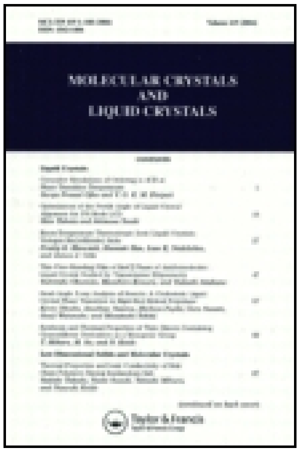

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Liquid Crystallinity in the Electro-active Polymer, Poly(3-dodecylthiophene)

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The liquid crystallinity of poly(3-dodecylthiophene) was studied systematically at selected temperatures with manually controlled shearing, using optical microscopy and differential scanning calorimetry, to determine the necessary conditions for the formation of liquid crystallinity. Poly(3-dodecylthiophene) did not show thermotropic liquid crystalline behavior under conditions which are usually used in the study of thermotropic liquid crystallinity. When a shear stress was applied to a solvent cast film, a Schileren texture was observed *in situ*. A finer texture was observed as the annealing temperature and time of the sample film were increased. There was no direct relationship between the melting behaviors in differential scanning calorimeter thermograms and the liquid crystalline behavior of poly(3-dodecylthiophene).

Keywords: Liquid crystallinity; electrically conducting polymer; polyalkylthiophene

1. INTRODUCTION

An understanding of the structural features in electrically conducting polymers has become essential because the electronic structure and chain conformation strongly interact with each other and because various applications are greatly dependent on these properties. Nevertheless, detailed studies on the structural properties have been restricted by the insolubility and non-meltability of these polymers. The alkylation of these stiff conjugated polymers has provided the desired solubility and processibility due to the reduction of strong interactions between main-chains and due to an increase in flexibility [1, 2]. The structure, thermo- and solvato-

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*Corresponding author.

chromisms of alkylated electro-active polymers, especially poly(3-alkylthiophene)s have been extensively studied [3 – 6].

Poly(3-alkylthiophene)s can be compared with alkylated polyesters which have been widely investigated for their liquid crystalline behavior. The mesogenic units are neither in the side chains as in the traditional side-chain liquid crystalline polymers nor in the polymer backbone as in the main-chain liquid crystalline polymers, but the liquid crystallinity arises from the cooperation of the stiff main chain and the flexible side chains which act as a bound solvent. In these comb-like polymers, which are also described as hairy rods, the anisotropy is based on two factors according to Ballauff [7, 8]: the stiffness of the polymer backbone and the repulsion between the polar backbone and the non-polar alkyl chains. The structural features have been described as having a smectic-like layered arrangement of the chains in which the distance between the main chains is determined by the length and the degree of intercalation of the side chains. The layers are organized in three dimensional packing, and the side chains may form hexagonal paraffin-like crystals within the layers. With an increase in the thermal energy the side chain crystals melt, and the further disordering of these side chains causes a slippage between the layers resulting in a two-dimensional ordering. The final isotropization temperature has been shown to be strongly dependent on the degree of packing of the main chains and the number of carbons in the side chains.

The conjugated structure in the electro-active polymers would indicate that these polymers could behave in a fashion similar to the above mentioned liquid crystalline comb-like polymers. The X-ray diffraction measurements and thermal analysis for poly(3-alkylthiophene)s show a layer formation [3, 9]. The diffraction at a low angle was shown to be dependent on the length of the side chains. Tashiro *et al.*, observed transitional states with temperature controlled X-ray measurements, which they were related to a formation of an anisotropic phase. Zheng *et al.*, observed a similar dependence with *N*-alkylated polyanilines [10]. In spite of these possibilities for liquid crystalline phases, there have been few reports on the texture of liquid crystalline phases of poly(3-alkylthiophene)s. Qian *et al.*, reported that a Schlieren texture was observed when the sample of poly(3-hexylthiophene) was heated to 190 ~ 220°C for 10 minutes and then quenched to room temperature, and when the melt was slowly cooled to 145°C and annealed at that temperature for 6 hours [11].

