

MORPHOLOGICAL AND KINETIC STUDIES OF PHASE TRANSITIONS OF A SIDE-CHAIN LIQUID CRYSTALLINE POLYMER

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Abstract The morphological changes of a side-chain liquid-crystalline polymethacrylate during isotropization and liquid-crystallization transitions were studied by means of polarizing microscopy. These transitions were found to be composed of the initiation of a new phase at local places of the old phase matrix and the growth of the new phase domains. The kinetics of the liquid-crystallization of the polymer from an isotropic melt to a smectic mesophase was also investigated. The isothermal process of the transition can be described by the Avrami equation. The values of the Avrami exponent were found to be around 2.6, which is lower than the value usually obtained for crystallization transition of polymers, but larger than that reported for liquid-crystallization transition of main-chain polymers. These results may indicate the difference in growth geometry of new phase during transition between crystallization and liquid-crystallization in general and between liquid-crystallization of main-chain and side-chain polymers. It was found that the liquid-crystallization of the used side-chain polymethacrylate may occur at small undercoolings with high transformation rate similar to that of main-chain polymers and small-molecule liquid crystals, while the crystallization of polymers can only proceed at large undercoolings. These phenomena can be explained by the idea that the surface free energy of nucleus during liquid-crystallization transition is less than that for crystallization, and evidence was obtained from analysis of the temperature dependence of the transformation rate.

Keywords Mesophase transition, Kinetics, Polarizing microscopy, Side-chain liquid crystalline polymer

INTRODUCTION

Mesophase transitions are characteristic for liquid-crystalline polymers. These transitions could be the transition from the isotropic liquid phase to the liquid-crystalline phase, which may be termed the liquid-crystallization transition, the crystallization transition from the mesophase and also transitions between mesophases, in the case of poly mesomorphism. Studies on the phenomena related with these transitions will undoubtedly gain an insight into the mesomorphic behavior of polymers.

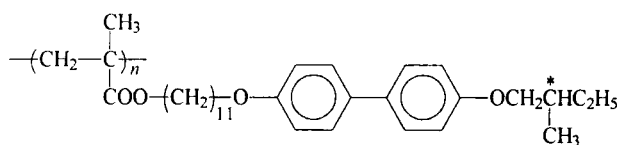
The morphological changes during transitions between isotropic and anisotropic melts of some main-chain liquid-crystalline polyesters have been studied in detail by means of polarizing microscopy and SALS^[1-3]. A special kind of two-phase morphology was observed in the transition temperature ranges. It was found that these transition processes are composed of the initiation of a new phase at local places of the old phase matrix and the growth of the new phase domains. Similar results have been obtained in a recent work related to the transitions of a side-chain liquid crystalline polymer^[4] which exhibits a nematic mesophase above its melting point. Kinetic studies on the liquid-crystallization transition have been reported for a main-chain liquid-crystalline

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polymer by Bhattacharya *et al.*^[5] and a side-chain one by Pracella *et al.*^[6]. In a previous paper we studied the kinetics of both the crystallization from mesophase and the liquid crystallization from isotropic melt for fractions of an aromatic thermotropic polyester^[7]. It was found that the values of the Avrami exponent n are quite different for crystallization and liquid-crystallization transitions, and the surface free energy of mesophase domains is much less than that of crystallites which may explain the large difference between the transformation rates of the two transitions. In this work the morphological changes and kinetics during transitions were investigated for a side-chain liquid-crystalline polymer which exhibited smectic mesophases above its melting temperature.

EXPERIMENTAL

The polymer used in this work was a chiral polymethacrylate, PN11n, which has mesogenic units longitudinally attached to the backbone via flexible spacers and has chiral groups at the end of the mesogens. Its structure is given below:



The method and procedure for synthesis of the polymer and its monomer have been described elsewhere^[8,9]. The apparent molecular weight of the polymer was measured to be 2.5×10^4 with the GPC technique. The solvent used was tetrahydrofuran, and polystyrene standard samples were used for calibration.

Thin film specimens with a thickness of about 10 microns were prepared by casting a 5% polymer solution in chloroform. The morphology of the specimens during phase transitions was studied by using an Olympus BH-2 polarizing microscope equipped with a Mettler FP-52 hot stage. The heating rate was programmed at about $1^\circ\text{C}/\text{min}$. A Perkin-Elmer DSC-4 differential scanning calorimeter was used to obtain the thermograms of the samples and the kinetic data of phase transition in isothermal processes.

