

## Studies on the Morphology of Poly(terephthalate)s

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**ABSTRACT:** The effect of temperature on the crystalline morphology of melt-crystallized poly(hexamethylene terephthalate) (PHT) and poly(decamethylene terephthalate) PDT was studied. An isothermal crystallization of both polymers was carried out within a wide range of temperatures. Microscopic and small-angle light scattering studies of the crystallized samples have shown the rod-like morphology as the prevailing one. Optical properties of the morphological entities evidently depend upon the crystallization temperature. At temperatures close to the maximum crystallization rate temperature  $T_{max}$ , only the structures of type 45 occur. At temperatures much lower or higher than  $T_{max}$ , structures of type 0-90 or mixtures of both 45 and 0-90 were observed. An explanation for this phenomenon is offered.

**KEY WORDS** Polyterephthalates / Crystallization / Morphology / Rod-like Structures /

Crystallization temperature is one of the most important factors affecting the morphology of crystallizing polymers.<sup>1</sup> Various morphologies as well as different sizes of morphological entities are usually observed when crystallization is carried out at different temperatures. Since crystalline morphology strongly affects many physical properties of the polymeric material, it is important to understand the phenomena controlling its formation. In particular, the effects of the crystallization temperature on the morphology of isothermally crystallized poly(hexamethylene terephthalate) (PHT) and poly(decamethylene terephthalate) (PDT), are studied in the present work.

This study, as a part of a wider investigation concerning the effect of cross-linking on the crystallization of polyterephthalates, confines itself to initial, uncross-linked polymers. Crystallization of these polymers has not been extensively studied in the past. Only a very few results concerning crystallization kinetics and the morphology of PHT,<sup>1</sup> as well as some X-Ray studies of its structure do exist,<sup>2,3</sup> but such results for PDT are lacking.

For this reason, a more complete study of the crystallization of polyterephthalates was undertaken at our laboratory. The aim of this paper is to summarize the results concerning the dependence of

the morphology of two polyterephthalates on temperature and the chemical structure of the polymers.

### MATERIALS AND PROCEDURES

Poly(hexamethylene terephthalate) and poly(decamethylene terephthalate) were prepared by the transesterification of dimethyl terephthalate with corresponding glycols, hexamethylene glycol and decamethylene glycol followed by polycondensation of glycol esters, obtained in the first step.

The reaction was carried out in the presence of a glycol excess to obtain polymers with -OH end groups exclusively. This is necessary for further cross-linking of the polymers, with triisocyanate. The analysis performed by NMR and IR spectroscopy showed that -OH groups were indeed the only end-groups existing in the material.

Molecular weights of the polymer samples were determined by the end group analysis. The results of these measurements are reported in Table I, along with the melting temperatures, obtained by the differential thermal analysis.

Using the known relationships, both the glass-transition temperature,  $T_g^{4,5}$  and the temperature of

the maximum crystallization rate,  $T_{\max}^{6,7}$  were estimated from the melting temperature,  $T_m$ , by the following formulas.

$$T_g = 0.66 \sim 0.67 T_m$$

and

$$T_{\max} = 0.82 \sim 0.85 T_m$$

The corresponding values are also reported in Table I. The melting temperatures shown here are evidently lower than the corresponding ones given in the literature.<sup>8,2</sup> Since, in both cases, similar methods were applied, this deviation may be due to the substantial differences in molecular weights (relatively low molecular weights in the present paper as compared to those in the papers in ref 2 and 8). This viewpoint is consistent with the results of a separate study<sup>9</sup> on the dependence of melting temperature on the molecular weight obtained for narrow fractions of PHT and PDT in the range of 1000–3000. The results<sup>9</sup> show that the melting temperature does increase with an increase in molecular weight.

Samples for morphological studies were prepared in the following manner. First, the polymer was melted between microscope cover glasses for 5 minutes at a temperature, 20°C higher than the corresponding melting temperature. After melting, the samples were quickly transferred to a bath filled with silicone oil adjusted to the desired crystallization temperature.