In this paper, the liquid crystalline behavior of poly(3-dodecylthiophene) was systematically studied, using optical microscopy and DSC, to find which factor is most critical for the liquid crystalline behavior of this material and whether or not this material is truly a thermotropic liquid crystalline polymer. Recently we have studied the crystallization of poly (3-dodecylthiophene) film by thermal treatments in detail [12], and observed a order – disorder transition of poly(3-dodecylthiophene) by thermochromism.

2. EXPERIMENTAL

The poly(3-dodecylthiophene) (P3DDT) substituted in the 3-position by *n*-dodecyl units was prepared by the oxidative polymerization utilizing $FeCl_3$ as an oxidant. The starting material 3-dodecyl thiophene was prepared by the coupling of alkyl magnesiumbromide with 3-bromothiophene in anhydrous diethylether in the presence of a phosphine complex of nickel chloride. P3DDT was synthesized by ferric chloride catalyzed dehydrogenation of the 3-alkyl derivative of thiophene. The reaction was carried out in a rigorously deoxidized and dehydrated chloroform for 30 minutes at 0°C and poured into methanol. The precipitate was filtered and washed with methanol several times. Molecular weights and molecular weight distribution of the P3DDT relative to polystyrene standards were determined by using gel permeation chromatography at 25°C. The results are shown in Figure 1. The films of P3DDT were cast on micro slides from chloroform solution and dried at atmospheric conditions for optical microscope observations. The as-cast films were a deep red color and homogenous when observed through an optical microscope. A cover glass was placed on the film to apply shear stress on the sample and to prohibit direct contact with air in the hot stage. A Nikon F2 optical microscope was used to study the liquid crystalline behavior of P3DDT. Formation of structures was observed during the isothermal heat treatment of the films. For this purpose the as-cast films were placed on a Mettler hot stage (FP82) with a programmable temperature controller (FP80). Thermal transition of the polymer was determined by a Perkin-Elmer TAS7 DSC with a cooling unit. The sample, which was usually 10 mg in weight, was placed in a sealed aluminum pan and the measurements were carried out in a nitrogen atmosphere using a heating and cooling rate of 10°C/min.

3. RESULTS AND DISCUSSIONS

The thermal behavior of P3DDT was analyzed by DSC experiments. DSC thermograms of P3DDT samples which were heated and cooled cyclically

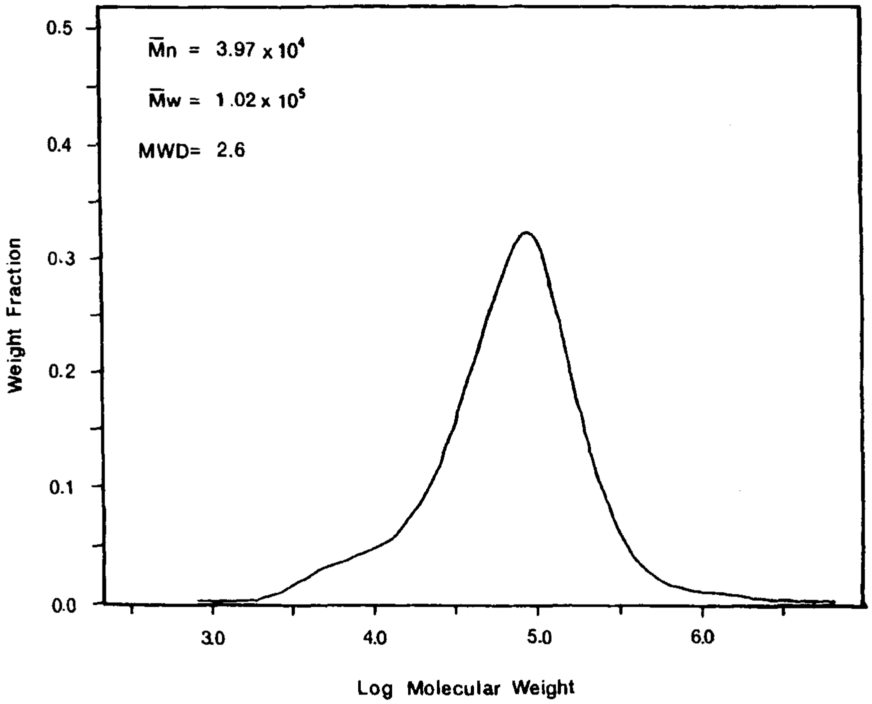


FIGURE 1 Molecular weight distributions of the sample, poly(3-dodecylthiophene).

