

Notes

**MORPHOLOGICAL STUDIES OF A THERMOTROPIC
SIDE-CHAIN LIQUID CRYSTALLINE POLYMER
DURING MESOPHASE TRANSITIONS***

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Abstract The morphological features of a side-chain liquid crystalline polymer during the mesophase transitions were investigated by using the DSC technique. The polymer used was polyacrylate with mesogens of three benzene rings attached to the main chain through a flexible spacer. A special two-phase texture was observed in the transition temperature range. Similar to main-chain liquid crystalline polymers the transition process of the side-chain liquid crystalline polymer was 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.

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

INTRODUCTION

For a liquid-crystal forming polymer, one or more mesophases exist above the melting point of the crystals. With further increasing temperature the mesomorphic polymer may become isotropic at the so-called clearing point or isotropization temperature. Its counterpart is the liquid crystallization of the polymer from its isotropic melt state. These transitions are specific for liquid crystalline polymers, and studies on these phenomena will undoubtedly provide an insight into the mesomorphic behavior of polymers.

The morphological changes during mesophase transitions have been studied for thermotropic main-chain aromatic polyesters^[1-3]. A special kind of two-phase morphology was observed in this transition temperature range. It was found that these transition processes are composed of the initiation of the new phase at local places of the old phase matrix and the growth of the new phase domains. In this work the morphological features of a side-chain liquid crystalline polymer during mesophase transitions was investigated.

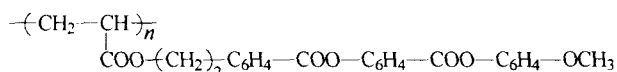
EXPERIMENTAL

The polymer used in this study is a polyacrylate with mesogens of three benzene rings attached longitudinally to the backbone through a short flexible spacer. The structure of the polymer is shown below, and its synthesis procedure has been described elsewhere^[4].

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The apparent number average molecular weight of the sample was measured to be 4.1×10^3 with the GPC technique. The solvent was tetrahydrofuran, and polystyrene standard samples were used for calibration. Thin film specimens with a thickness of about $10 \mu\text{m}$ were prepared by casting 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, and its heating or cooling rate was about $1^\circ\text{C}/\text{min}$. Thermograms of the samples were obtained by using a Perkin-Elmer DSC-4 differential scanning calorimeter with a heating or cooling rate of $20^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The thermogram of the sample is shown in Fig. 1. The endothermal peak at 72.2°C in the heating process can be identified as the melting transition from crystalline state to a mesophase, T_{KN} , and the peak at 222.7°C is considered as the clearing point, T_{NI} . The existence of a mesophase range between T_{KN} and T_{NI} was proved by direct morphological observations under polarizing microscope. The typical threaded texture of nematic mesophase was observed. In the cooling process an exothermal peak at 215°C was observed, which can be attributed to the liquid crystallization of the sample from its isotropic melt state, T_{IN} , according to the small supercooling and the optical texture of the specimens at temperatures below T_{IN} . No crystallization transition was observed in the cooling process, and a glass transition was detected at about 51°C . It means that the specimens are in an anisotropic glassy state after melting treatment.

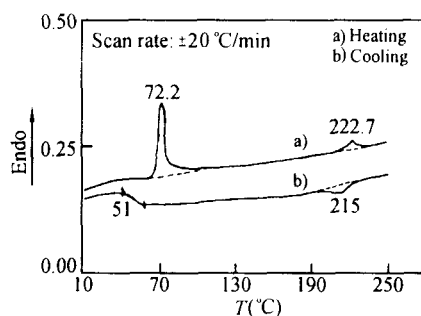


Fig. 1 Thermograms from DSC analysis of the polymer

The morphological changes of the specimens in the T_{NI} and T_{IN} transition temperature ranges were observed. Results of the heating process are given in Fig. 2. At the beginning of the transition a two-phase texture appears after an ambiguous texture of short time period. Dark isotropic domains are formed at local places of high thread concentration due to intersection of threads or thread coiling. The size and darkness of these domains increase with temperature. These growing isotropic domains then contact and amalgamate with each other. Finally, a conversion occurs from an anisotropic continuous matrix to an isotropic matrix. The size of the mesophase domains decreases with temperature and they disappear at high temperatures of the transition range.

Polarizing micrographs for the reverse process, the liquid crystallization from the isotropic melt, are given in Fig. 3. Two-phase textures were also observed in the T_{IN} transition temperature range. At the first stage of the transition small bright spots appear in the dark background, indicating the initial formation of mesophase in the isotropic melt. With decreasing temperature the size and number of the bright spots increase continuously. They may contact and amalgamate with

each other and form large domains. Then the mesophase becomes predominant and forms a continuous phase.

