

CRYSTALLINE MORPHOLOGY IN A SERIES OF CH₃-SUBSTITUTED THERMOTROPIC AROMATIC POLYESTERS WITH EVEN AND ODD FLEXIBLE SPACERS*

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Abstract Crystalline morphology in a series of CH₃-substituted main chain thermotropic aromatic polyesters with even and odd numbered methylene spacers has been studied by polarizing optical microscopy (POM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). On crystallization from solution evaporation spherulites of radial structure were observed in the polymers with even numbered spacers, but spherulites with concentric rings form in the polymer with odd numbered spacers. Both spherulites have a lamellar structure, which is about 10 nm in thickness. On crystallization from nematic glassy state spherulites can not be grown; lamellar structure was only observed around disclinations in a specimen during crystallization. In the case of crystallization from nematic melt two types of spherulites can be observed for the sample with even numbered spacers. For the sample with odd numbered spacers spherulites can not be formed, but only irregular crystallites.

Keywords Crystalline morphology, Spherulite, Even-odd flexible spacers, CH₃-Substituted thermotropic aromatic polyester

INTRODUCTION

A liquid crystalline polymer (LCP) containing mesogenic units in the backbone chain is a rather rigid chain. The molecular chains in the nematic state are assumed to be essentially fully extended. Recently it has proved of considerable interest to study the crystalline morphology of LCP. The crystalline morphology of main chain lyotropic LCPs obtained from their nematic solutions has been studied in many cases, such as poly(1,4-phenylene terephthalamide) (PPTA)^[1-3], poly(1,4-benzamide) (PBA)^[4] and poly(γ -methyl-L-glutamate) (PMLG)^[5-7], etc. Large spherulites could be grown from nematic solutions and the crystalline morphology is not very much different from that of flexible chain polymers.

For the crystalline morphology of thermotropic LCPs, Cheng *et al.*^[8, 9] were able to compare the crystallization from the isotropic state and from the nematic state of thermotropic polyethers containing flexible spacers of various lengths. As these LCPs are monotropic, so that the nematic-isotropic transition temperature T_{N-I} is lower than the melting temperature T_{K-L} , it is possible to perform isothermal crystallization both from an isotropic melt and from a nematic melt. Crystallization from the isotropic state showed spherulitic morphology analogous to spherulites crystallized from flexible chain polymers while lamellar morphology was observed for crystallization from the nematic state^[8]. For crystallization from the nematic state of aromatic polyesters containing long flexible spacers^[10, 11], the observed lamellar morphology leads to the possibility of chain folding during crystallization or its presence even in the nematic state^[11]. If the polymer in the nematic state can be

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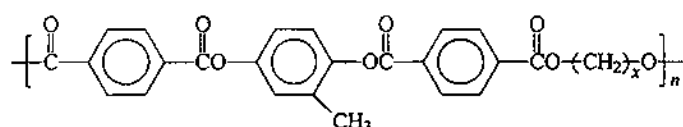
frozen into a nematic glass, the subsequent thermal crystallization will lead to a lamellar morphology which reflects the disclinations present in the nematic state, known as the lamellar decoration for studying disclination first used by Thomas^[12]. Spherulitic morphology was observed for crystallization at a temperature $T_c < T_{K-N}$ from the nematic state in the case of thermotropic halogen substituted aromatic polyesters by Chen *et al.*^[13, 14]. For thermotropic LCPs with short flexible methylene spacers, it has been found that the parity (odd-even) effect of the methylene spacer significantly affects the orientation order of the liquid crystalline mesophase^[15-18].

Up to now, the crystalline morphology grown from nematic melt of LCPs has not been well studied and understood. Furthermore, it should be noted that there has been no further report on the influence of the odd-even effect on crystalline morphology of thermotropic aromatic polyesters crystallized from a solution cast specimen, and especially crystallized from a nematic melt. In the present paper the effect of the odd-even effect on the crystalline morphology of thermotropic aromatic polyesters grown from solution evaporation, from the glassy state and from the nematic melt has been studied.

EXPERIMENTAL

Materials

The samples used in this work are thermotropic aromatic polyesters containing a triad phenylene ring mesogen and methylene flexible spacers of different length in the main chain. They have the following chemical constitution in the molecular chain:



The polymers are denoted as Pd- x ($x = 5\sim 10$). The values of intrinsic viscosity of these polymers determined in phenol-1,1,2,2-tetrachloroethane (1:1) at 30°C and the transition temperatures measured by DSC are listed in Table 1.