between −40°C and 175°C at a rate of 10°C/minute are shown in Figure 2. The difference between the first heating curve and the second shows the large effect of previous history. The second heating curve shows a single glass transition temperature at about −16°C, a bimodal lower transition region covering the temperature range of about 30∼75°C, and higher double endothermic processes having peak temperatures of 133°C and 140°C. The lower transition range indicates the melting of the side chain crystals, and its broad shape represents a large distribution of the degree of packing in the crystals. The bimodal shape may imply that two packing features exist, which are determined by the main chain arrangement. The structural features of the more ordered phase could be described with a smectic-like layered arrangement of the chains in which the distance between the main chains is determined by the side chain length. The layers are organized in three dimensional packing and the side chains may form hexagonal paraffin-like crystals within the layers, of which the melting temperature is higher

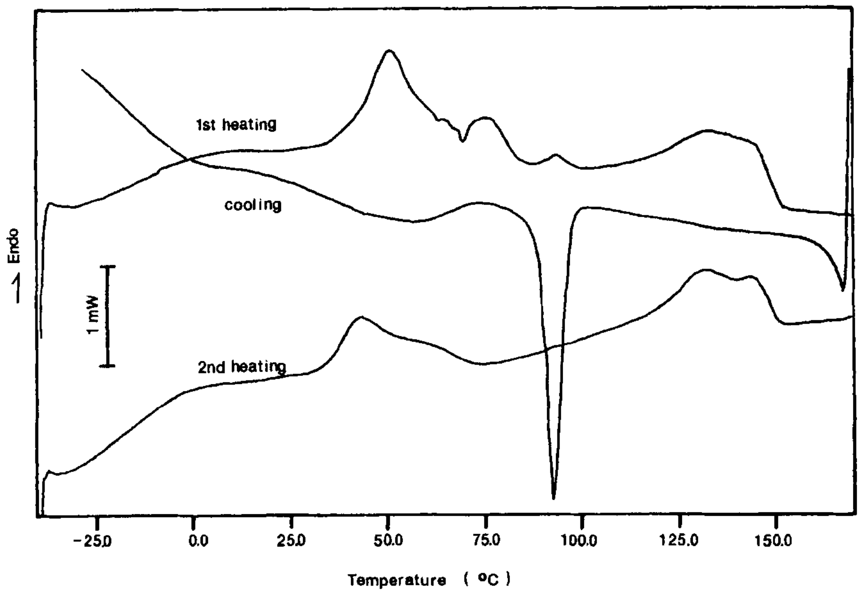


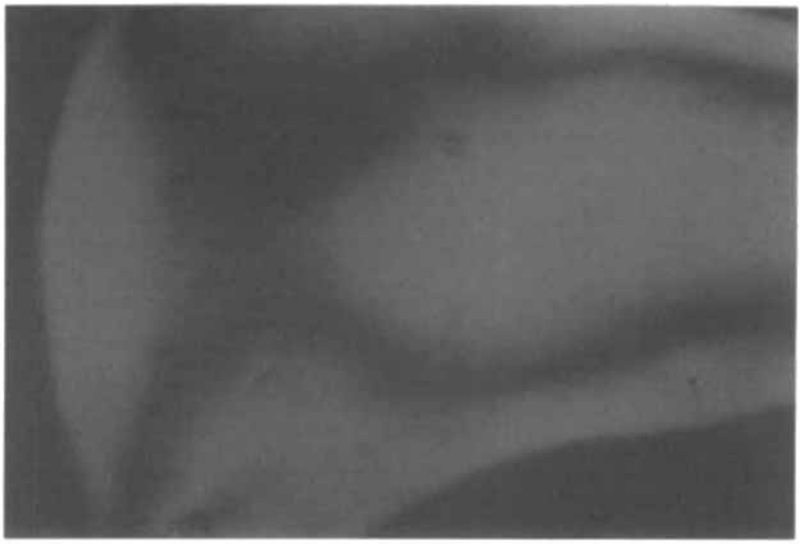
FIGURE 2 DSC thermograms of the poly(3-dodecylthiophene) with a heating and cooling rate of 10°C/min.

