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Effect of solvent and plasticizers on the rheology and morphology of a thermotropic liquid crystalline polymer with low temperature transitions*

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The effect of solvent and of small molecule plasticizers on the rheology and morphology of a main chain thermotropic liquid crystalline polymer with low melting transition has been studied. Of the two plasticizers used, diphenylisophthalate (DPIP) has a melting temperature (T_m) in the same range as that of the polymer, while diphenylterephthalate (DPTP) has a much higher T_m of 198°C. Incipient crystallization occurs in the starting samples when solvent cast, whereas the melt-pressed initial samples were amorphous. The influence of the crystallinity of the starting material and the concentration of the plasticizers on the time-dependence of the rheological parameters, η^*, G' and G'' are discussed. Differential scanning calorimetry, X-ray diffraction and optical microscopy were used in parallel to rationalize the rheological behaviour in terms of the crystallinity and the morphology of the samples. It is shown that the relative molecular conformations of the polymer and the plasticizer molecules can affect the morphology and hence the rheological behaviour of the composite. The twisted conformation of the DPIP can disrupt the ordering of the chains whereas the 'rodlike' shape of the DPTP molecule can facilitate intercalation with the polymer chains, leading to enhanced ordering of the polymer. Although the rheological characteristics of the TLCP were affected by the plasticizers, the glass transition temperature was not. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: liquid crystal; plasticizer; crystallization)

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) with low temperature transitions (i.e. a few degrees above ambient) are the subject of emerging interest. They combine the liquid crystallinity of rigid polymers with the mechanical properties of flexible chains and are applicable to numerous technologies. One of the strategies used in the design of such polymers is the introduction of methylene spacers of different lengths[1]. While the mesogenic units promote liquid crystallinity, the presence of aliphatic spacers lowers the extent of ordering and imparts attributes characteristic of a flexible polymer. Thus, by decreasing the packing order, these polymers offer the advantage of processability at lower temperatures, as well as increased solubility in common organic solvents, while retaining their liquid crystalline properties. A series of such polymers for use as toner resins for imaging applications have been described by Mahabadi and Alexandru[2]. These polymers typically have a glass transition temperature (T_g) of about 50°C and a melting temperature (T_m) up to 200°C. The large drop in their melt viscosity over a small temperature range, and their shear thinning behaviour are examples of the rheological properties of these TLCPs which are of interest in imaging technology.

The rheological and morphological studies of one of these TLCPs, with two spacers, were described recently[3]. It was shown that the increase in η^*, at constant strain amplitude and temperature, depends only on time and not on shear. X-ray diffraction studies showed that shear causes the polymer chains to orient in the shear direction and that both frequency and strain amplitude induce a gradient of crystallinity in the bulk of the sample, with crystallization being predominant near the surface.

Plasticization of polymers is a well established technology and is commonly used to tailor their T_gs and their processability[4]. The effect of plasticizers on the dynamic relaxations of a number of polymers has been reported[5]. The relative stiffness and polarity of the polymer and the plasticizer have a profound influence on the resulting properties, if it acts as a plasticizer or antiplasticizer[6]. A recent study[7] on roll-extruded, plasticized amorphous polymers with low T_gs showed that beyond a certain limit of compatibility the

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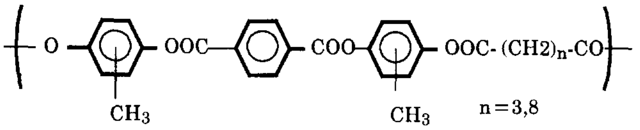
excess plasticizer was dispersed as crystallites, and that these crystallites were oriented along the direction of extrusion, in the polymer matrix. In this case, the crystallites of the excess plasticizer act as particulate fillers. In the absence of such aggregation as crystallites, the plasticizer can be viewed as a molecularly dispersed filler, of the size of a few angstroms. Since the effect of the plasticizer is to act as a 'lubricant' in the host matrix, it is expected that plasticization would exhibit interesting features in the behaviour of liquid crystalline polymers.

In this paper, we describe the effect of plasticization on the rheological and morphological behaviour of a TLCP with low thermal transitions, reported earlier by Drappel *et al.*[3]. Two plasticizers were used, one with T_m about the same as that of the polymer, while the other had a higher T_m.

EXPERIMENTAL

The synthesis of the TLC copolyester with two spacers (i) has been described previously[3]. This polymer shows a nematic mesophase, has a T_g of 48°C and an isotropic clearing temperature (T_i) of 235°C. The molecular weights, measured by gel permeation chromatography (g.p.c.) and reported in terms of polystyrene standards, were $M_n = 7591$ and $M_w = 48\,914$. The T_m depends on annealing history and varies[3] from 130 to 155°C.



(i)

The two plasticizers selected for this study are diphenyl isophthalate (DPIP) which has a melting point of 141°C as determined by differential scanning calorimetry (d.s.c.) and diphenyl terephthalate (DPTP) with a melting point of 198°C. The plasticizers were incorporated in the matrix polymer by solution blending in dichloromethane at concentrations of 2, 5 and 10 wt%. This procedure assured a molecular dispersion since both components were soluble in the solvent. The resulting blends were dried under ambient conditions for 24 h and then under vacuum at 60°C for an additional 24 h. They were then ground using a coffee mill and dried again under the same conditions. Throughout the duration of this study, the samples were kept under vacuum and removed just prior to the actual experiment.

The rheological characterization was carried out on a Rheometrics Mechanical Spectrometer RMS-800 with the parallel-plate geometry using disposable plates (25 mm diameter). The parallel-plate geometry was chosen, since the results are not as sensitive to small variations in sample thickness caused by thermal expansion as they are with the cone and plate geometry[8]. All the rheological tests were based on dynamic measurements using small amplitude oscillatory shear deformations.

Consistency in the sample preparation procedure is critical in obtaining reproducible results. It is known that the rheology of thermotropic liquid crystalline polymers is greatly dependent on the thermal and shear history of the sample[9–12] and the state of the specimen at the beginning of the rheological measurements depends on the preparation itself[12]. The polymer disks were made under identical conditions using the following procedure: 1 g of polymer was placed in a compression die with a diameter of 25 mm between two thin polytetrafluoroethylene (Teflon) sheets. The die was placed in a press, preheated to 120°C and left for 5 min, with no load, for temperature equilibration. A pressure of 17.2 MPa (2500 psi) was then applied for 5 min. The compression die was then removed and immersed in liquid nitrogen.

An exact procedure for loading the sample into the rheometer was also followed throughout. The sample was loaded into the preheated rheometer chamber and exactly 5 min were allowed for temperature equilibration and gap setting, after which the experiment was started. The gap was maintained at 1.5 mm for all samples in order to avoid discrepancies in the results due to gap variations, as previously noted by Kalika *et al.*[13]. One data point was taken every minute. At the end of the experiment, the sample was immediately quenched with liquid nitrogen, the temperature of the sample reaching sub-ambient within 30–40 s.

The rheological experiments were conducted as a function of elapsed time. All tests were time sweeps for a period of 60 min, at a constant temperature of 130°C, with a strain amplitude of 5% and a frequency of 1 rad s^{-1}. It has been established previously[3] that under these conditions there was a maximum in the degree of crystallinity of the melt pressed neat polymer.

X-ray diffraction patterns were recorded with a Statton-type Warhus flat film camera (William Warhus Co., Wilmington, DE), under vacuum, in order to eliminate air scatter, using CuK$_\alpha$ radiation with a wavelength of 0.1542 nm. The sample to film distance was either 5.3 cm or 12.3 cm. Both 'edge view' and 'through view' configurations were used for qualitative determination of the degree of crystallinity as well as the degree of molecular orientation. In the former, the X-ray beam traverses the sample through the thickness, parallel to its surface and in the through view, the beam is normal to the sample plane.

D.s.c. analysis was carried out using a TA Instruments DSC10 differential scanning calorimeter, at a heating rate of 20°C min^{-1}. Some scans were also made at a rate of 5°C min^{-1}. After the first scan from room temperature to 180°C, the sample was quenched with dry ice to 0°C and scanned again to 180°C. Both scans were recorded. For the materials containing the DPTP plasticizer (which has a T_m of 198°C), the maximum temperature was 220°C, to detect if any excess plasticizer was present.

Small angle light scattering (SALS) was used primarily to detect the spherulitic crystalline morphology. This technique involves the photometric measurement of the scattered intensity, which arises mainly from fluctuations in anisotropy and density in the crystalline domains, as a function of scattering angle. The setup, described by Jabarin and Stein[14], includes a 15 mW He–Ne laser with $\lambda = 0.6328\,\mu$m (Spectra-Physics Model 120), a rotatable analyser, and a photographic setup for Polaroid 4 × 5 Land film. The vertically polarized incident laser beam was passed through a 2 mm pinhole to avoid stray radiation and the pattern was recorded with the optical axis of the analyser kept horizontal (H_v

mode). The average size of the spherulites is given by[15]:

$$4\pi(R/\lambda)\sin(\Theta/2) = 4 \qquad (1)$$

with

$$\Theta = \tan^{-1}(d/D) \qquad (2)$$

Here R is the radius of the spherulite, λ is the wavelength of the laser beam, d is the distance on the H_v photograph from the centre of the incident beam to the point of maximum intensity on the four-leaf clover pattern and D is the sample to film distance.

Optical Microscopy (OM) was performed with a Zeiss Axioplan OM, equipped with a Leitz Wetzlar hot stage, using cross polarized illumination. The samples were prepared by dissolving a small amount of the material in dichloromethane and letting the solution dry on a microscope slide. The slides were covered to allow a slow evaporation of the solvent. For each material, three slides were prepared.