The range of crystallization temperatures was chosen between 20°C and 110°C for PHT, and between –5°C and 100°C in case of PDT. In order to obtain the final “equilibrium” degree of crystallinity and the final morphology corresponding to each temperature, a long enough crystallization time was chosen for each experiment. At relatively low undercoolings (lower than 20°C), the crystallization time was about 30 hours, whereas at high undercoolings, it was only from 2–5 hours. Finally, the samples were cooled to room temperature. The morphology of the crystallized samples was studied at room temperature, using a polarizing microscope, and by means of small-angle light scattering (SALS).

## RESULTS AND DISCUSSION

Typical morphologies, as seen under microscope,

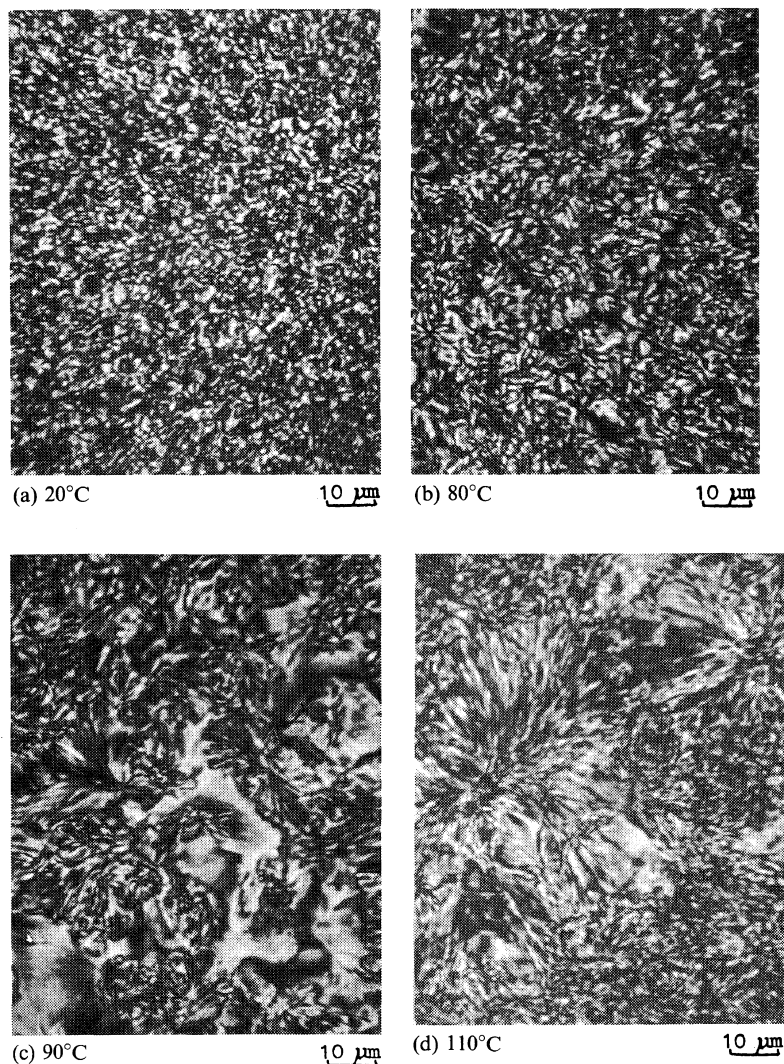
are shown in Figure 1 for PHT, and in Figure 2 for PDT. As can be seen in both figures, the existence of rod-like entities in the majority of cases studied is the characteristic feature of the morphology. The entities formed at a low crystallization temperature seem to be quite small (Figures 1a and 2a) compared to those grown at higher temperatures. This may result from the variation in the ratio of the nucleation rate to the crystal-growth rate with temperature. It is quite probable that at low undercoolings, the low nucleation rate is accompanied by relatively high crystal-growth rate, which would cause growth of not too numerous, but large entities. At higher undercooling, however, the nucleation rate may dominate, causing the formation of a much greater number of nuclei at the initial step of crystallization, and consequently the final structure is filled with a great number of small entities. It can be also noted that the morphological entities are practically monodisperse with respect to their size. This might be considered as evidence of athermal nucleation, or at least may suggest that nucleation process does not overlap in a time scale with the growth of morphological entities.