than that of the side chains in the less ordered phase. This can also be confirmed by the double peaks of the higher transitions which represent two principal kinds of main-chain ordering as first observed by Kim [13]. Detailed studies of the thermal behavior of P3DDT showed that P3DDT sample contained two kinds of ordered phases and the contents of the more ordered phase increased as the annealing temperature and annealing time were increased [12]. It was concluded that these two kinds of ordered phases are the cause of the double peaks appearing in the higher temperature region in DSC thermograms.

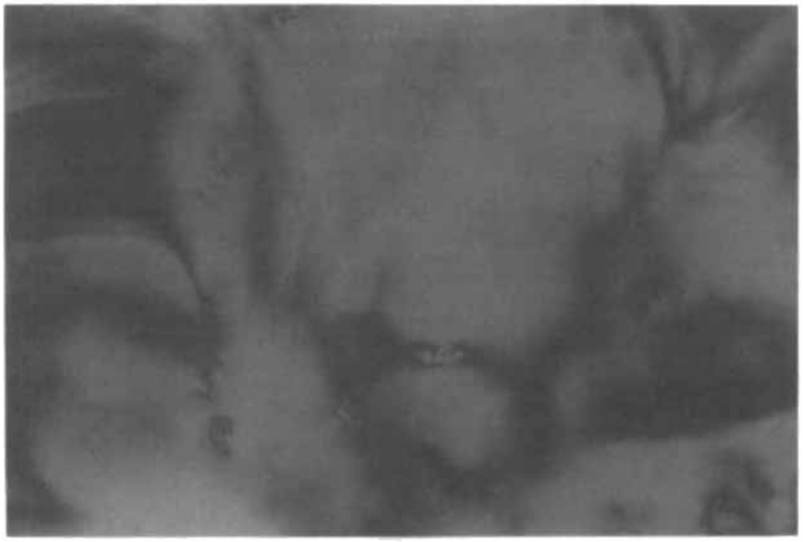
Although the liquid crystalline state of P3DDT at these temperatures has been proposed by several researchers [4, 14, 15], experimental evidence for the liquid crystalline texture of poly(3-hexylthiophene) has only been observed by Qian *et al.* [11]. We investigated the thermotropic liquid crystalline state of P3DDT, but we were unable to observe any texture of the melt under cross polarized microscopy [12]. We thus consider that P3DDT may not a conventional thermotropic liquid crystalline material under normal conditions. In general, traditional thermotropic liquid crystalline materials have relatively short and regular mesogenic units. These properties facilitate the ordering of these mesogenic units by intra- and inter-chain arrangements at a specific temperature range. However, P3DDT has long mesogenic units if the anti-conformation is taken as the most stable one [16–18], and the mesogenic units become irregular in length due to the interruption of conjugation, which partitions a polymer chain into sub-chains having a distribution of smaller conjugating lengths. The density and length of the side-chains also influence the packing of the mesogenic units. A single chain of P3DDT is so bulky that it is very difficult for the whole chain to move over a certain length. It is also very difficult for the side chains to pack densely at temperatures above the side chain melting temperature. Hence, in these temperature ranges the side chains act effectively as a bound-solvent, which lowers the interactions between the main chains, and leads to a large increase in entropy when dissolving or melting the polymer. All of these factors seem to make it difficult for P3DDT to show the liquid crystalline phase under normal conditions.