Preliminary calculations were performed on the preferred conformations of the polymer and the plasticizer molecules, using the Polygraf© (versions 3.1 and 3.2, Molecular Simulations Inc.) molecular modelling code. The atomic force field used here is the Dreiding II potential, with the parameters described by Mayo *et al.*[16].

RESULTS AND DISCUSSION

Solvent cast vs *melt-pressed samples of the neat polymer*

We have previously presented the time-dependent rheological characteristics of the melt-pressed low melt TLCP with two flexible spacers[3]. Since the samples in the present study were prepared by solution blending the polymer and the plasticizer, a comparison was made of the rheological and thermal behaviour of a sample of the neat polymer which was solution cast, and another which was melt-pressed. Even though it is the same polymer, there are numerous differences between the behaviour of these samples. *Figure 1* illustrates the change in the complex viscosity η^* and damping factor tan δ with time. The change in elastic modulus G' and viscous modulus G'' are shown in *Figure 2*. The neat polymer which was not predissolved in the solvent (i.e. directly melt-pressed) has an initial viscosity of $\sim 1 \times 10^4$ Pa s at time zero and there is a continuous increase in the values of η^* and G' with a slope (a measure of the crystallization rate) of $\sim$ 1.25 over the first 1000 s of shearing. Thereafter, there is a slowdown of the crystallization process and the rheological parameters reach asymptotic values. During the entire period of shear of 60 min, η^* and G' increased by about two orders of magnitude. However, in the case of the solution cast sample, the initial viscosity is $\sim 2 \times 10^4$ Pa s at time zero and the slope of η^* is $\sim$ 1.8 only for the first 3–4 min of shearing, after which the slope changes dramatically. The increase in η^* over the entire period of time is just over one decade. For the melt-pressed polymer, the damping factor tan δ (i.e. G''/G') decreases continuously from a high value of 1.35, when G'' is predominant, to a crossover point at about 200 s and to a value of 0.3 after 900 s. Then there is a more gradual decrease over a time period of 1 h. For the solution cast polymer, tan δ shows a similar behaviour, with the exception that at time zero, which actually represents the 5 min already allowed for temperature equilibration, the highest value is 0.43 and reaches a constant value of 0.27 after the first 300 s.

The differences in the variations in G' and G'' of the two samples (*Figure 2*) are similar to those in η^*. In each case, G' increased faster than G'', indicating an increase in the relative elasticity of the system. At time zero, the elastic modulus G' of the solvent cast neat polymer is half an order of magnitude higher than that of the 'dry' polymer, while the G''s of the two polymers are identical. Recall that the former was dried at 60°C for 24 h, put in a compression die and kept for 5 min at 120°C (250°F), then pressed into a disk with a pressure of 17.2 MPa (2500 psi) for 5 min, and subsequently kept under

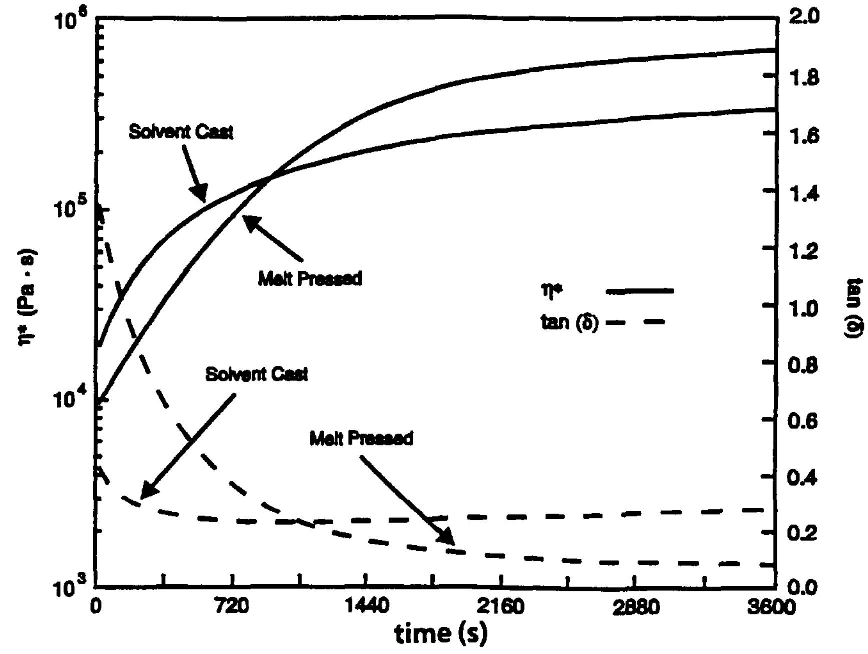


Figure 1 Complex viscosity η^* and tan δ vs time at 130°C, 1 rad s^{-1} and 5% strain, of the melt-pressed and solvent cast polymer samples

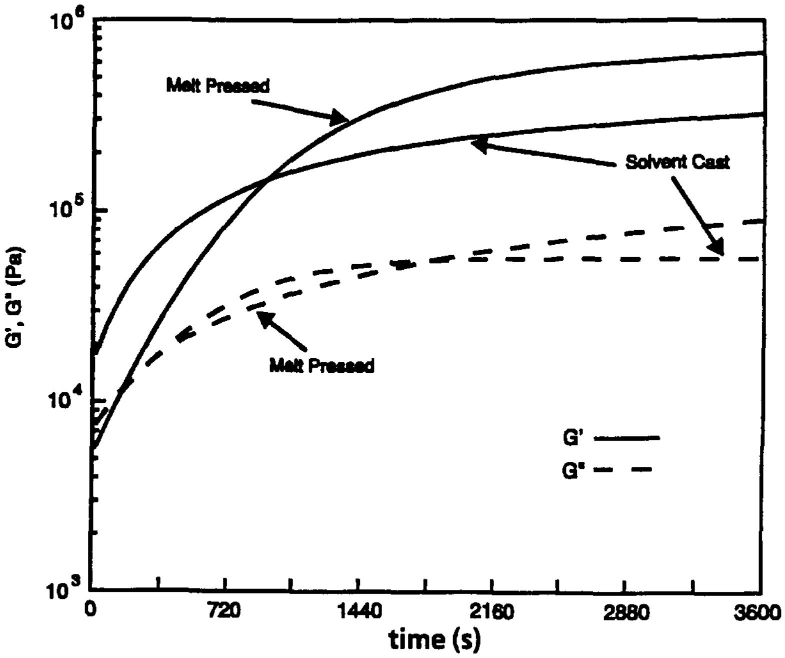


Figure 2 Storage modulus G' and loss modulus G'' vs time at 130°C, 1 rad s^{-1} and 5% strain, of the melt-pressed and solvent cast samples

vacuum for several days. In spite of this protocol, d.s.c. and X-ray diffraction analysis of the solution cast film indicated that solvent induced crystallization had occurred. Although the crystallinity, as discerned from visual inspection of the diffraction patterns, is small, it seems to be enough to account for the higher melt viscosity. The melt-pressed/quenched films were, however, amorphous. Hence, the initial viscosity of this sample is lower than that prepared by the solution route. Crystallization occurs in the melt-pressed sample during the first 5–10 min, reaching an asymptotic value in about 15 min.

The rate of crystallization, as seen from the slope of the curves for η^*, is higher for the initially amorphous melt-pressed sample, as compared with the solution cast film. This is seen from *Figure 3*, in which the rates of change of η^* and G' (not their logs) are shown as a function of time, for the 'dry' (*Figure 3a*) and solvent cast (*Figure 3b*) films. The $\mathrm{d}(\eta^*)/\mathrm{d}t$ and $\mathrm{d}(G')/\mathrm{d}t$ for the 'dry' sample increase sharply with time, exhibiting a maximum at ~ 1300 s and decreasing thereafter. These rates gradually decrease with the solvent cast film.

This rheological behaviour seems to parallel the previously published results on a two step crystallization process[17,18]. The first step is rapid until the sample is physically crosslinked. In the present case, this time is ~ 1300 s for the melt pressed polymer and ~ 300 s for the solvent cast film. This effect also suggests that the solvent cast film was already partially crystalline which affected the magnitude of the elastic modulus G' at time zero. The slowdown of the crystallization rates afterwards has been attributed to a second step of the transformation which is controlled by a slow diffusional process and occurs over more than 10^7 s of annealing time, until the sample reaches the maximum degree of crystallinity[17].

Teh *et al.*[19] have recently employed the modulus G' to characterize nucleation and crystallization in conventional flexible polymer systems. The change in the slope of G' with time has been related to the different stages of crystallization, viz. nucleation, development of spherulites from the nuclei and the growth of the spherulites. The time scale for the maximum observed with the 'dry' sample in *Figure 3a* is of the same range (1000 s) as that measured by Teh *et al.*[19] for the rapid spherulite growth in polypropylene. Such a maximum in G' is not seen in *Figure 3b*, since the sample was already partially crystalline. In the present case, after 60 min of shearing, the final viscosities of both the 'dry' and solvent cast neat polymers are similar (*Figure 1*), indicating a slower crystallization rate in the dry polymer.