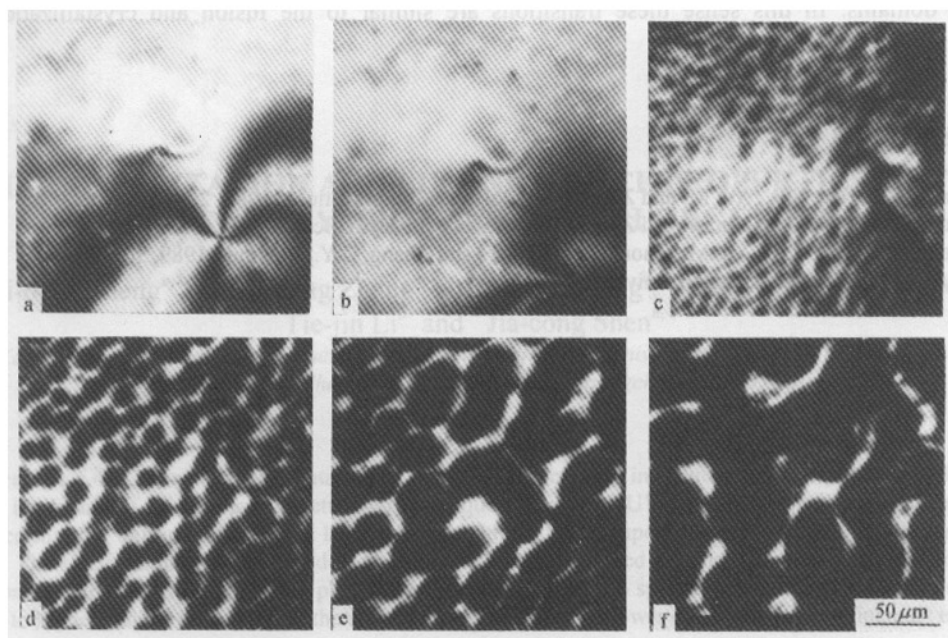


Fig. 2 Polarizing micrographs of a polymer specimen at different temperature in a heating process a) 210°C, b) 213°C, c) 217°C, d) 218°C, e) 219°C and f) 220°C

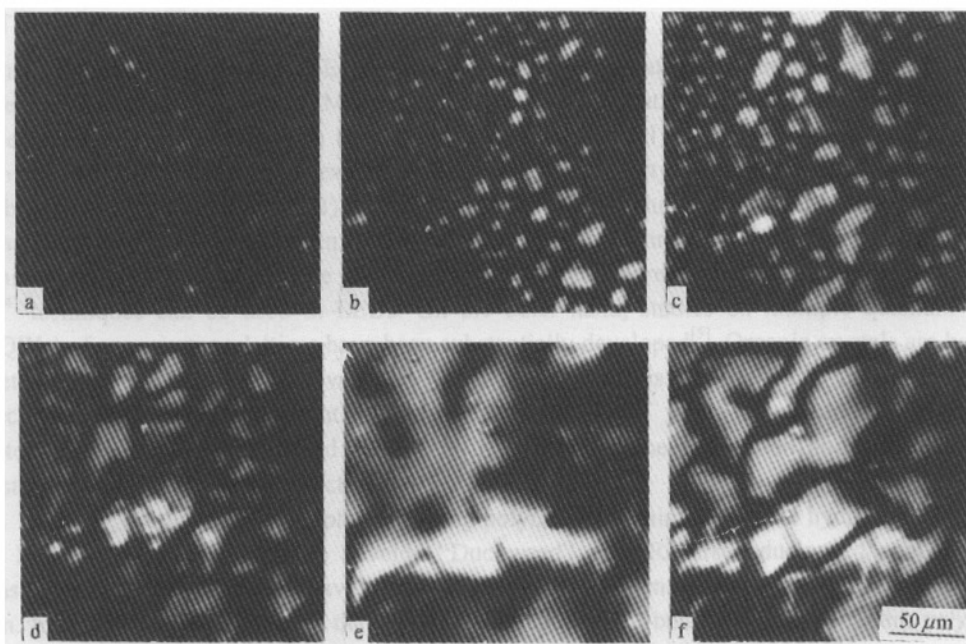


Fig. 3 Polarizing micrographs of a polymer specimen at different temperature in a cooling process a) 214°C, b) 213°C, c) 212°C, d) 211°C, e) 209°C and f) 205°C

These morphological features are similar to those observed for main-chain aromatic polyesters^[1-3]. This may imply that the transitions between the anisotropic and isotropic melts of

both the main-chain and side-chain thermotropic liquid crystalline polymers 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 these transitions are similar to the fusion and crystallization of conventional polymers.

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