RESULTS AND DISCUSSION

The thermograms of the polymer are given in Fig. 1. The original solution cast specimen shows three endothermal peaks in the heating process. The first peak appeared at about 68°C corresponds to the melting of crystals. The mesomorphic nature of the polymer above that temperature was evidenced by the liquid-crystalline texture under polarizing microscope. The third peak appearing

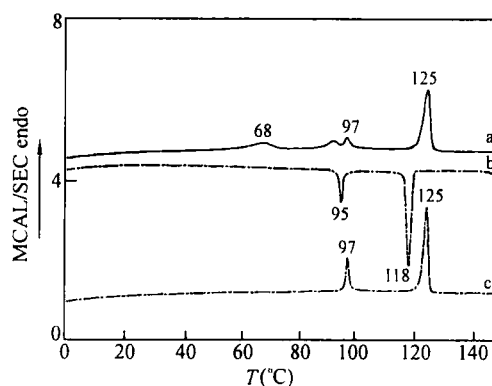


Fig. 1 Thermograms of the polymer in heating and cooling processes with scanning rates of $\pm 10^\circ\text{C}/\text{min}$

at about 125°C is the clearing point. There are two smectic mesophases for the sample which have been attributed to an S_C^* and an S_A phase^[8], respectively. The endothermal peak at about 97°C is the transition between the two mesophases. In the cooling process only two exothermal peaks were observed at about 118°C and 95°C, which were the liquid crystallization transition and the transition from S_A to S_C^* respectively, and no crystallization transition was observed. The polarizing micrographs of the specimen in the temperature ranges of the two smectic phases are given in Fig. 2. Focal conic texture typical for smectic phases can be observed for both cases, and additional ring structure was observed for specimen of S_C^* phase (Fig. 2b).

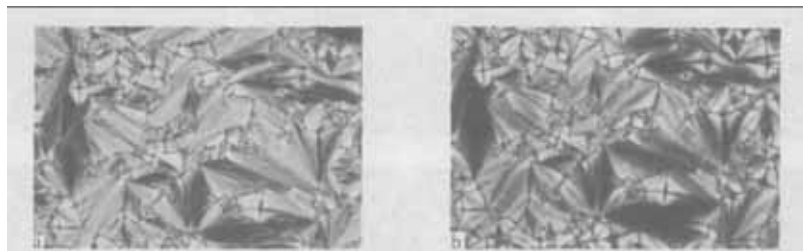


Fig. 2 Polarizing micrographs of specimen prepared by cooling from the isotropic melt state to a) 110°C and b) 70°C, respectively

Polarizing micrographs of the sample at different temperatures during the isotropization transition are given in Fig. 3. At the beginning of the transition corresponding to the onset temperature of the transition peak in the thermogram, the new isotropic phase appears as dark domains separately distributed in the mesophase matrix. The size of these dark domains in Fig. 3a is about 10 μm . The size of the domains increases rapidly with increasing temperature. These growing domains then contact and combine with each other. A conversion occurs from an anisotropic continuous matrix to an isotropic matrix before the final disappearance of the bright mesophase. The morphological change of specimens in the reverse process, liquid crystallization from the isotropic melt, has also been observed under polarizing microscope. Figure 4 shows the progress of transition in an isothermal experiment at 123°C. The specimen was cooled down quickly from its melting state at 150°C. At the initial stage of the transition small bright spots appear in the dark background. This indicates the primary formation of the mesophase in the