D.s.c. analysis of the solvent cast polymer displays an unusual behaviour as shown in *Figure 4* and *Table 1*. These results correspond to a heating rate of 20°C $\min^{-1}$. The dried and ground polymer shows a second transition at ~ 80°C, in addition to a major melting transition at ~ 125°C (*Figure 4a*). The heats of fusion (ΔH) of these two transitions are in the range of 4 J g^{-1} and 10 J g^{-1} respectively. Upon subjecting the material to a temperature of 120°C for 10 min for the disk making procedure, a single broad melting peak with a shoulder at ~ 125°C is observed with a ΔH of ~ 6.5 J g^{-1} (*Figure 4b*). Following the major endotherm, there are small but distinctive multiple melting peaks. Their origins will be discussed later. As previously described, the experimental procedure involved placing the polymer disk in the preheated rheometer chamber at the preset temperature of 130°C for 5 min for temperature equilibration, before starting the actual rheological measurements. When the disk was removed after this initial equilibrium period of 5 min, it exhibited only one small transition with a peak endotherm at ~ 138°C and a ΔH of ~ 0.6 J g^{-1} (*Figure 4c*). After shearing the disk in the rheometer for 60 min at a fixed temperature of 130°C, there is only one better defined endotherm at 144°C with a ΔH of ~ 4.1 J g^{-1} (*Figure 4d*).

Figure 5 shows a series of optical micrographs of the solvent cast film, recorded at different temperatures, during heating and subsequent cooling. At room temperature, spherulites of two distinct sizes are seen, one about 0.7–0.9 μm and the other 5–8 μm. The SALS

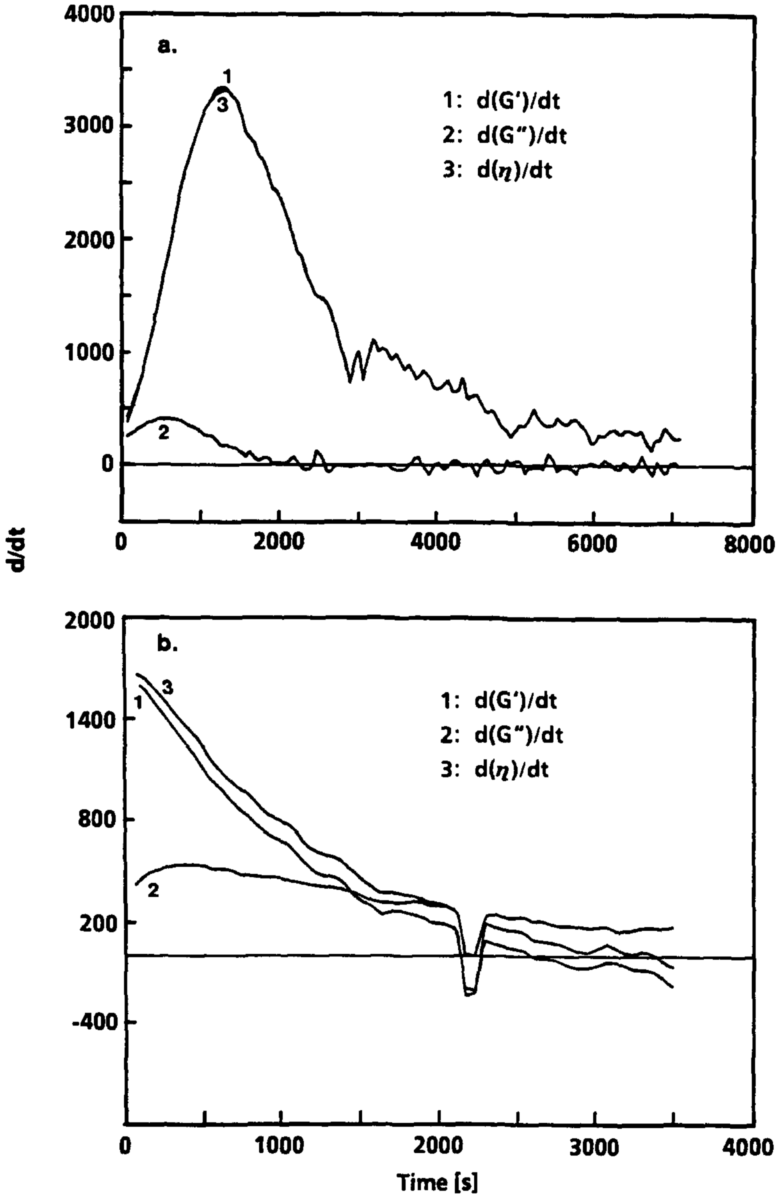


Figure 3 $d/dt(\eta^*)$, $d/dt(G')$ and $d/dt(G'')$ vs time at 130°C of the (a) melt-pressed and (b) solvent cast sample

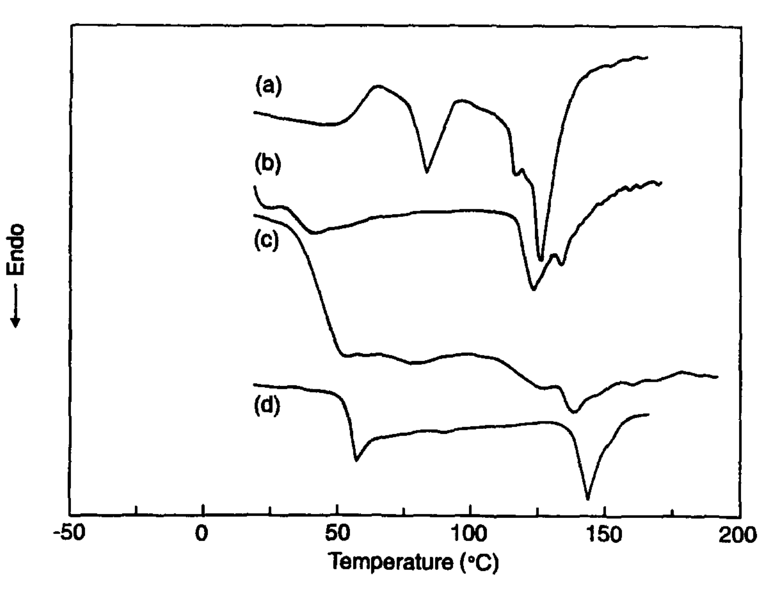


Figure 4 D.s.c. thermograms: (a) the solvent cast neat polymer; (b) following the preparation of the disk for rheological analysis; (c) heated for 5 min at 130°C; (d) sheared for 60 min at 130°C

Table 1 Results of rheological and thermal analysis of the samples, after shearing for 60 min at 130°C

Sample	η^* $\times 10^{-5}$	Ratio[a]	Melting point T_m (°C)	ΔH (J g^{-1})
Neat polymer, melt pressed	6.81	71.9	143.7	3.3
Neat polymer, solvent cast	3.35	17.5	143.7	4.1
Polymer + 2% DPIP	2.05	5.2	141.8	3.6
Polymer + 5% DPIP	1.56	3.4	142.9	2.9
Polymer + 10% DPIP	1.04	4.5	140.3	1.5
Polymer + 2% DPTP	2.32	4.4	143.1	3.7
Polymer + 5% DPTP	2.50	3.9	143.7	2.7
Polymer + 10% DPTP	3.43	6.1	142.8	2.5

[a] This ratio refers to η^* at 60 min/η^* at time zero

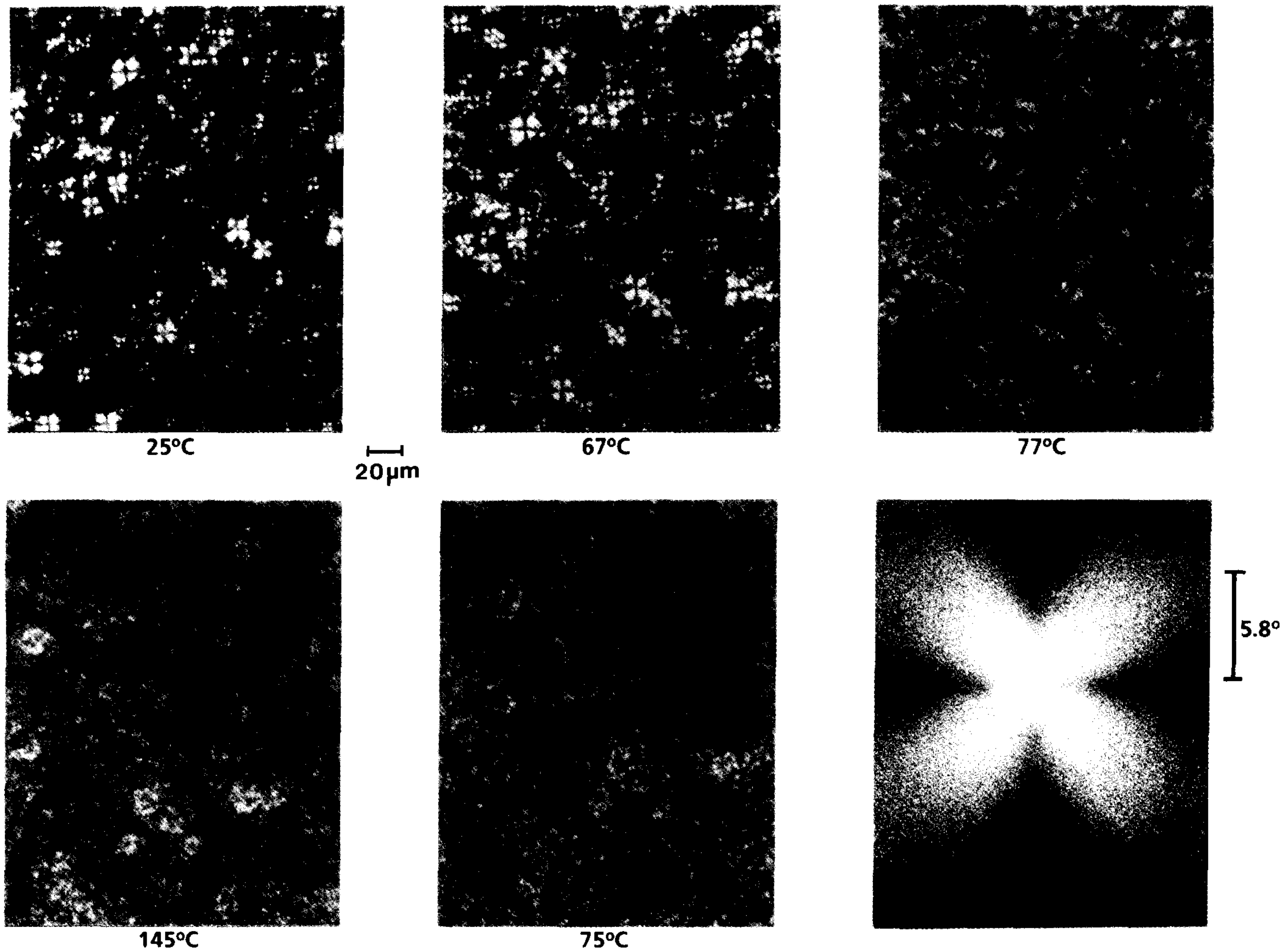


Figure 5 Optical micrographs of the solvent cast film recorded at different temperatures. The SALS pattern for 'a' is also shown. The scattering angle Θ is marked on the SALS pattern