Besides the observed rod-like elements mentioned above, plate-like entities could be distinguished in some samples (Figures 1c and 2d), usually in those crystallized at the highest temperatures. Sporadically, some spherulites were also found (Figures 1d and 2a) in a few cases.

In order to investigate the optical properties and organization of the structural entities, SALS studies were performed. Examples of  $H_v$  light-scattering patterns are shown in Figure 3, and the corresponding photometric curves in Figure 4.

As can be seen, the monotoneous decrease in scattered-light intensity with an increase in scattering angle,  $\theta$ , is observed for all cases. This behavior is typical for a system of randomly distributed rod-like elements.<sup>10,11</sup> It can be noted that different orientations of lobes with respect to the polarization plane of the incident beam are obtained in various cases (*cf.* Figures 3a and 3b). This effect can be attributed to the different orientations of polarizability tensors with respect to the rod axis. The pattern seen in Figure 3a, referred to as the “type 45” pattern, corresponds to those entities having polarizability tensors oriented either parallel or perpendicular to the rod axis (structure type 0-90). The pattern in Figure 3b (pattern “type 0-90”),

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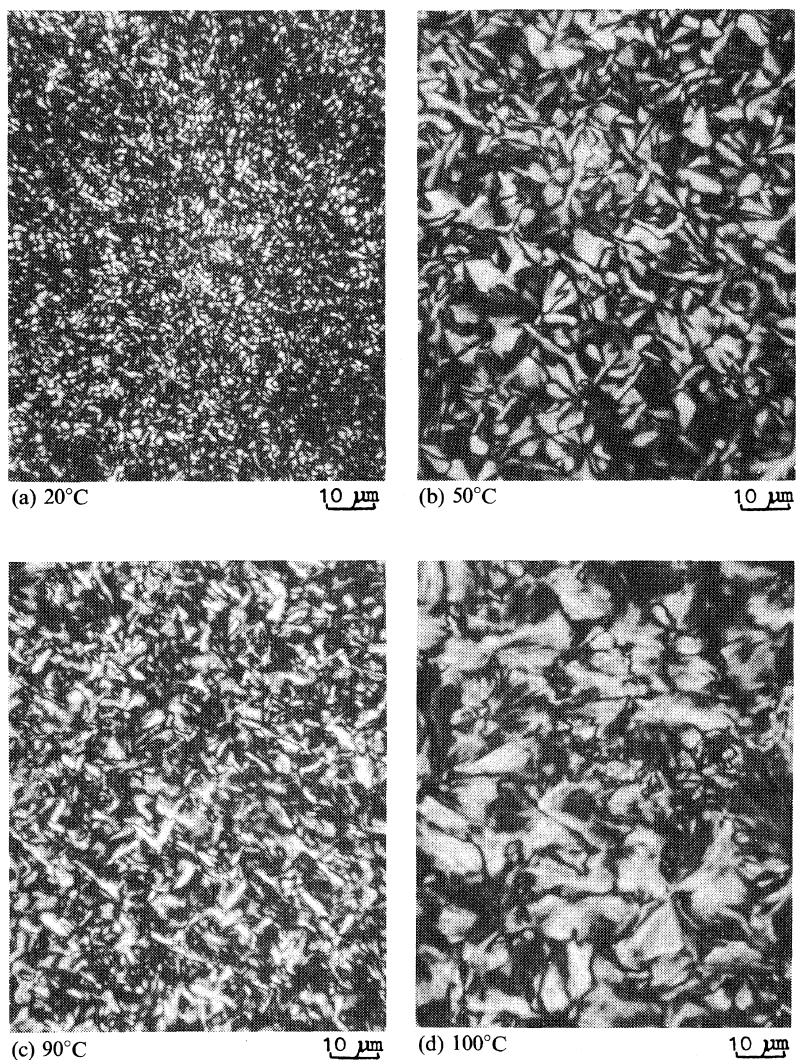