Table 1. The intrinsic viscosity and transition temperatures of materials

Samples	$[\eta]$ (dL/g)	T_m (°C)	T_i (°C)
Pd-5	0.30	170	215
Pd-6	0.30	180	257
Pd-7	0.30	157	190
Pd-8	0.31	194	244
Pd-9	0.29	119	188
Pd-10	0.29	145	213

Specimen Preparation

Crystallization from solution evaporation

A 1.0 wt% solution of the polymers in phenol-1,1,2,2-tetrachloroethane (1:1 W/W) was prepared. A few drops of the solution were dropped onto a glass slide, which was then placed in a desiccator at room temperature for growing spherulites under conditions of very slow evaporation of solvent. The crystalline morphology of the specimen was observed under a polarizing optical microscope (POM). For transmission electron microscopic studies, the crystalline specimen was first exposed to RuO₄ vapor for staining for 30 min at room temperature and then a thin layer of carbon was evaporated onto it. Afterwards, the specimen was transferred onto microscope grids for TEM observation.

Crystallization from the nematic glassy state

A few drops of the solution were deposited on a piece of microscope slide preheated and maintained at a constant temperature above T_m of the polymers. When the solvent had evaporated at this temperature a thin polymer film of ca. 100 nm thickness was obtained. Then the polymer film was quenched to room temperature to obtain a frozen nematic mesophase. The specimen was then annealed at T_c for a certain time for isothermal crystallization.

For TEM observation the crystalline specimen was first exposed to RuO_4 vapor for staining for 30 min at room temperature.

Crystallization from the nematic melt

The specimen for crystalline growth and morphology observations was prepared by fusing the sample between two pieces of cover glass at a temperature between T_m and T_i for 10 min. It was then rapidly transferred to a hot-stage at a predefined temperature for isothermal crystallization. The crystalline growth process and morphology of the spherulites were studied using a POM under crossed polarizers. For SEM observation the surface of the specimen was argon plasma etched and a gold layer was evaporated onto the surface of the specimen.

Instruments

The microscopes used in this work were an Olympus Model BH-2 polarizing microscope with a FP-52 hot-stage and a Hitachi Model H-800 transmission electron microscope (TEM) and a Hitachi Model S-570 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Crystallization from Solution Evaporation

Specimens obtained by slow evaporation of a dilute solution show the typical spherulite morphology observed in the POM under crossed polarizers. Spherulites are of round shape, and their size ranges from 10 μm to 100 μm . The size of spherulite for the specimen with even numbered spacers is larger than that of specimen with odd numbered spacers. It is interesting to note that the morphology of these spherulites was found to be dependent on the odd-even numbered spacers of the polymers. The spherulites of the specimen with even numbered spacers ($x = 6$) exhibit a fibril structure in radial direction (Fig. 1a), while the specimen with odd numbered spacers ($x = 7$) tends to grow spherulites with concentric rings (Fig. 1b). It can be seen from Fig. 1 that all these spherulites show a clear Maltese cross extinction pattern under POM. After inserting a compensator into the optical axis of the microscope, the interference color in the first and third diametrically opposed quadrants of the spherulites is orange, and the color in the second and fourth quadrants is blue. This indicates that these spherulites have negative birefringence. Dark concentric rings are distributed uniformly in the spherulites as shown in Fig. 1(b). The radial distance between neighbouring rings is about 1 μm . Similar ringed spherulites have been reported for flexible chain polymers crystallized under proper conditions and were explained as an optical effect of the lamellar orientation twists occurring regularly along the radial direction of spherulites^[19, 20].

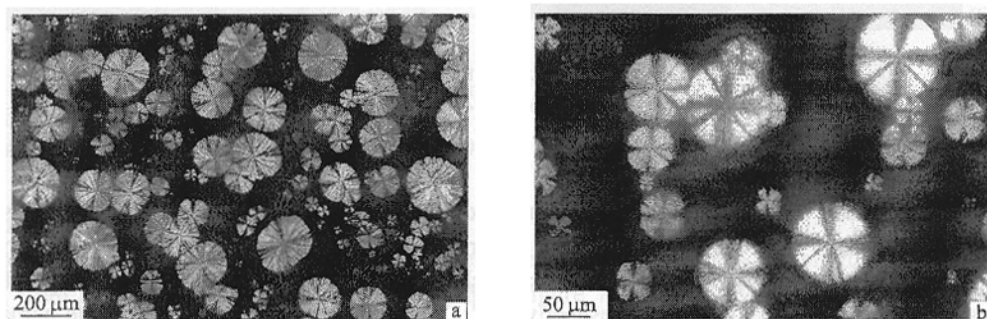


Fig. 1 POM microphotographs of the spherulites of thermotropic aromatic polyesters crystallized from solution evaporation
a) Pd-6; b) Pd-7