pattern at room temperature, consisting of the characteristic four-leaf clover due to spherulitic scattering, is also shown here. At 67°C there is an increase in the population and the size of the spherulites. At 77°C the small spherulites have melted. Beyond 145°C, a Schlieren pattern developed. This pattern remains upon cooling and the spherulites do not re-form. Upon cooling to 75°C, the polymer is frozen in a nematic glassy state. Thus the transition at 80°C can be attributed to the melting of the small spherulites. Moreover, the analysis of the samples after shearing in the rheometer for 60 min at 130°C show only a single endotherm at ~ 140°C, consistent with the observation that the small spherulites melt at ~ 80°C.

Effect of annealing temperature on the crystallinity of the solvent cast TLCP

A d.s.c. study on the effect of the annealing temperature on the heat of fusion and peak position of the melting endotherm was conducted. The temperature range was from 60 to 150°C in increments of 10°C. The neat polymer was predissolved in dichloromethane at a

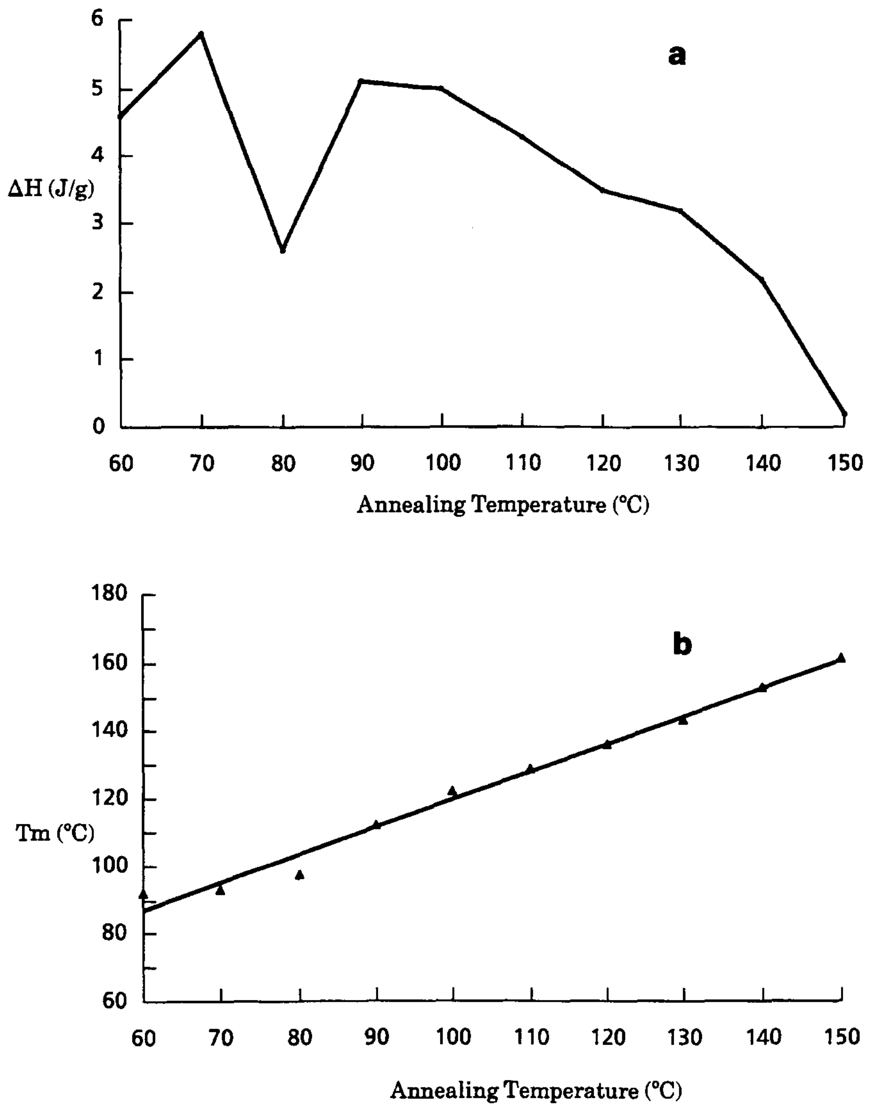


Figure 6 Effect of annealing temperature on: (a) the heat of fusion ΔH; (b) peak position of the melting endotherms

concentration of 10%, stirred with a magnetic stirrer for 24 h and processed as described in Experimental. A small sample of approximately 10 mg was placed in a d.s.c. pan. To check the reproducibility two samples were prepared for each temperature. For consistency with the rheological measurements, the rheometer chamber was used for annealing.

We have previously shown[3] that the TLCP polymer, in the absence of the solvent, is amorphous and a maximum growth rate of stable nuclei was observed at 130°C. Below the temperature of 100°C, no crystallinity was detected. In the case of the solvent cast resin, annealing was performed starting at 60°C. The ΔH and T_m following annealing at specified temperatures are shown in *Figures 6a* and *6b* respectively. The overlay plot of the d.s.c. curves of these samples are presented in *Figure 7*. *Figure 6a* shows that in this case two maxima occur in the heat of fusion. The ΔH increases from 60°C and reaches a peak at 70°C. Consistent with the OM observations, there is a small endotherm at 80°C, and then there are two broad transitions at 90°C and 100°C with a ΔH of $\sim 5\,\mathrm{J\,g^{-1}}$ representing the second plateau. *Figure 7* shows that the endotherm for the sample annealed at 110°C becomes narrower, suggesting that this is the optimum temperature for crystal growth. Even though the heat of fusion continues to decrease steadily, the breadth of the transition starts again to increase and a small shoulder can be detected at 130°C. A commonality between the melt-pressed and solvent cast polymers is that the peak positions of the melting endotherms are identical over the same temperature range and increase linearly with increasing annealing temperature (*Figure 6b*). Up to the temperature of 90°C and at 140°C, following the major endotherm, the distinctive multiple small melting peaks are seen again. They occur with the two small molecules as well, being more pronounced with the DPTP plasticizer (see below).

Effect of the diphenyl isophthalate (DPIP) and diphenyl terephthalate (DPTP) plasticizers

Rheological behaviour. The changes in the viscosity η^*, the elastic modulus G' and the viscous modulus G'' are illustrated in *Figures 8a*, *8b* and *8c* respectively, for composites with 2, 5 and 10% concentration of DPIP in the polymer. Several interesting features are observed in their behaviour. At time zero, in all three cases, the relative values of η^*, G' and G'' of the filled systems are higher than those of the neat polymer. However, they are in the reverse order of what one

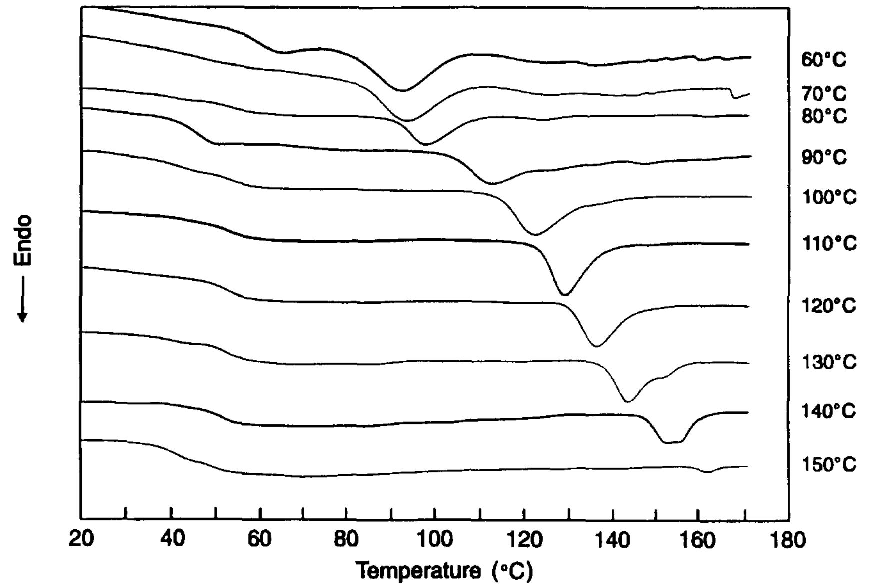


Figure 7 Overlay of d.s.c. thermograms of the solvent cast film as a function of annealing temperature

would expect and they decrease with increasing plasticizer concentration. During the first 300 s, the rate of crystallization is slower for the filled systems, as seen in the slopes of η^* which are ~ 1.8 for the neat polymer and ~ 0.9 for the DPIP/polymer systems. After 60 min, η^*, G' and G'' decrease with increasing concentration of DPIP in the polymer, indicative of the plasticizing effect of the small molecule. The effect of the plasticizer in this case is to decrease the rate of crystallization and the crystallinity of the polymer and to lower the viscosity of the TLCP upon shearing at 130°C as seen in the values of ΔH presented in *Table 1*.