**Figure 1.** Microscope photographs showing the morphology of PHT crystallized at various temperatures.

corresponds to those entities having polarizability tensors tilted  $45^\circ$  towards the rod axis (structure type 45).<sup>10,12-15</sup> The present investigation reveals that the type of structure evidently depends upon crystallization temperature. The curves presented in Figure 5, show hypothetical plots of the crystallization rate vs. temperature dependences for both polymers studied. These curves were plotted with reference to the measured melting temperatures,  $T_m$ , the estimated values of the glass transition,  $T_g$ , and the maximum crystallization rate,  $T_{max}$ , tempera-

tures (*cf.* Table I). Crystallization rates were assumed to be higher for PDT than for PHT. Since there are no results for PDT, this choice can be justified by comparison of the general trends known to exist in this and other homologous series of polymers.<sup>2</sup>

The range of temperatures in which crystallization experiments were carried out is indicated by a heavy line. According to our observations, there exist a specific range of temperatures for each polymer, in which the only structures of type 45 do



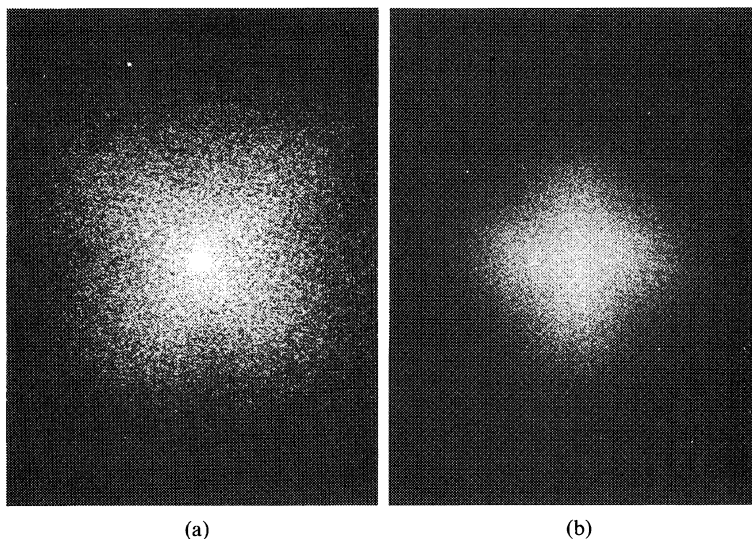
**Figure 2.** Microscope photographs showing the morphology of PDT crystallized at various temperatures.

crystallize. This range is marked in Figure 5 with a double line.