In our subsequent approach, we applied a shear stress to the melted thin film of P3DDT sandwiched between a cover glass and micro slide at various temperatures. The formation of a Schlieren texture and other anisotropic morphologies was observed *in situ* after applying a shear stress. These structures remained after quenching the samples to 25°C. This state is a consequence of the long relaxation time of the P3DDT because of its bulkiness as well as the freezing of molecular motion. The shear stress was applied by a press and shear method: first, the cover glass was pressed on the sample to force the molecules to become packed and then the cover glass was sheared to deform the sample. Hence, the shear stress applied to the samples in this study is not a simple shear, but it is closer to rubbing the cover glass in a controlled direction.

Figure 3 shows the Schlieren texture of the P3DDT samples, which developed after applying a shear stress at different temperatures. All of the samples were annealed at pre-determined temperatures before applying the shear stress to remove the metastable thermal history from solvent casting. Figure 3(a) shows a Schlieren texture at 25°C. The shear stress was applied to the as-cast film without any further annealing treatment because the sample films had been at room temperature for several days. The texture seemed to be stable with further shearing at this temperature. The picture of the texture shown in Figure 3(b) was taken at 60°C. The shear stress was applied to the sample after annealing for 15 hours at 60°C. This annealing time was chosen to confirm the equilibrium state of the sample. The texture of the sample at 60°C was coarse, and it showed a diffuse extinction line of the texture, which means that the ordering on the molecular level was not

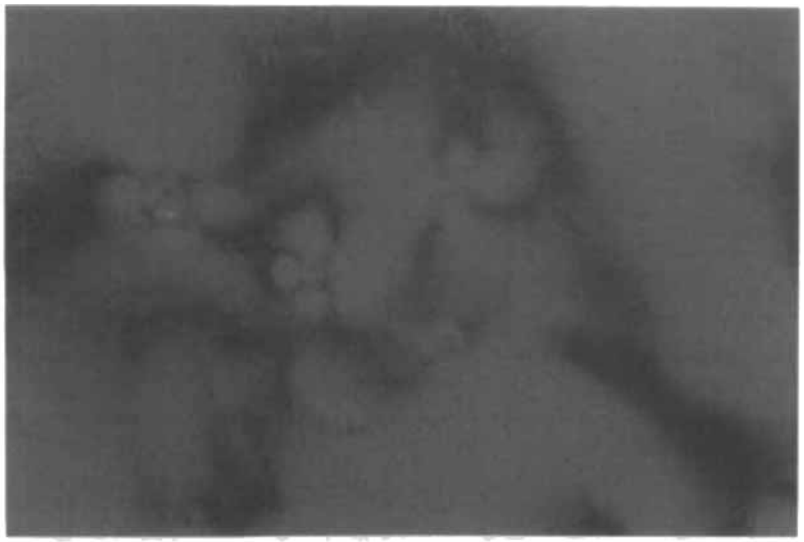


(a)

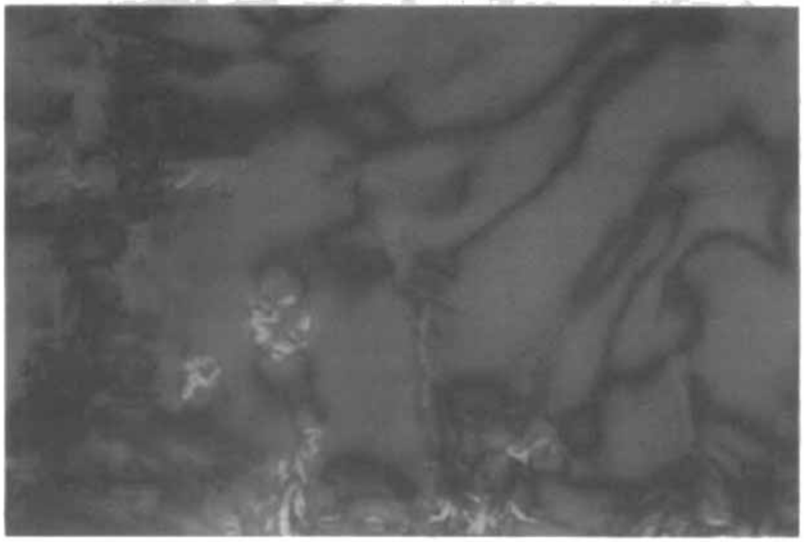


(b)