The variations in η^*, G' and G'' with time for various concentrations of DPTP in the polymer are shown in *Figures 9a*, *9b* and *9c* respectively. The melting temperature of this plasticizer is approximately 55°C higher than that of the polymer itself. *Figure 9a* shows that for the first 300 s, the rate of crystallization is again slower in the presence of the plasticizer and has the same slope as with the polymer/DPIP system. After 60 min of shear the differences between the samples are not as pronounced as in the DPIP case. While the η^* and G' values increase slightly with increasing plasticizer concentration, the magnitude of G'' decreases, consistent with their heats of fusion (*Table 1*). The higher value of η^*, with 10% DPTP compared to 2 or 5% concentration, would also indicate that the plasticization decreases the η^* compared to the neat polymer, but the excess plasticizer begins to act as a reinforcing filler and increases the overall viscosity of the system.

Thermal properties. Several thermal studies were also performed on the plasticized TLCP system. First, let us consider the case of 'as prepared' samples of the DPIP/polymer composite. The d.s.c. curves for the solvent cast films with 2, 5 and 10 wt% DPIP (*Figure 10a*) show the two endotherms at ~ 80°C and ~ 125°C, as in the case of the neat polymer. Following the second endotherm, distinctive small multiple melting peaks are observed. These small transitions are similar to those reported in the literature for lower transition TLCPs by Hu *et al.*[20] and Marsano *et al.*[21]. These are probably due to the formation of a broad range of crystal modifications (i.e. various sizes and degrees of order), in this case promoted also by the plasticizer molecules. This interpretation seems to be confirmed by the second scan, where they were not seen in the samples with 2% and 5% DPIP, but detectable with the 10% loading, where there is excess plasticizer beyond the compatability limit.

In the next series of experiments, an explanation was sought for the decrease in the values of η^*, G' and G'' at time zero, with increasing plasticizer content. A set of disks with 2, 5 and 10% DPIP were placed in the rheometer and removed after the initial 5 min of temperature equilibration, as previously described, and their thermal properties (*Figure 10b*) were determined (as noted above, the solvent cast neat polymer showed that after 5 min of annealing at 130°C, the heat of fusion dropped from a ΔH of $\sim 6.5\,\mathrm{J\,g^{-1}}$ to a ΔH of $\sim 0.6\,\mathrm{J\,g^{-1}}$). With 2% DPIP loading, the thermogram displays a very broad endotherm with a ΔH of $\sim 1.9\,\mathrm{J\,g^{-1}}$ and two major peaks, the first at ~ 125°C, (as with the neat sample) and the second, more predominant peak at ~ 140°C. With the 5% sample, the endotherm is not quite as broad and has a ΔH of $\sim 1.5\,\mathrm{J\,g^{-1}}$. Although the two endotherms are still present at the same peak positions as with the 2% loading, the first transition is predominant. At 10% loading, the peak corresponding to the second transition is shifted to ~ 136°C. The heat of fusion of this endotherm, which is $\sim 1.7\,\mathrm{J\,g^{-1}}$, indicates as well the presence of excess plasticizer. This increase in the value of ΔH in the case of the plasticized polymer as compared to the value of $\sim 0.6\,\mathrm{J\,g^{-1}}$ for the neat polymer, accounts for the higher viscosity of the former at time zero.

Upon shearing the samples at 130°C (*Figure 10c*), there is only one principal endothermic transition at ~ 141°C for the 2% and 5% plasticizer loading. For the 10% sample, there is a double endotherm, with peaks at ~ 129°C and ~ 141°C. Since the pure plasticizer has a T_m of ~ 141°C, a slower heating rate of $5\,\mathrm{°C\,min^{-1}}$ was employed to get a better separation between the two peaks (*Figure 10d*). Even though the data are noisier, the

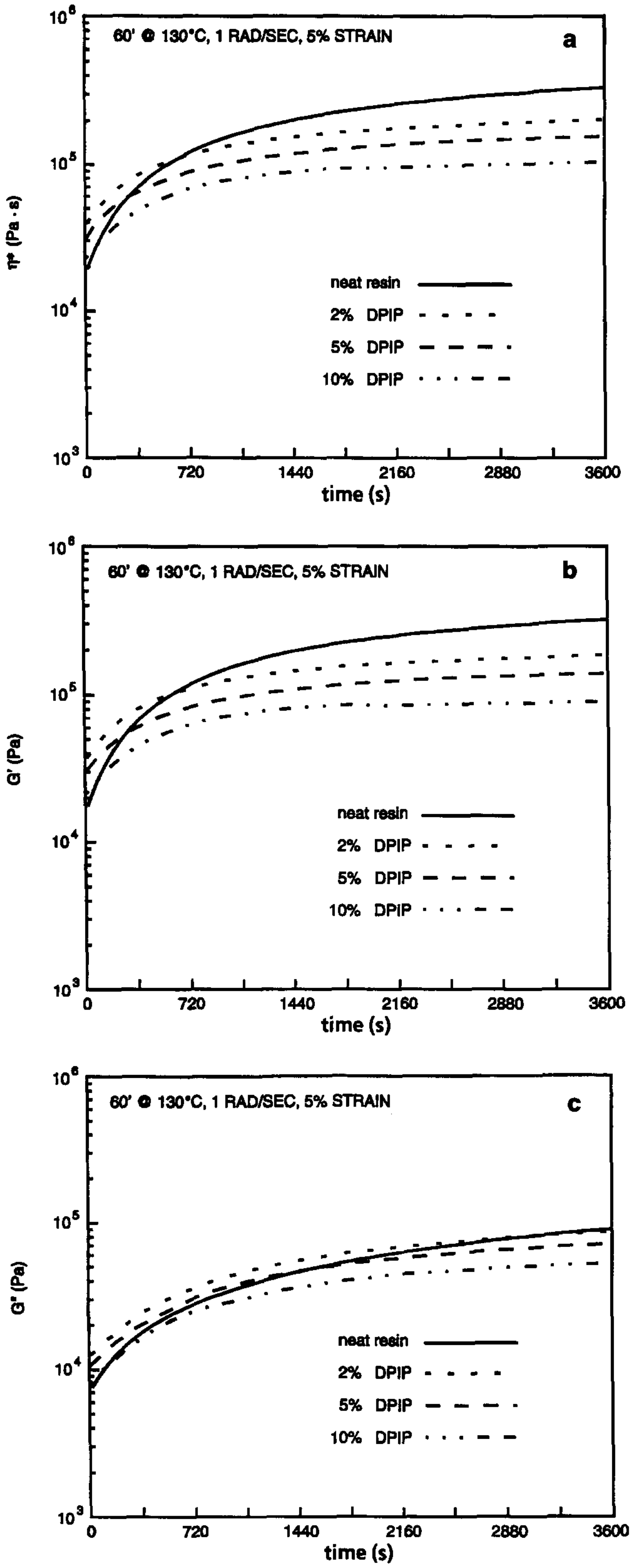


Figure 8 Complex viscosity η^* (a), storage modulus G' (b) and loss modulus G'' (c) vs time at 130°C of the solvent cast neat polymer and polymer/DPIP composites