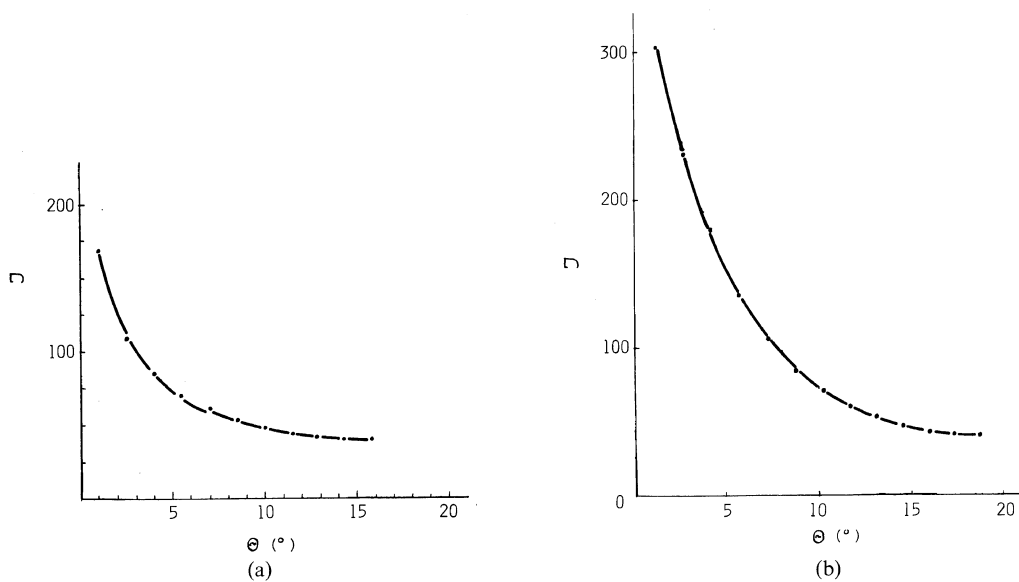
As can be noted, this range for the PHT polymer covers temperatures between 50°C and 70°C. At slightly lower temperatures (between 40°C and 50°C), both structure types were observed simultaneously, whereas at temperatures lower than 40°C but higher than 70°C, only 0-90 structures were found. Type 45 structures for PDT were observed in temperatures between 20°C and 80°C. At tempera-

tures lower than 20°C and higher than 80°C, both structure types were found. Despite the fact that structures of 45-type are not very common in polymer systems, they have been reported in a few cases, and they seem to be typical for polyterephthalates. The occurrence of such structures in poly(ethylene terephthalate) was reported by Baranov and coworkers.<sup>14,15</sup> Stein and others<sup>16</sup> as well as the present author<sup>17</sup> also found them in poly(butylene terephthalate). In all cases men-

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**Figure 3.** Typical examples of  $H_V$  small-angle light-scattering patterns observed in PDT and PHT: (a), pattern type 45 (structure type 0-90); (b), pattern type 0-90 (structure type 45).



**Figure 4.** Photometric curves taken from SALS patterns at angle corresponding to the maximum intensity of the lobe: (a), pattern type 45,  $\mu = 45^\circ$ ; (b), pattern type 0-90,  $\mu = 0^\circ$ .

tioned, however, the observed entities had the form of spherulites.

Considering the range of the existence of type 45 structures, as plotted in Figure 5, one may draw conclusion that this range coincides with the range

of temperatures close to the maximum crystallization temperature. A similar conclusion may also be made on the basis of results presented by other authors.<sup>14-17</sup> It can also be noted that this range is wider for PDT than for PHT. This effect is possibly

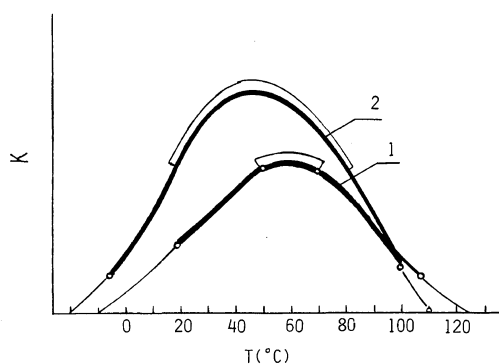


Figure 5. Crystallization-rate dependence upon temperature, estimated for PHT (curve 1), and PDT (curve 2).

Table I.

| Polymer | $M_n$ | $T_m$ | $T_g$     | $T_{max}$ |
|---------|-------|-------|-----------|-----------|
|         |       | °C    | °C        | °C        |
| PHT     | 1900  | 124   | -11 ~ -7  | 52 ~ 64   |
| PDT     | 1700  | 110   | -20 ~ -16 | 41 ~ 52   |

connected to the over-all crystallization rate which is quite different between those two polymers. One may suppose that there exists some critical crystallization rate, above which only 45-type structures grow. According to this, the higher the crystalli-

zation rate, the wider the range of crystallization of such structures. This kind of behavior is indeed observed in the present paper, since faster crystallizing PDT exhibits a wider range accessible to the crystallization of 45-type structure.

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