Figure 2 shows SEM microphotographs of the spherulites in Figs. 1(a) and (b) etched by argon plasma, respectively. In Fig. 2(a) the less ordered interfibrillar regions were etched by argon plasma to show up the fibrils. In Fig. 1(b) the spherulite shows the wave-like structure which is similar to that of common ring spherulite

in flexible polymers. This implies that the lamellae in the spherulite are twisted regularly along radial direction of spherulite. In order to reveal the lamellar structure more clearly in the spherulites of thermotropic aromatic polyester, the spherulites were observed by using TEM with RuO_4 staining technique shown in Fig. 3. The thickness of the lamellae is about 10 nm. Taking into account the negative birefringence nature of the spherulite, we suppose that the molecular chains are perpendicular to the axes of radially outward growing lamellae, and chain folding may occur at the lamellar surface.

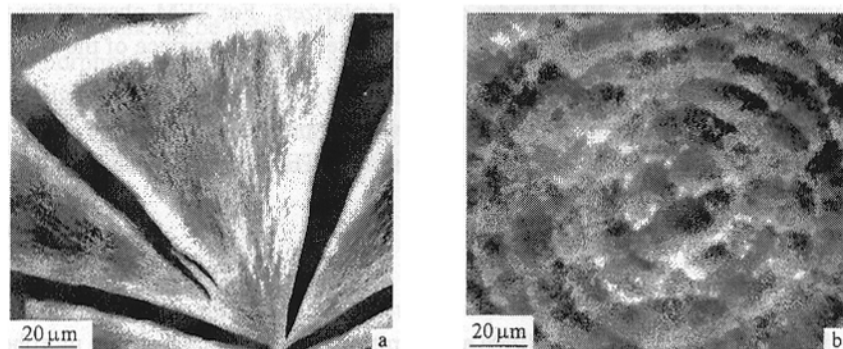


Fig. 2 SEM microphotographs of the spherulites of Fig. 1 after argon plasma etching

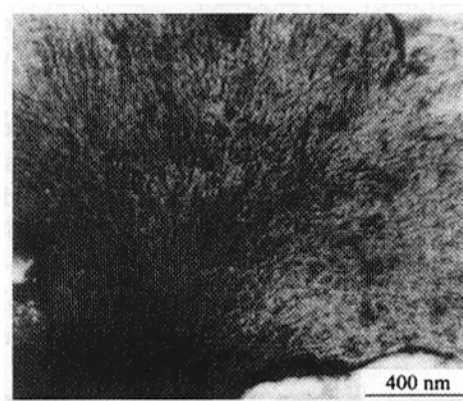


Fig. 3 TEM microphotograph of the lamellar structure in the spherulite of Pd-6 stained by RuO_4

Crystallization from the Nematic Glassy State

The thermotropic aromatic polyesters used in this study exhibited a nematic mesophase and were easily frozen into the nematic glassy state from which the schlieren texture could be observed under a POM as shown in Fig. 4 for the sample of Pd-10. It shows two and four dark brushes emanating from a nucleus, corresponding to the disclination strength $s = \pm 1/2$ and $s = \pm 1$, respectively^[21]. Spherulite can not be grown in the nematic glassy state when it is annealed at crystallization temperatures, but lamellar structures could form around disclinations in the nematic glassy state during crystallization. Figure 5 shows a TEM microphotograph of lamellar structure crystallized from the nematic glassy state of $x = 10$ polymer after annealing at 90°C for 2 h to ensure complete crystallization. It can be seen that the lamellar structure was arranged in a special shape which corresponding to that of the molecular director fields around disclinations described by Frank^[21]. The thickness of lamellae is about 10 nm, which coincides with the size of the lamellar structure observed in spherulites crystallized from solution evaporation. The polymer chains are perpendicular to the long direction of the lamellae, which was

checked by selected area electron diffraction. It is interesting to note that the microphotograph of Fig. 5 shows the lamellar decoration of $s = \pm 1/2$ disclinations as originally developed by Thomas *et al.*^[10, 12] to show the singularity in the chain orientation around the disclinations in the frozen nematic glassy state of thermotropic aromatic polyesters^[22-24]. The types of disclinations with $s = \pm 1$ and some pairs of disclinations have also been observed in this polymer^[12]. Figure 6 shows the director field around a disclination of strength $s = +1$, $c = \pi/4$. This type of disclination is rarely observed in LCP.