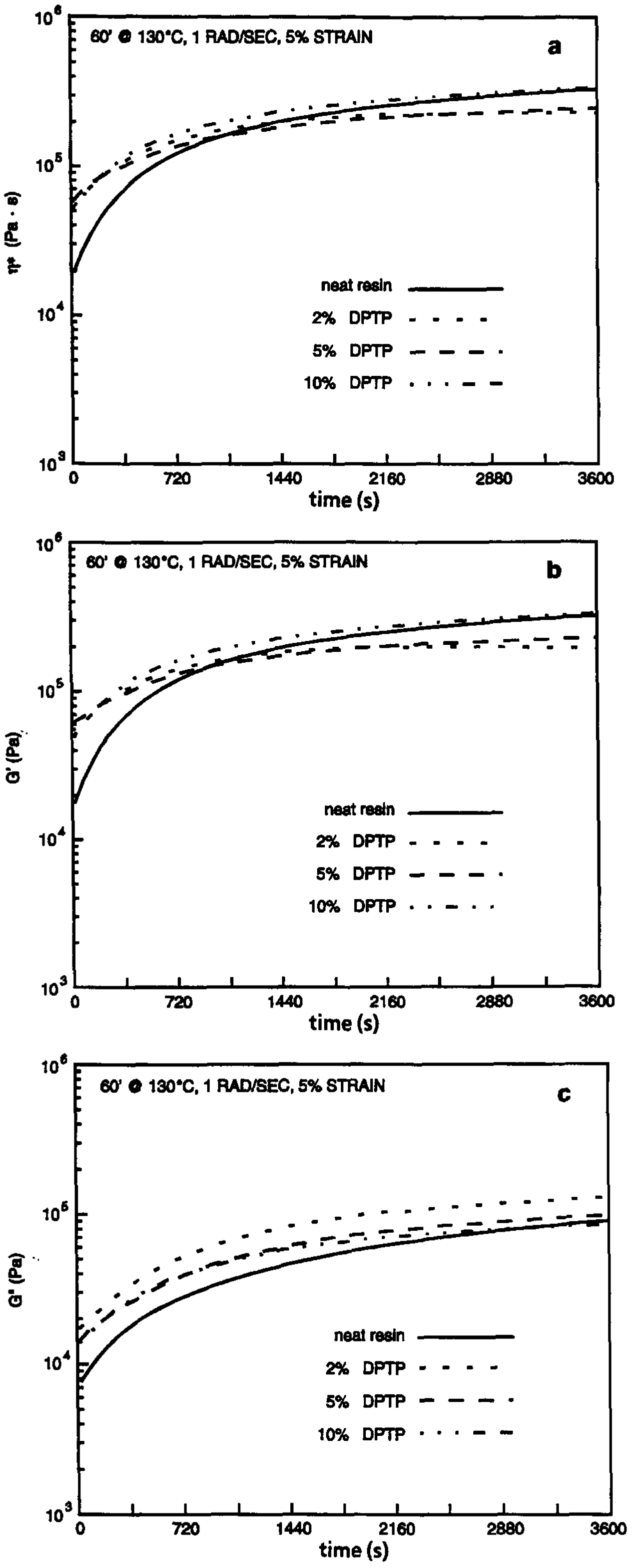


Figure 9 Complex viscosity η^* (a), storage modulus G' (b) and loss modulus G'' (c) vs time at 130°C of the solvent cast neat polymer and with DPTP

transition is shifted to ~ 136°C for the 2% and 5% loading, while for the 10% sample, there is a secondary peak at 131°C, which is ~ 10°C below the melting temperature of the plasticizer, suggesting a reverse plasticization of the small molecule by the polymer. Such a depression of the T_m of the plasticizer by the polymer was noted in the case of plasticized (styrene/acrylate) polymers[6]. At the scan rate of 5°C min^{-1}, a small peak at ~ 150°C with a ΔH of ~ 0.3 J g^{-1} is present in all cases. This temperature is above the melting points of both polymer and plasticizer. The origin of this peak is not known at this time.

D.s.c. thermograms of the TLCP/DPTP composites show characteristics similar to those of the polymer/DPIP system. The solvent cast films with 2%, 5% and 10% DPTP (*Figure 11a*) display two transitions as well. The first endotherm is at ~ 88°C, the second one however, is shifted by ~ 4°C with increasing plasticizer concentration. Multiple peaks are seen above the T_m of the polymer and a broad transition at 185°C, due to the excess plasticizer, is observed with the 10% concentration of plasticizer. The degree of crystallinity of the materials sheared at 130°C does not seem to be affected by the presence of the small molecule, the main endotherm being at ~ 143°C and a ΔH of ~ $3\,J\,g^{-1}$, similar to that of the neat polymer (*Figure 11b*). The T_g of all these samples does not appear to be affected by the plasticizer and therefore the small molecule acts as a filler and not plasticizer.

An isothermal annealing study where samples were kept for 60 min at a set temperature was also carried out. The results for the plasticized systems, presented in *Figures 12* and *13*, and in detail in *Table 2*, show a behaviour similar to that of the solvent cast neat polymer. The minimum in ΔH at 80°C and the maximum crystallization rate at 90–100°C are observed with both plasticizers and the peak position of the melting endotherm increases linearly with increasing annealing temperature. However, the overlay plot (*Figure 14*) for the composite with 5% DPIP shows that the transitions are broader than in the case of the neat polymer, and there are double endotherms at almost

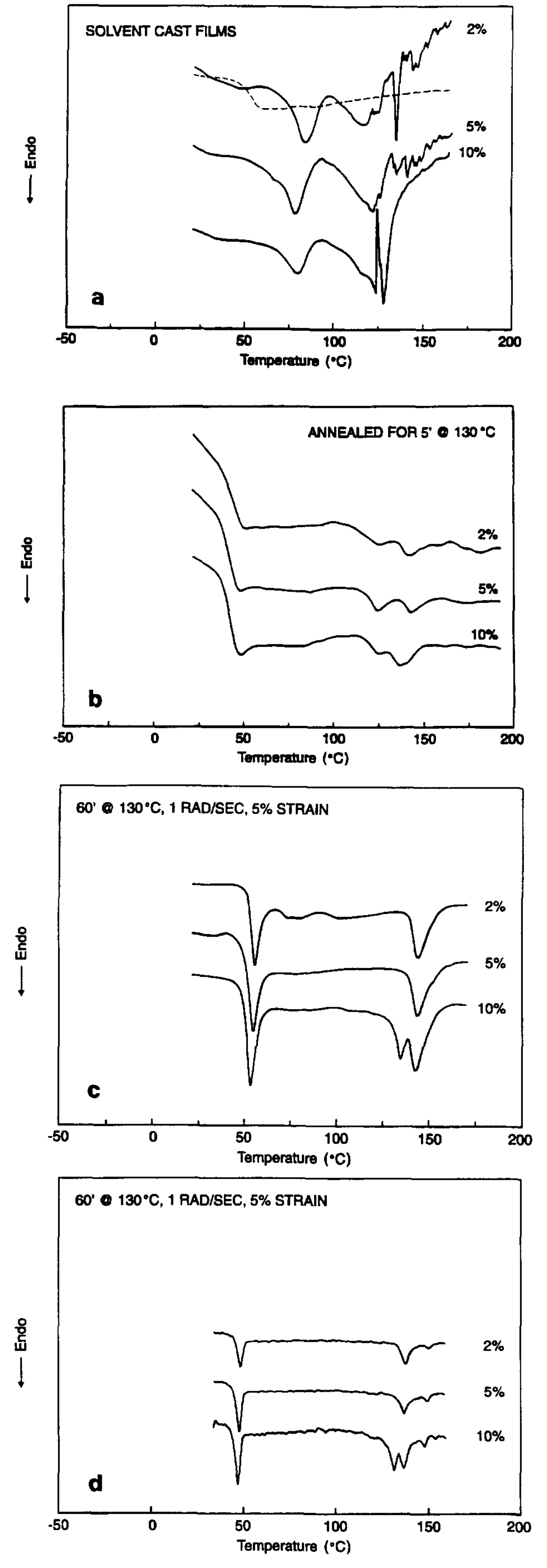


Figure 10 D.s.c. thermograms of the composites with 2%, 5% and 10% DPIP: (a) solvent cast films; (b) disks heated for 5 min at 130°C; (c) and (d) disks sheared for 60 min at 130°C. Heating rates were $20°C\,min^{-1}$ for (a), (b) and (c) and $5°C\,min^{-1}$ for (d). The dashed curve in (a) corresponds to the second scan with 2% DPIP

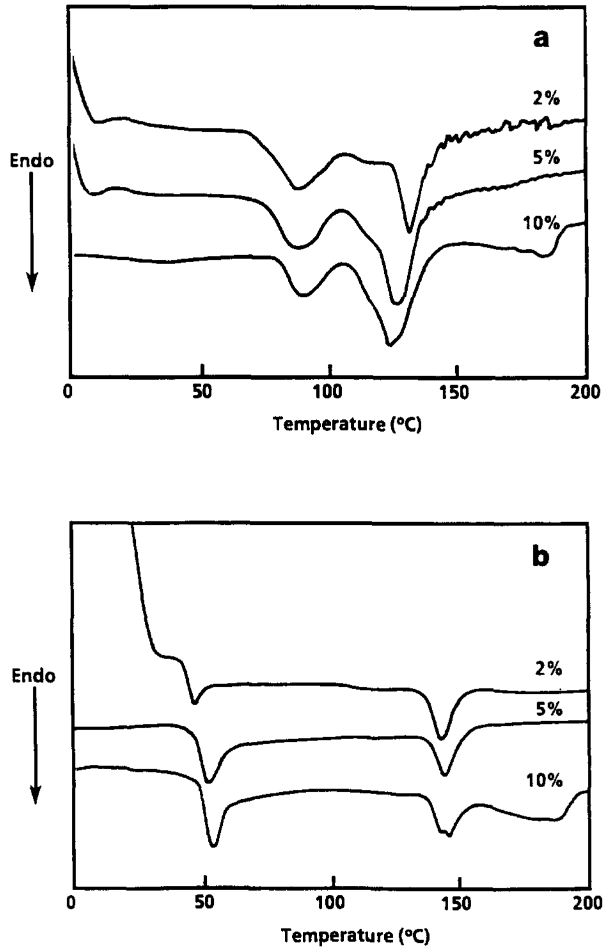


Figure 11 D.s.c. thermograms with 2%, 5% and 10% DPTP of: (a) the solvent cast films; (b) sheared disks for 60 min at 130°C

all temperatures, with the exception of the transition at 120°C when the endotherm becomes narrower, suggesting that this temperature is the optimum for a more perfect crystalline structure.