FIGURE 3 Optical micrographs of poly(3-dodecylthiophene) films with crossed polarizers ($^{A}X^{P}$) at different temperatures after applying shear (Magnification, X 300); (a) 25°C, (b) 60°C, (c) 100°C, (d) 120°C. (See Color Plate VII).



(c)



(d)

FIGURE 3 (Continued).

well developed. The sample which was annealed for 16 hours at 100°C, as in Figure 3(c), shows a more developed texture than the previous two. This texture clearly shows the disclination line perpendicular to the film surface and well developed dark brushes. These dark brushes correspond to the region having the extinction conditions between the crossed polarizers where the directions orient either parallel or perpendicular to the electric vector of the polarizer or analyzer. The pattern resulting from the dark brushes reflects a spatial distribution of the disclination lines which were essentially oriented normal to the surface of the thin film samples. A more detailed disclination will be given in the explanation part of Figure 4. Figure 3(d) shows the finest Schlieren texture in this experiment. The shear stress was applied to the sample after annealing for 3 hours at 120°C. This series of micrographs shows that the higher the annealing temperature, the finer the texture that was observed, although the texture also depends on the degree of the shear stress. The influence of the annealing time was also investigated: the longer the annealing time, the finer the texture that developed, but there is no effect when the annealing time is longer than a certain time. At this point, it is worth noting that it is impossible to quantize the degree of shear stress applied to each sample because the shear stress was applied manually.

Figure 4 shows a different part of the sample annealed at 120°C. The non-cross polarizing micrograph in Figure 4(a) shows the color of the sample at 120°C. The bright circles may be considered to be of relatively thin thickness. These thin domains are caused by two factors. One is that the as-cast film has excess surface area and free energy. Thus when it is brought to the liquid crystalline state, it tends to minimize the surface-to-volume ratio by increasing the thickness and decreasing the surface area. The other reason is that the shear stress forces the sample to spread so that the surface-to-volume ratio is increased by force. This process is not a preferred thermodynamic state. Figure 4(b) is the cross polarizing micrograph, which clearly shows the relationship between the mother phase texture and the spherulite-like structure. The regular patterns of dark brushes are also shown. The pattern resulting from the dark brushes reflects a spatial distribution of the disclination lines essentially oriented normal to the surface of the film sample. The disclination strength $|S|$ and the sign of the disclination were determined by observing a number of dark brushes emanating from the disclination lines and by observing the direction of the rotation of the brushes accompanied by the rotation of the crossed polarizers. In this micrograph, it is clearly shown that specific kinds of the disclination, which have strengths $S = +1/2$ and $S = +1$, and a particular relationship between $S = +1/2$ and $S = +1$ exist. This fact may imply that