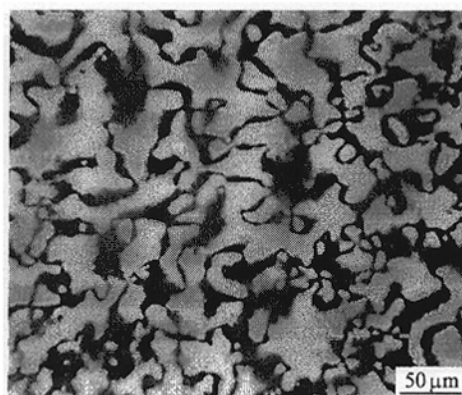


Fig. 4 POM microphotograph of schlieren texture of Pd-10 polymer in nematic glassy state



Fig. 5 TEM microphotographs of lamellar structure crystallized from the nematic glassy state of Pd-10 polymer after annealing at 90°C for 2 h, stained by RuO₄



Fig. 6 TEM microphotograph of lamellar decorated disclination $s = +1$, $c = \pi/4$, showing the director field

Crystallization from the Nematic Melt

In the two different isothermal crystallization temperature regions, two types of spherulites can be formed by quenching from the nematic melt of the Pd-8 polymer. Figure 7(a) shows the POM photograph of the type 1 spherulites. It is interesting to note that the undercooled nematic texture remained as the background of spherulites, and the size of the spherulites is very large, at least in the order of 10^2 μm diameter. These spherulites exhibit a clear Maltese cross pattern under crossed polarizers, showing a negative birefringence. It can be clearly seen that the spherulites of type 1 grow with a morphology of radial radiation. This morphological feature of type 1 spherulites is very similar to that of flexible chain polymers.

The spherulites of type 2 (shown in Fig. 7b) exhibit radially outward growing structure, but no Maltese cross pattern was observed under crossed polarizers. Such spherulites can grow up to several millimeters so that they can be seen by the naked eye. This case is very similar to that of the lyotropic aromatic polyamides formed from

anisotropic solutions^[4].

The morphological difference of these two types of spherulites was found to be independent of the starting melt temperature, but strongly dependent on the crystallization temperature. When the crystallization temperature is above 170 °C, for example $T_c = 185$ °C only the type 1 spherulites can be formed. At crystallization temperatures lower than 160 °C, for example at 150 °C, only type 2 spherulites can be formed. At intermediate temperatures of crystallization between these two limiting temperatures (170 °C and 160 °C), both types of spherulites could be observed simultaneously in the same specimen.

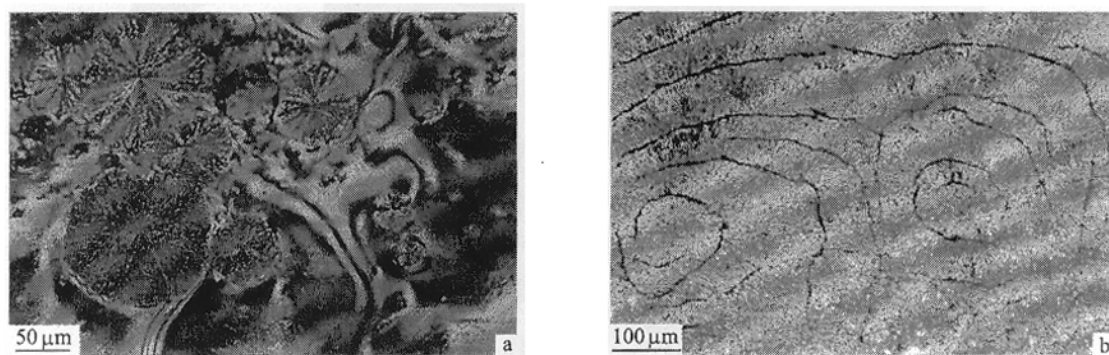


Fig. 7 POM microphotographs of type 1 spherulites (a) and type 2 spherulites (b) of Pd-8 polymer crystallized at 185 °C and at 150 °C, respectively

The spherulitic morphology can also be observed in the Pd-6 polymer crystallized from nematic melt as shown in Fig. 8. The morphology and size of these spherulites are similar to that of type 2 spherulites of Pd-8 polymer, but no spherulite like that of type 1 spherulites of Pd-8 polymer could be observed at any temperatures of crystallization. On the other hand, no typical spherulites of any type were formed in polymers with odd numbered spacers crystallized from the nematic melt, but only irregular crystallites were formed as shown in Fig. 9.