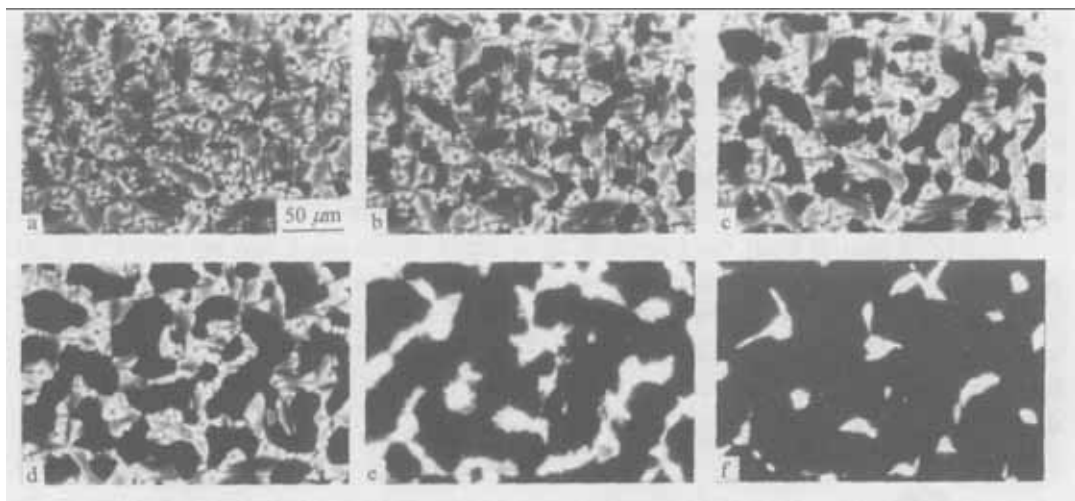


Fig. 3 Polarizing micrographs of a solution cast specimen at different temperatures in a heating process
a) 122.0°C, b) 122.5°C, c) 122.8°C, d) 123.8°C, e) 124.5°C and f) 125.0°C

isotropic melt. The size of these mesophase domains increases slowly with time at this temperature. It was about $10\ \mu$ after 35 min. In the first stage these domains are almost circular in shape. In the growing process some of the domains may be combined together to form an irregular rod-like structure. Finally the mesophase becomes continuous, and the typical liquid-crystalline texture of this sample can be obtained (Fig. 4h).

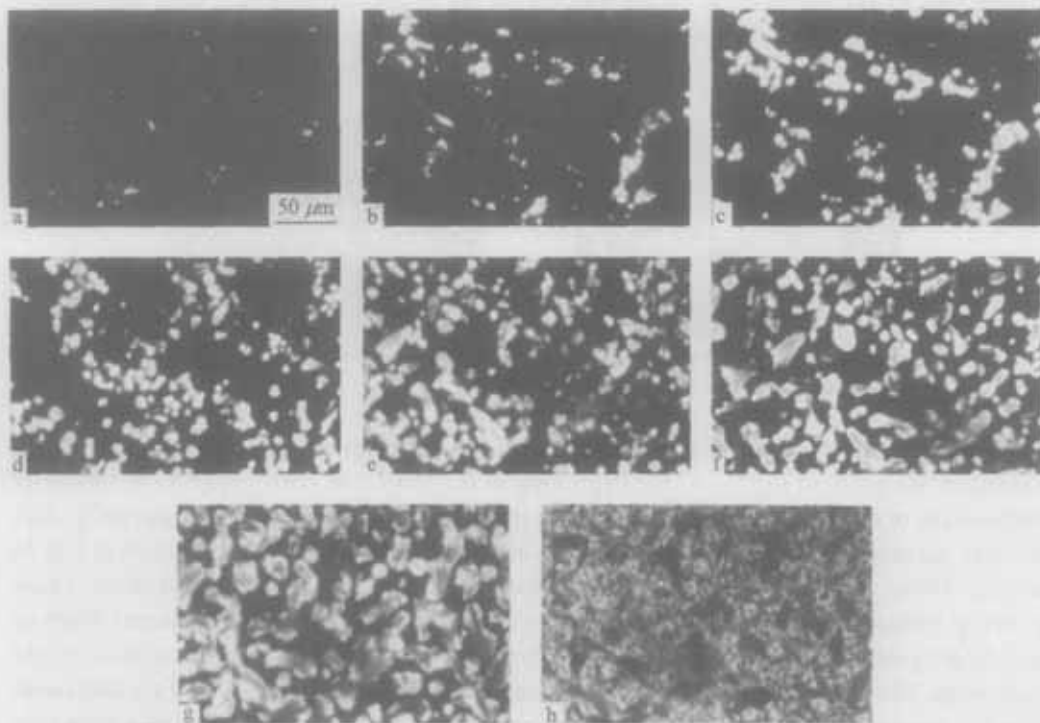


Fig. 4 Polarizing micrographs of a specimen from the melt state in an isothermal process at 123°C

a) 0 min, b) 10 min, c) 20 min, d) 35 min, e) 50 min, f) 10 h, g) 14 h and h) 24 h

These results of morphological changes during transitions between isotropic and anisotropic melts are similar to those obtained previously in studies of main-chain liquid-crystalline polyesters^[1-3] and a side-chain polymer^[4]. This may imply that these transitions are composed of an initiation of the new phase at local places of the old phase matrix and a growth process of the new phase domains. In this sense they are similar to the fusion and crystallization of conventional polymers. The transitions between the two mesophases were also studied. However no obvious variations were detected due to their almost identical optical textures.

