diameter ellipsoids or the finer features observed by TEM may consist of the molecular segments arranged in a spherulitic structure.

The crystallization mechanism discussed above has strong implications on the processing of these polymers. Since both the enthalpy and the entropy are small at the melting point, therefore a small amount of latent energy is exchanged in a heating or a cooling process and the change in dimensions during this transformation would be small. The orientation in these polymers is accompanied by a large change in melting endotherms that occur at temperatures lower then the melting point of the crystals formed under zero strain.

Acknowledgement

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Table 1

Data for Crystal Nematic Transformation of the Copolyester

	Heating*	Cooling*
Melting/Freezing Peak, °C	251	207
Melting/Freezing Enthalpy, J/gm	1.34	2.42

*Heating and cooling rates were 10°C/minute

Table 2

Values for the Avrami Exponent, n, for Various Types of Nucleation and Growth

n	
3+1=4	Spherulitic growth from homogenous nucleation (n $\propto t^1$)
3/2+1=5/2	Diffusion controlled spherulitic growth from homogenous nuclei
3+0=3	Spherulitic growth from heterogenous nucleation
3/2+0=3/2	Diffusion controlled spherulitic growth from heterogenous nuclei
2+1=3	Disc-like growth from homogenous (sporadic) nuclei
2/2+1=2	Diffusion controlled disc-like growth from homogenous nuclei
2+0=2	Disc-like growth from heterogenous nuclei
2/2+0=1	Diffusion controlled disc-like growth from heterogenous nuclei
1+1=2	Rod-like growth from homogenous nuclei
1/2+1=3/2	Diffusion controlled rod-like growth from homogenous nuclei
1+0=1	Rod-like growth from heterogenous nuclei
1/2+0=1/2	Diffusion controlled rod-like growth from heterogenous nuclei

Table 3

Isothermal Crystallization Enthalpy at Different Temperatures, after cooling from 277°C.

Crystallization Temperature (°C)	Enthalpy J/gm	Avrami Parameters	
		Intercept	Slope
215	0.89	-	-
217	0.96	-	-
218.5	1.34	25.7	4.24
220	1.25	20.7	3.32
222	1.30	19.5	3.04
225	1.34	22.6	3.48