

EVIDENCE FOR THERMOTROPIC LIQUID CRYSTALLINITY OF A FUSIBLE POLYDIACETYLENE *

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ABSTRACT

The thermotropic liquid crystalline behavior of a fusible polydiacetylene has been studied by using polarizing optical microscopy and wide angle X-ray diffraction. It was found that the typical threaded texture can exhibit in the melt and the banded texture can be observed when applied a gentle shear to the melt. The results indicate that this polydiacetylene is really a thermotropic liquid crystalline polymer.

INTRODUCTION

Polydiacetylene (PDA) can be obtained in the form of perfect macroscopic single crystals by solid state polymerization. The polymer chain with a conjugated backbone consists of a sequence of double, single and triple bonds to exhibit the special optical property and one-dimensional order. Due to the macromolecular chain is rod-like, most PDAs are insoluble and infusible. Patel et al.^[1] synthesized some soluble and fusible PDAs, one of them is poly {5, 7-dodecadiyne-1, 12-diol bis [((3-butoxycarbonyl)-methyl)urethane]} which is abbreviated as P-3BCMU. Although the reports on solubility and solution properties^[2,3] and optical properties^[4,5] of PDA may be found in the earlier literature, but general interest in the liquid crystallinity has been taken only recently. For the soluble and/or fusible conducting polymer of fully conjugated chains of

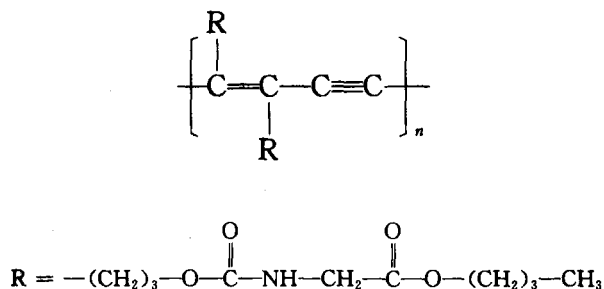
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heterocyclic monomer units, it is reasonable to expect the formation of either a lyotropic or a thermotropic liquid crystalline state. Recently it has been reported that these conducting polymers can exhibit a lyotropic or thermotropic nematic mesophase^[6-9]. The present work studied the thermotropic liquid crystalline behavior of P-3BCMU. The results show some evidences for a thermotropic liquid crystalline state of P-3BCMU.

EXPERIMENTAL

The polymer used in this work was a soluble and fusible P-3BCMU with chemical structure as follows:



The weight average molecular weight $M_w = 1.36 \times 10^6$ is measured by light scattering of the yellow solution in CHCl_3 ^[3]. The melting temperature T_m is 185°C by DSC, at which the polymer color changes from red to yellow.

The melting behavior of the polymer is observed under polarized optical microscope (POM) with a Mettler FP-52 type hot-stage. Oriented film specimens were obtained by shearing the polymer melt at above T_m of the polymer between two slides and subsequently quenched to room temperature. The banded texture formed was observed using an Olympus Model BH-2 polarizing optical microscope. Wide angle X-ray diffraction (WAXD) spectrum of the specimen quenched from melt of 200°C was recorded by using a Rigaku Model DMAX-36 X-ray diffractometer with Cu anode.

RESULTS AND DISCUSSION

P-3BCMU is a fusible PDA, it gives a dark red solid state. The dramatic color change from red to yellow could be observed at the phase

transition temperature (185°C) when the polymer was heated. In the temperature range slightly above the melting temperature, we tried carefully to observe in a POM whether there is a texture typical of a thermotropic liquid crystalline phase. We found that the polymer melt of 200°C can exhibit strong birefringence (yellow field) between crossed polarizers. It shows the disclination in the form of winding threaded texture with loops and occasional sharp cusps as shown in Fig. 1. This is a typical threaded texture of nematic mesophase, that is a good evidence of a thermotropic liquid crystals for P-3BCMU polymer.