It is of interest to study the kinetics of these phase transitions. It was not possible to get isothermal kinetic data of the transition between the two mesophases due to the very small undercooling of the transition. The isothermal DSC curves for liquid-crystallization from melt state are given in Fig. 5. The fraction X_t of the sample liquid-crystallized at time t can be determined as the ratio of the area of the exotherm at time t to that of the overall exotherm. The data were then used for kinetic analysis on the basis of the Avrami equation:

$$1 - X_t = \exp(-Kt^n) \quad (1)$$

where K is a kinetic constant of the transformation process, and n is a parameter dependent on the type of nucleation and growth geometry. The plots of $\lg[-\ln(1-X_t)]$ versus $\lg t$ at different temperatures are given in Fig. 6. The experimental data can be described by straight lines up to sufficiently high conversions. This may imply that the mechanism of liquid-crystallization from

melt state is nucleation followed by growth, similar to that for the crystallization of conventional polymers. The parameters K and n were determined according to Eq. (1), and the results are given in Table 1. The average value of Avrami exponent n was found to be around 2.6, which is close to that reported for a side-chain polyacrylate, 3.0 ± 0.3 ^[6], and also to the values, around 2, for small-molecule liquid crystals in kinetic studies of transitions from the isotropic melt to mesophases^[10–12]. At the same time average values of Avrami exponent, from about 0.7 to 2.4, have been obtained for main-chain liquid-crystalline polyesters^[7, 13, 14]. In kinetic studies of polymer crystallization the average values of Avrami exponent of 3–4 and even higher were usually reported. This may imply a relatively low-dimensional growth of mesophase in the liquid-crystallization transition process, especially for main-chain liquid-crystalline polymers.

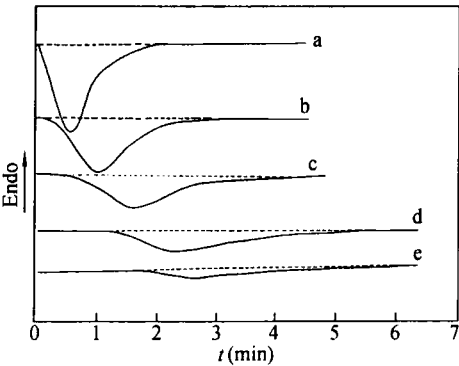


Fig. 5 Isothermal liquid-crystallization thermograms for specimens from the melt state
a) 120.0°C, b) 121.0°C, c) 121.5°C, d) 122.0°C and e) 122.3°C

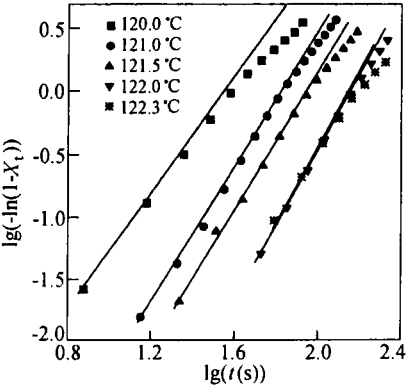


Fig. 6 Avrami plots of isothermal data for liquid-crystallization from isotropic melt

Table 1. Kinetic parameters of the I-S_A phase transition of PN11n

T_l (K)	n	K	$t_{1/2}$	Avrami corr. coeff
393	2.21	3.02×10^{-4}	55.81	0.9998
394	2.64	1.41×10^{-5}	82.19	0.997
394.5	2.58	8.69×10^{-6}	120.30	0.998
395	2.71	1.30×10^{-6}	175.7	0.999
395.3	2.70	1.17×10^{-6}	216.73	0.9999