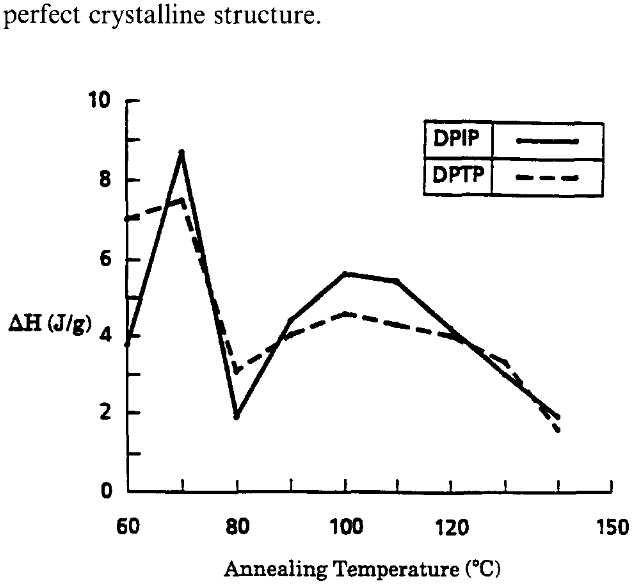


Figure 12 Effect of annealing temperature on the heat of fusion ΔH for the sample with 5% DPIP (—) and with 5% DPTP (- - -)

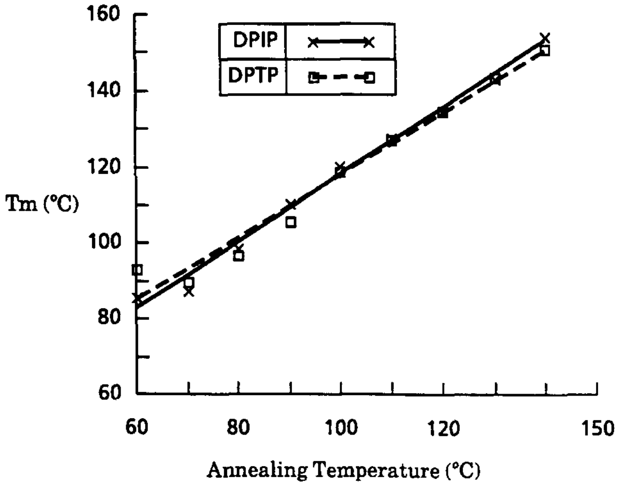


Figure 13 Effect of annealing temperature on the peak position of the melting endotherm for the samples with 5% DPIP (—) and with 5% DPTP (- - -)

The overlay plot of the 5% DPTP/polymer sample is shown in *Figure 15*. The multiple small peaks are again seen up to annealing temperatures of 90°C and again at 140°C. This suggests that a more ordered crystalline domain is being developed only within a certain range of annealing temperature, i.e. 100–130°C. An interesting aspect is the absence of the double peaks in the thermograms for this material as opposed to the DPIP/

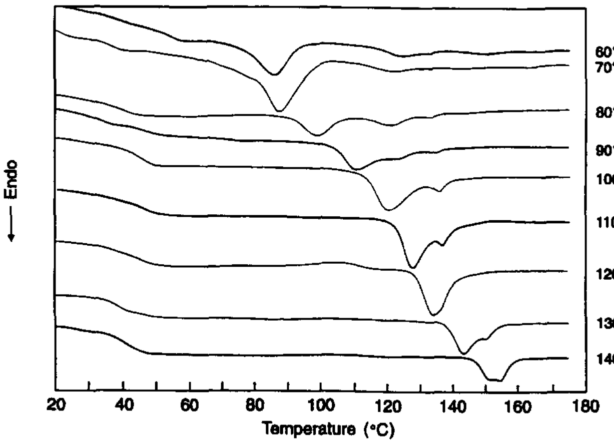


Figure 14 Overlay of d.s.c. thermograms of the polymer with 5% DPIP as a function of annealing temperature

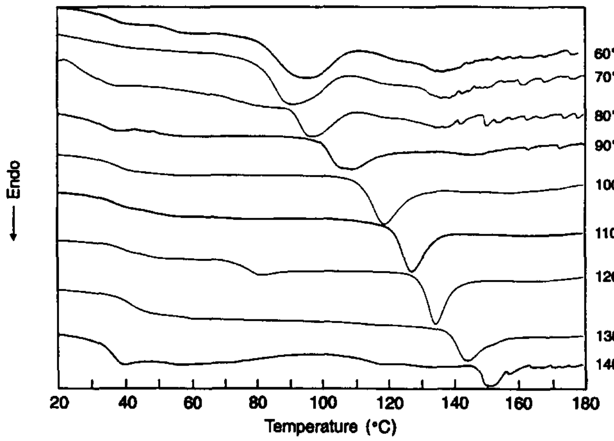


Figure 15 Overlay of d.s.c. thermograms of the polymer with 5% DPTP as a function of annealing temperature

Table 2 Results of thermal analysis of plasticized TLCP, after annealing at various temperatures

Annealing temperature (°C)	Solvent cast, neat polymer, peak T_m (°C)	Solvent cast, neat polymer, ΔH (J g^{-1})	Polymer + 5% DPIP, peak T_m (°C)	Polymer + 5% DPIP, ΔH (J g^{-1})	Polymer + 5% DPTP, peak T_m (°C)	Polymer + 5% DPTP, ΔH (J g^{-1})
60	91.9	4.6	85.9	3.8	93.2	7.0
70	93.0	5.8	87.4	8.7	89.8	7.5
80	97.8	2.6	98.7	1.9	96.8	3.1
90	112.4	5.1	110.7	4.4	105.6	4.0
100	122.2	5.0	120.1 136.1	5.6	119.1	4.6
110	129.2	4.3	127.8 138.3	5.4	127.5	4.3
120	136.4	3.5	134.7	4.2	134.6	4.0
130	143.7	3.2	143.3	3.0	143.8	3.3
140	152.9	2.2	154.5	1.9	151.1	1.6
150	161.7	0.2	162.1	0.3	161.5	0.3

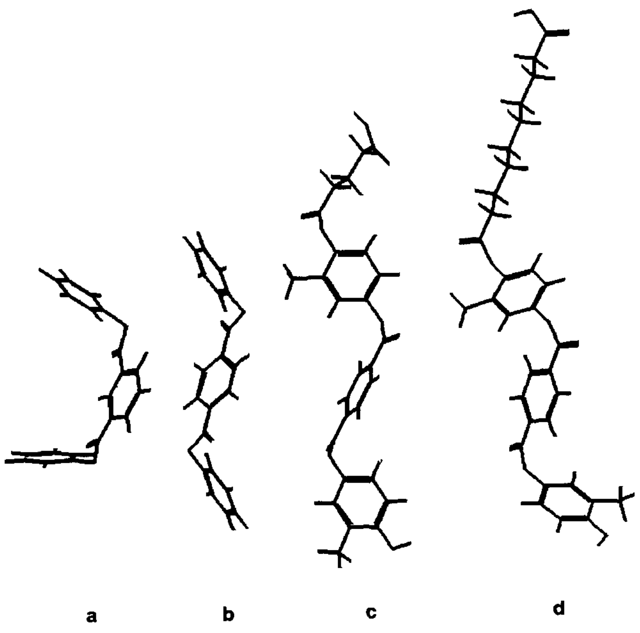


Figure 16 Minimum energy conformations of: (a) DPIP; (b) DPTP; (c) TLCP segment with 3 methylene spacer; (d) TLCP segment with 8 methylene spacer

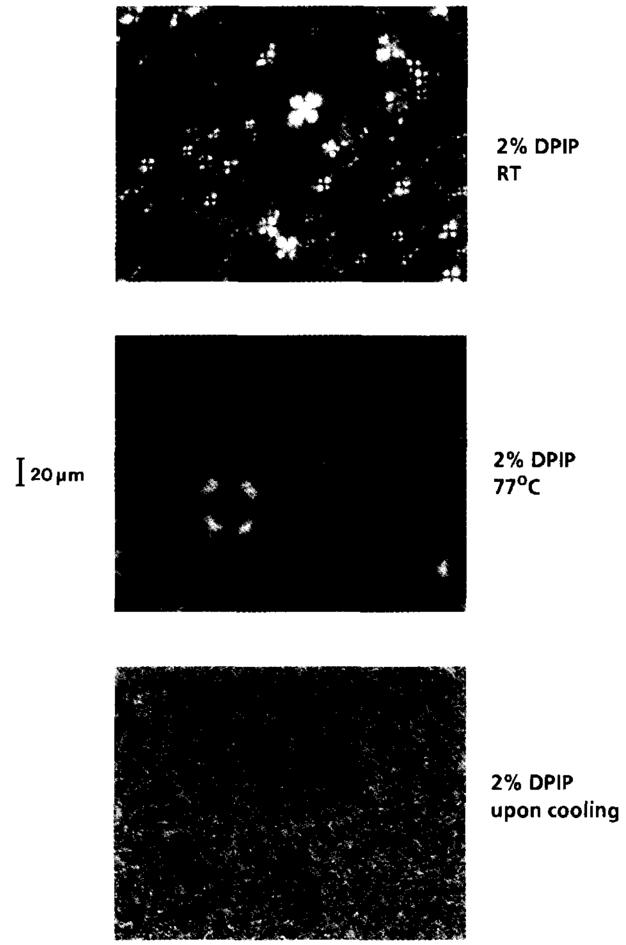


Figure 17 Optical micrographs of the film with 2% DPIP recorded at different temperatures

polymer system. This behaviour, as well as the increase in the crystallization of the polymer in the case of DPTP as compared with that of DPIP, can be rationalized on the basis of their molecular conformations.