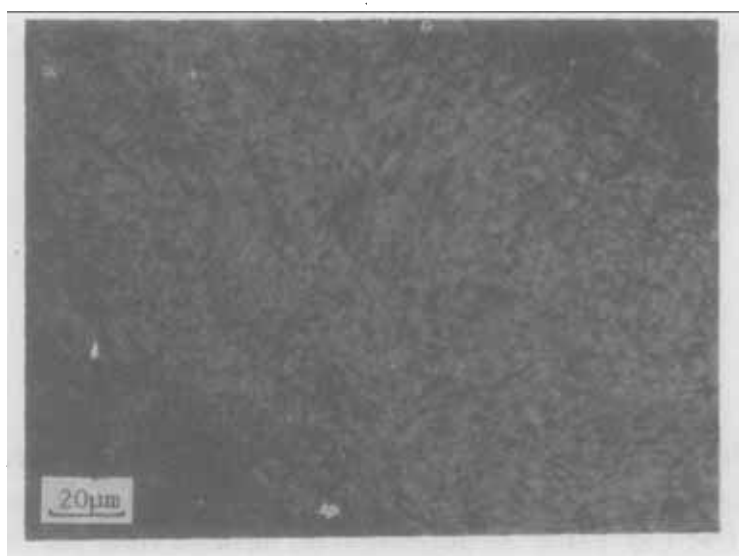


Fig. 1 POM micrograph of threaded texture of P-3BCMU melt at 200°C , under crossed polars

P-3BCMU is usually considered as partial crystallization in its solid state^[10,11]. When it was heated above its melting point (185°C) and then quenched to room temperature a frozen liquid crystalline state could be obtained. Fig. 2 shows a WAXD spectrum of the frozen liquid crystalline state of P-3BCMU quenched from nematic melt at 200°C . It is clearly seen that WAXD spectrum only shows a diffuse peak at 20° in two theta, no peaks of crystallization can be seen in the WAXD spectrum. This diffuse peak, which is corresponding to the space of 0.47nm is a characteristic WAXD spectrum for a nematic mesophase. This datum is a good evidence of a thermotropic liquid crystals for P-3BCMU polymer.

In the same time when we applied a gentle shear to the anisotropic melt

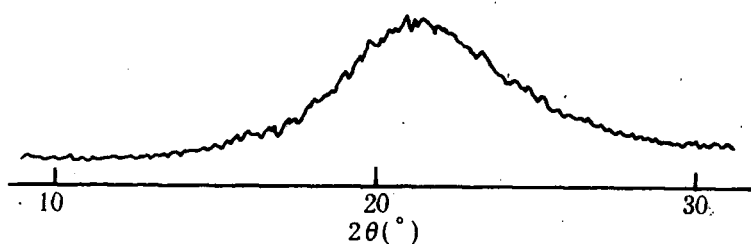
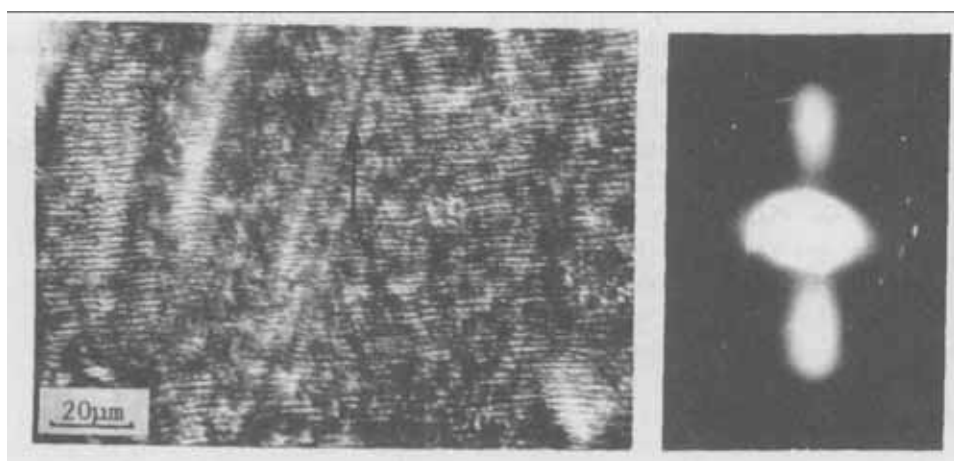


Fig. 2 WAXD spectrum of P-3BCMU quenched from melt of 200°C



(a)

(b)

Fig. 3 POM micrograph of banded texture of P-3BCMU formed by shear, under crossed polars and corresponding light scattering pattern

layer of P-3BCMU sample sandwiched between two glass slides at 200°C and then air quenched to room temperature, we did observe banded texture typical of main chain liquid crystalline polymers. The bands are perpendicular to the shear direction with a band width of 1μm as shown in Fig. 3a. Fig. 3b is a small angle light scattering pattern of the banded texture in Fig. 3a. It can be seen that the banded texture gave an SALS pattern of two strong and narrow light scattering lobes normal to the bands. The fact that a banded texture appears under an external force field has been viewed as a feature of typical liquid crystal of polymers^[12-14]. Consequently the appearance of banded texture in Fig. 3 is a strong argument for the existence of nematic state of P - 3 BCMU melt . The above results demonstrate that P-3BCMU is really a thermotropic liquid crystalline polymer.

Keywords:

Thermotropic liquid crystals; Polydiacetylene; Nematic mesophase

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