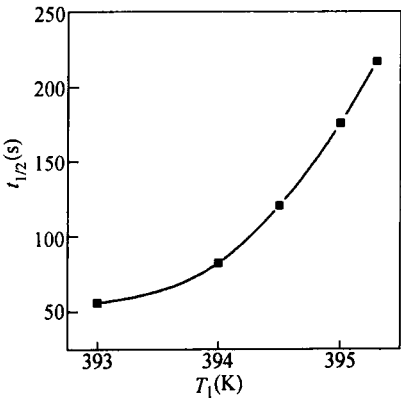


Fig. 7 Dependence of half-time on liquid-crystallization temperature

The half-time $t_{1/2}$ of the liquid-crystallization transition is given in Fig. 7 as a function of temperature. The $t_{1/2}$ values increases with temperature and were found to be around 50–200 s at undercoolings less than 10°C, which are comparable with $t_{1/2}$ values for liquid crystallization of small-molecule liquid crystals at low undercoolings (1–2°C)^[10–12]. Similar results have been reported for main-chain and side-chain liquid crystalline polymers^[6, 7, 14].

The influence of temperature on the rate of a transition composed of nucleation and growth has been discussed by many authors^[15, 16], and the overall transition rate expressed as $1/t_{1/2}$ can be correlated with the temperatures of isothermal experiments through a general equation:

$$\ln(1/t_{1/2}) = A - B_k(T_i^0)^k / T(\Delta T)^k \quad (2)$$

where T_i^0 is the equilibrium temperature of transformation and ΔT is the degree of undercooling. $k = 1$ or 2 for different nucleation models. Parameter A depends on the density of nucleation and on the energy of transport of molecules, and can be considered constant in a small undercooling range. B_k depends on the average surface free energy σ and the heat of transition of the phase formed in the transition process in the following way:

$$B_k \sim (\sigma)^{k+1} / \Delta H^k \quad (3)$$

It is clear that B_k is a parameter characterizing the difficulty of nucleation of the new phase.

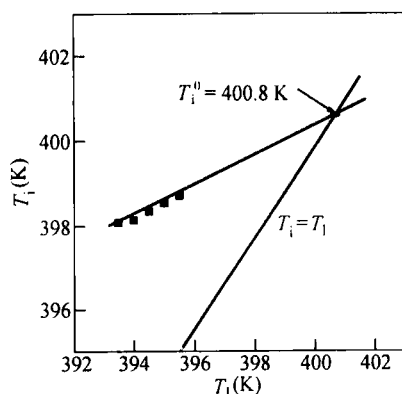


Fig. 8 Dependence of T_i on T_l and the extrapolation

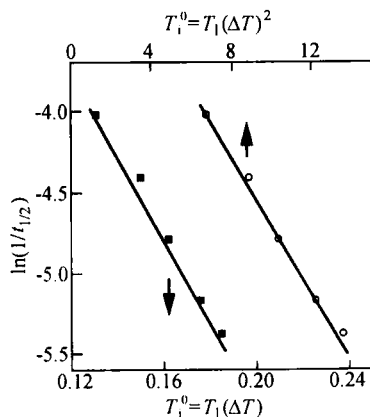


Fig. 9 Plots of $\ln(1/t_{1/2})$ versus $T_i^0/T_l\Delta T$ and $(T_i^0)^2/T_l(\Delta T)^2$

The experimental data were analyzed according to Eq. (2). The equilibrium temperature of isotropization, $T_i^0 = 400.8$ K, was obtained by extrapolating the isotropization temperature T_i to $T_i = T_l$, T_l is the temperature at which the specimen has been isothermally liquid-crystallized (Fig. 8). The data can be fitted by straight lines (Fig. 9) for both plots of $\ln(1/t_{1/2})$ versus $T_i^0/T_l\Delta T$ and $\ln(1/t_{1/2})$ versus $(T_i^0)^2/T_l(\Delta T)^2$. The B_k values were then determined from the slope of the lines. It was found that $B_1 = 25.8$ K and $B_2 = 0.21$ K respectively. These values are about one order of magnitude less than those for crystallization transition of liquid-crystalline polymer^[7] or conventional polymers^[15, 16]. These results support the idea that the surface free energy of nucleus during liquid-crystallization should be much less than that in the case of crystallization. It may explain the experimental fact that liquid-crystallization can proceed with high transformation rate at very small undercoolings, whereas crystallization only proceeds at very large undercoolings. It was interesting to find that the B_k values obtained in this work are very close to those reported for main-chain polymers in transition from isotropic melt to nematic mesophase^[7, 14]. It may imply that the surface free energy of nucleus during liquid-crystallization transition is almost independent on the locations of mesogenic units in the polymer molecules and the type of the mesophases.

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