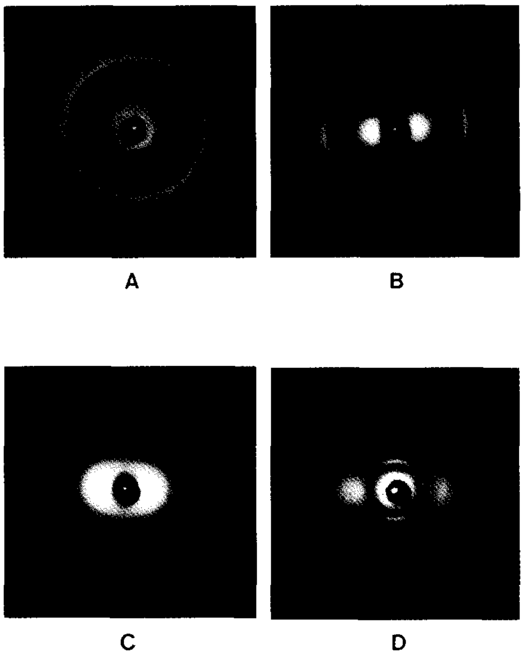


Figure 18 X-ray diffraction patterns of disks sheared for 60 min at 130°C of: (A) the neat polymer in through view; (B) composite with 5% DPIP in through view; (C) edge view; (D) increased sample–film distance in through view respectively

Figure 16 shows the minimum energy conformations of the polymer and plasticizer molecules used here. The conformation of DPIP is twisted and thus can disrupt the ordering of the chains. However, the shape of the DPTP molecule is 'rod-like'. Apart from the methyl substitutions on the backbone phenyl groups, the mesogenic segment of the TLC polymers used here has the same chemical structure as that of DPTP. Hence, the latter can promote or even intercalate with the ordering of the polymer. Thus, the molecular shape of plasticizers could have a profound influence on the morphological and mechanical behaviour of polymers.

Both with the solvent cast neat polymer and with polymers with the DPIP or DPTP plasticizer, the maximum in ΔH occurs at a lower temperature than the temperature of 130°C observed[3] in the case of the neat polymer prepared from the melt. This is perhaps due to the incipient crystallization which occurs in the solvent cast films and the resulting presence of spherulites in the starting sample. We have not investigated in detail the morphological origin of the minimum in ΔH observed at 80°C both with the solvent cast neat polymer film and with the plasticizers, but for the fact that the smaller spherulites melt in this temperature range.

The d.s.c. results given in *Tables 1* and *2* indicate relatively low enthalpies for all these melting transitions. These are similar to those of the previous studies with TLCPs and several explanations have been given. Blundell[22] attributed this phenomenon to imperfections within the crystal lattice due to the non-regular nature of the copolymers causing a poor cohesion of the chains. This leads to weaker intermolecular interactions within the crystalline state, compared to conventional flexible polymers, and to the persistence of these intermolecular interactions even in the isotropic state[20–23].

The presence of double peaks has been observed with many polymeric systems[24]. This behaviour, seen in both conventional and liquid crystalline polymers, briefly reviewed by Carpaneto *et al.*[23], has been attributed to the presence of different degrees of crystal perfections, to crystal reorganizations or to different morphological components formed in the two stages of crystallization. In the case of TLCPs, the same phenomenon has been reported by other authors. Marsano *et al.*[21], Nam *et al.*[25] and Lin and Winter[26] attributed this to a melting–recrystallization process of the solid crystal–nematic mesophase–new crystal phase transition, and the development of a more ordered crystalline structure during annealing.

Another interesting feature seen in *Figures 10c* and *11b* is that the T_g is unaffected by the presence of the plasticizers. Alexandru *et al.*[6] have shown that, in the case of flexible polymers, the same plasticizers as those used in this study depress the T_g of polymers such as styrene/methacrylate copolymers. With TLCPs, the T_g, which is usually measured on the second heating scan, does not seem to be visibly affected by the plasticizer concentration. A possible explanation is that since the molecular ordering is not perfect in the low melt TLCPs due to poor packing of the chains, the presence of the plasticizer does very little to affect this order. However, the small molecule crystallites act as particulate fillers and affect their viscoelastic properties.

Optical microscopy and X-ray diffraction analysis of plasticized TLCP. The optical micrographs of the films of the TLCP/DPIP composite shown in *Figure 17* indicate that the population of the visible spherulites (over 4 μm in size) in the film containing 2% and 5% DPIP is smaller than that for the neat polymer (see *Figure 5*). Visual inspection of the films showed two regions. One is transparent and the spherulites in this area have radii of 5–8 μm. The second is opaque with spherulites of an average radius of 0.7 μm, as measured by SALS. Another opaque area showed the existence of impinging spherulites. As the temperature was increased, the small spherulites melted at ~ 75–80°C. Upon heating the sample to 145°C and cooling it to room temperature, a frozen nematic structure was obtained.

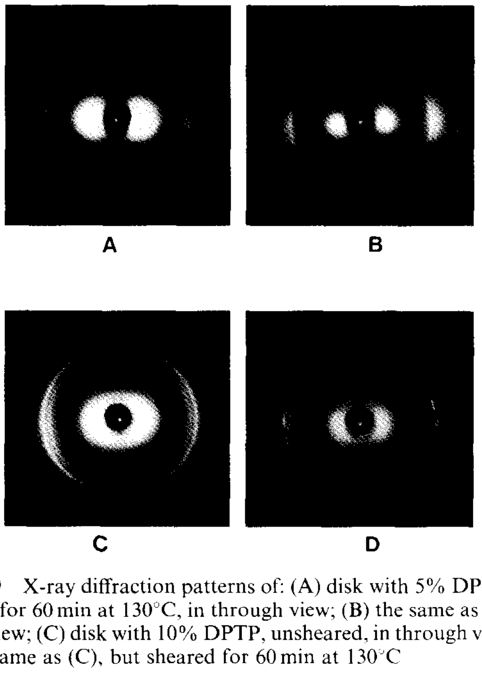


Figure 19 X-ray diffraction patterns of: (A) disk with 5% DPTP after shearing for 60 min at 130°C, in through view; (B) the same as (A), but in edge view; (C) disk with 10% DPTP, unsheared, in through view; and (D) the same as (C), but sheared for 60 min at 130°C

The optical micrographs (not included here) of the solvent cast films of the TLCP/DPTP system also showed the presence of spherulites, with sizes ranging from 5–20 μm. Upon increasing the temperature, the films remained transparent, the spherulites grew up to a factor of 50%, and melted at ~ 75–80°C, when the samples became opaque. D.s.c. results confirm that at this temperature, melting of the solvent induced spherulites occurs. With continued heating, a nematic mesophase, seen as a Schlieren texture was observed at about 145°C, when, according to d.s.c. results, all crystallites have melted, similar to the case of DPIP/polymer.

The X-ray diffraction patterns of the neat solvent cast polymer exhibits two crystalline reflections with spacings of 4.99 and 6.67 Å, as shown in *Figure 18A*. The crystallinity is gradually reduced by the addition of DPIP, consistent with the decrease in ΔH (see *Table 1*). *Figures 18B* and *18C* show the through view and edge view patterns from a sample containing 5% DPIP and sheared at 130°C for 60 min. Significant amorphous scattering is noted. Also of interest is the orientation which has developed due to the shearing. Both through and edge view patterns show orientation, in contrast to the case reported previously[3] for the melt quenched 'dry' polymer, in which only the edge view showed orientation. Thus, the decrease in η^* with an increase in the concentration of DPIP can be attributed to the combined effect of the decrease in the crystallinity and the orientation caused by shearing. The X-ray patterns above do not indicate the presence of any significant crystalline aggregate of the plasticizer.

By increasing the sample–film distance, a highly oriented reflection, with a spacing of 14.92 Å is obtained (*Figure 18D*). The orientation of the 14.92 Å reflection is normal to that exhibited by the 4.99 Å reflection. The latter is characteristic of the distance between the polymer chains in the nematic mesophase. Preliminary conformational analysis of the monomers of the present LCP showed that the length of the mesogen in this case is 15 Å. The presence of the 14.92 Å reflection would then imply that the samples which were sheared develop smectic ordering.

The X-ray diffraction patterns from the DPTP plasticized polymer shows features which differ from those of the DPIP case. Addition of DPTP improves the crystallinity of the polymer. *Figures 19A* and *19B* show the through view and edge view patterns from the sample containing 5% DPTP and sheared at 130°C for 60 min. In comparison to the diffraction pattern from the solvent cast neat polymer (*Figure 18A*), a larger number of reflections are seen. In this case also, both edge and through view patterns show orientation due to shearing. The smectic orientation, similar to that in *Figure 18D*, was also seen in this case. With 10% DPTP, prior to any shearing, the sample shows much improved crystallization, as seen in *Figure 19C*. A number of reflections due to the polymer is seen, along with those due to the excess plasticizer (spotty reflections are due to the latter). In contrast to the previously discussed cases, the sample with 10% DPTP does not show orientation upon shearing. Thus, the increase in viscosity of this sample can be attributed to the enhanced crystallization and the lack of orientation during shearing.

CONCLUSIONS

We have described the effect of a solvent and of two plasticizers on the morphology and rheology of a TLCP with low temperature transitions. In contrast to the melt-pressed starting sample, where no initial crystallinity was detected, the solvent cast films indicate an inherent solvent induced crystallization, as determined by d.s.c., OM, SALS and rheological studies. However, the time sweep study at constant temperature, frequency and strain amplitude indicated that after 60 min of shear, the 'dry' and 'solvent cast' samples reach the same asymptotic values of η^*, G' and G'', indicating a slower crystallization rate in the 'dry' polymer. The two plasticizers used in this study do not affect the T_g of the polymer. The molecular shape however, can affect the morphology and rheology of the composite. The twisted conformation of the DPIP can disrupt the ordering of the chains which results in a decrease in the rate of crystallization of the polymer and a lower viscosity of the sheared material. However, the 'rod-like' shape of the DPTP molecule can intercalate with the ordering in the polymer, resulting in a more ordered crystalline structure. Due to its higher T_m, this plasticizer acts as a reinforcing filler as well, affecting the viscoelastic properties of the composite.

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