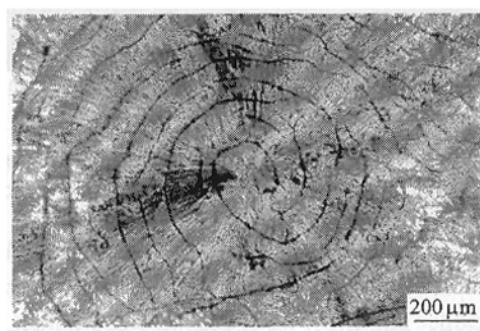


Fig. 8 POM microphotographs of the spherulites of Pd-6 polymer crystallized at 150 °C

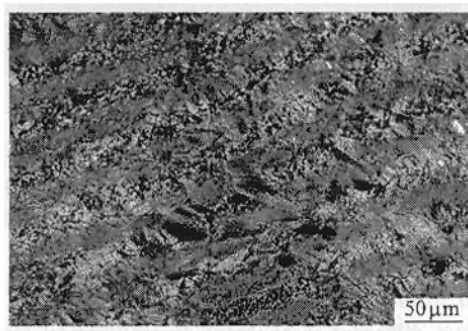


Fig. 9 POM microphotographs of the crystalline morphology of Pd-5 polymer crystallized at 100 °C

It should be noted that circumferential cracks and microcracks emerged in type 2 spherulites when the sample was cooled to room temperature, but not in type 1 spherulites. Circumferential cracks and microcracks can also be observed in the specimens of Pd-6 polymer crystallized at a lower temperature of 160 °C. This phenomenon in type 2 spherulites is similar to that in polyhydroxybutyrate spherulites discussed by Barham *et al.*^[25]. However, in the present case, the cracks and microcracks will disappear when reheated to the

crystallization temperature. Apparently, the appearance of cracks and microcracks is the result of a large coefficient of thermal expansion along the radial direction of the spherulites.

SEM microphotographs of these two types of spherulites of Pd-8 polymer are shown in Fig. 10. Type 1 spherulites show negative birefringence, the molecular chains are oriented perpendicular to the radial direction. These oriented chains pack into periodical compact fibrils of about 150 nm diameter along their orientation directions and exhibit ripple-like concentric morphology as shown in Fig. 10(a). In type 2 spherulites (Fig. 10b), radially growing crystallites can be observed between two adjacent circumferential cracks. The size of the crystallite is about 500 nm. These crystallites form no periodicity in the radial direction like those in type 1 spherulites.

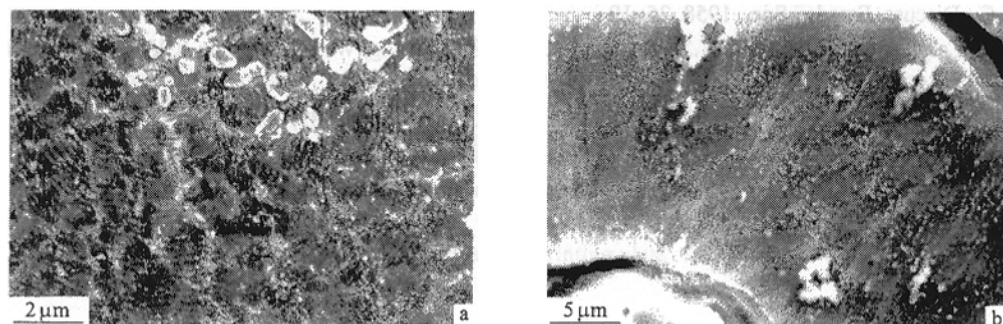


Fig. 10 SEM microphotographs of the spherulites of Pd-8 polymer crystallized at different temperatures (a) 185°C and (b) 150°C

The distinctive difference between these two kinds of spherulites crystallized at different temperatures from the nematic state is a puzzling and important question to be understood. A possible explanation can be depicted as the difference in the reorientational mobility of the nematic domains with oriented molecular chains at different degrees of supercooling during crystallization. At higher crystallization temperatures, the lower supercooling provides adequate opportunity for domains to reorientate, and form ordered fibrils which aggregate and form spherulites with a high degree of order. At lower crystallization temperatures, $T_C < 160^\circ\text{C}$, the higher supercooling helps the crystallization to proceed readily. As a result, crystallization takes place in the aggregating domains with very limited reorientation. The spherulites observed should be of much lower degree of order. Further research is certainly needed to better understand the formation mechanism of these two types of spherulites.

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