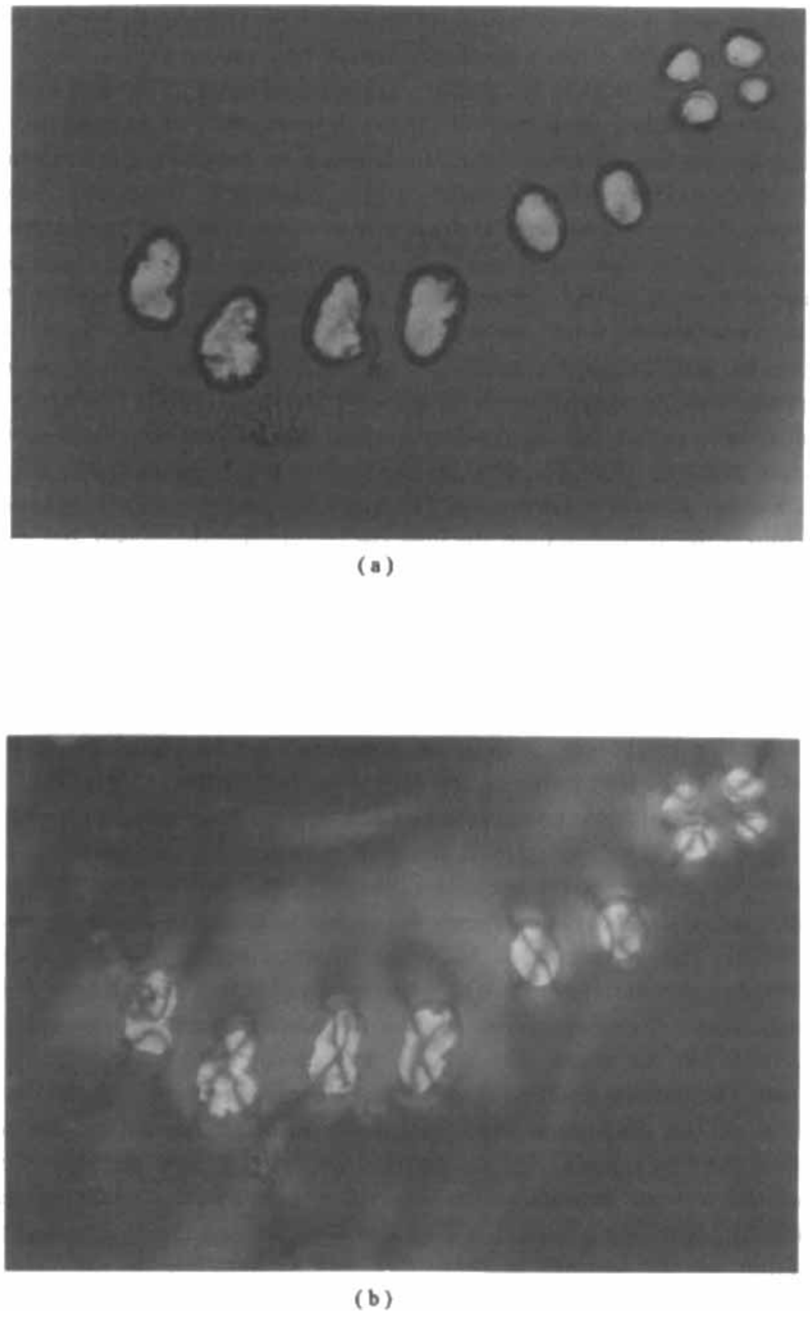


FIGURE 4 Optical micrographs of poly(3-dodecylthiophene) film at 120°C after applying shear (Magnification, X 300); (a) Non-crossed, (b) Crossed. (See Color Plate VIII).

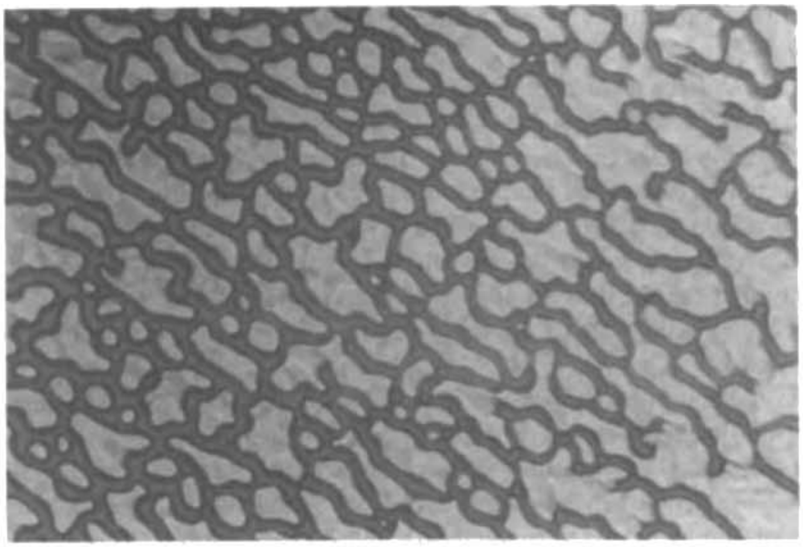
the disclination strengths and their relationship are unique to the molecular structures.

The Schlieren textures developed at 120°C under shearing conditions were held at 125°C for several days and at 25°C for several months to investigate the stability of the Schlieren texture. There were no apparent changes in the Schlieren texture of the sample held at 25°C after 4 months. The Schlieren texture held at 120°C slowly diffused with time though changes in the Schlieren texture could not be detected until after 2 days. These results imply that the shear stress applied to the sample was slowly released, and that the releasing rate of the stress became slower as the temperature was decreased.

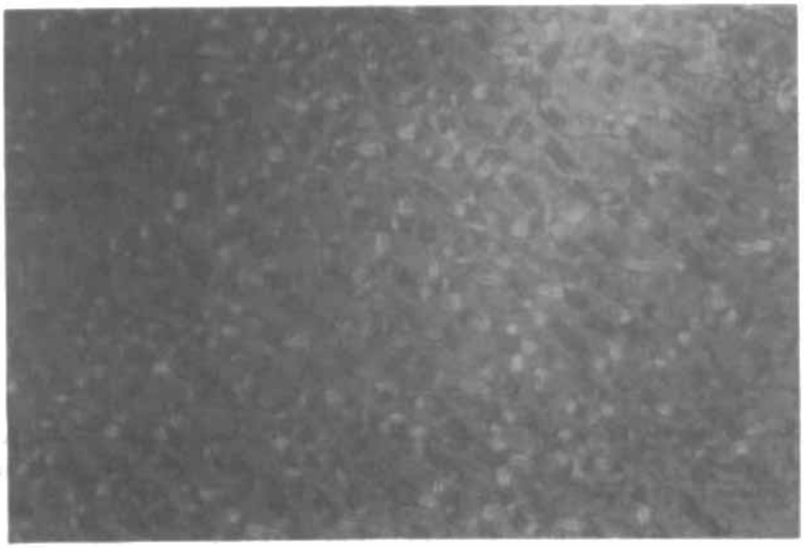
As the annealing temperature was increased above the melting temperature of the main chains, a different optical phenomenon was observed. The boundary temperature between the Schlieren texture and this additional anisotropic behavior is at about 135°C. As shown in Figure 5, thread-like structures having a characteristic thickness developed. This structure was partially developed on the edge, which means that high shear deformation is needed to develop this structure. Figure 5(a) is a non-cross polarizing micrograph, which shows a yellow phase, which is the relatively thin part of the film, and a brown-red phase, which is the thick part. P3DDT has a yellow color at this temperature because the color is known to be dependent on the sample thickness. Some segments of the thread show bright "illumination" under cross-polarized light, as shown in Figure 5(b). There are two kinds of parts, the well developed strands and the bright spots. Thread-like structures were obtained by the cooperation of the applied shear stress, which spread the sample film, and the thermodynamic characteristics, which reduced the excess surface free energy, as mentioned above.

4. CONCLUSIONS

The liquid crystallinity of P3DDT was thoroughly studied by DSC and optical microscopy. When observed under cross-polarized light, the liquid crystalline texture was not observed without the application of shear stress. The Schlieren texture was only observed under sheared condition. Even at 25°C, the Schlieren texture was developed by moderate shear stress. A finer Schlieren texture developed as the annealing temperature was increased. Based on the results of thermal analysis and optical microscopy, there was no direct relationship between the melting behavior in DSC thermograms



(a)



(b)

FIGURE 5 Optical micrographs of poly(3-dodecylthiophene) film at 140°C after applying shear (Magnification, X 300); (a) Non-crossed, (b) Crossed. (See Color Plate IX).

and the liquid crystalline behavior of P3DDT. It was proposed that P3DDT may not be a thermotropic liquid crystalline material.

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