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Interactions of a liquid crystalline polymer with polycarbonate and poly(ethylene terephthalate)

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Thermal behaviour of blends of a liquid crystalline copoly(ester amide) (Vectra B950) with two isotropic polymers has been studied by differential scanning calorimetry. One of the isotropic polymers is an amorphous polymer – polycarbonate, the other is a semi-crystalline polymer – poly(ethylene terephthalate). It was found that the glass transition temperature of polycarbonate decreases with increasing Vectra concentration in the blend, suggesting a partial miscibility between the Vectra liquid crystalline polymer (LCP) and polycarbonate. The miscibility is enhanced through heat treatment at elevated temperatures presumably due to a transesterification reaction. Moreover, the presence of the amorphous polycarbonate hinders the crystallization of the liquid crystalline polymer in the blends. It was also observed that heat treatment of the Vectra LCP and poly(ethylene terephthalate) blends causes a loss in crystallinity and shifts in transition temperatures of poly(ethylene terephthalate), indicating that exchange reactions occur between Vectra B950 and poly(ethylene terephthalate). Based on these results, a new strategy, *in situ* compatibilization, is proposed to improve the interfacial adhesion between an LCP and an isotropic polymer.

1. Introduction

Blends of liquid crystalline polymers (LCPs) with flexible isotropic polymers offer the potential of improved melt processability and enhanced mechanical properties. In addition, under appropriate processing conditions, a composite structure can be generated from these blends in a single step, as opposed to the multiple step processes needed in the fabrication of conventional composites. We have been interested in developing high-performance materials from these blends. The processing, structure and mechanical properties of the blends based on thermotropic liquid crystalline polymers (Vectra LCPs) and two isotropic polymers: polycarbonate and polystyrene [1–6] were studied. Although the addition of a small amount of the LCPs into the isotropic polymers has produced a significant reinforcement effect, further improvement in mechanical properties has been hampered by the generally poor interfacial adhesion between the LCPs and the isotropic polymers. The purpose of this work was to investigate the interactions and possible chemical reactions in binary blends of a Vectra LCP (Vectra B950) with two isotropic polymers: polycarbonate and poly(ethylene terephthalate) (PET). The goal of this investigation was to establish a strategy to improve the interfacial adhesion between the LCPs and the isotropic polymers through processing.

The miscibility of LCPs and isotropic polymers has been a subject of controversy. Literature reports on the miscibility of an LCP and an isotropic polymer range from total immiscibility to complete miscibility. Many of the previous studies have found that LCPs are immiscible with polyolefin-type flexible isotropic polymers (polypropylene [7], polystyrene [8] and polysulphone [9]). However, LCPs with a two-phase structure, namely copolyesters of *p*-hydroxybenzoic acid (PHB) with poly(ethylene terephthalate) (PET), have been found to be partially miscible with a number of condensation polymers, including poly(ethylene terephthalate) [10, 11], poly(butylene terephthalate) [12], polyarylate [13], and polycarbonate [14, 15]. The liquid crystalline PHB/PET copolyesters themselves exhibit two amorphous phases: a PET-rich "flexible" phase and a PHB-rich "rigid" phase. Generally, the PET-rich phase of the liquid crystalline copolyesters is miscible with the isotropic polymers, while the PHB-rich phase is not miscible with the isotropic polymers. The partial miscibility has also been observed in blends of Vectra LCPs with poly(ether imide) [16, 17].

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Occasionally, LCPs were found miscible with isotropic polymers, such as polyesters [18–20], polycarbonate [21], and poly(ether imide) [22]. The miscibility was most often observed in blends prepared by solution casting. However, the blends thus prepared were usually metastable. They all underwent a phase separation process through spinodal decomposition when the chain mobility was enhanced by raising the temperature [18, 21, 22]. Finally, the miscibility of an LCP and an isotropic polymer can be enhanced through the compatibilization effect of copolymers resulting from the exchange reaction between the two polymers. This effect has been observed in blends of PHB/PET with poly(ethylene terephthalate) [23], poly(butylene terephthalate) [24], poly-hexemethylene terephthalate) [25], and polycarbonate [11], as well as in blends of aromatic liquid crystalline copolyesters (Vectra-A) with poly(ethylene terephthalate) [26, 27].

The presence of an LCP in a crystallizable isotropic polymer matrix can have a significant effect on the crystallization behaviour of the isotropic polymer. It has been observed that addition of an LCP to a crystallizable isotropic polymer accelerates the crystallization of the isotropic polymer [28–30], due to the nucleation effect of the LCP. However, the degree of crystallinity of the isotropic polymer can be increased [27] or decreased [29] with the addition of the LCP.

The objective of this work was to study the interactions and possible chemical reactions of a thermotropic liquid crystalline copoly(ester-amide) (Vectra B950) with two isotropic polymers, namely, amphous polycarbonate and semi-crystalline poly(ethylene terephthalate). We were also interested to investigate the effects of normally amorphous polycarbonate on the crystallization of the Vectra LCP, and the effects of thermal treatment on the interactions between the two components in the blends. To this end, we used differential scanning calorimetry to determine the thermal behaviour of the blends. We have found that Vectra B950 and polycarbonate are partially miscible. The miscibility is enhanced through heat treatment at elevated temperatures, presumably due to exchange reactions. Furthermore, the presence of amorphous polycarbonate in the Vectra/polycarbonate blends impairs the crystallization of the LCP. We have also found that heat treatment of the Vectra LCP and poly(ethylene terephthalate) blends causes a depression in melting temperature and an increase in the glass transition temperature of poly(ethylene terephthalate), indicating that exchange reactions also occur between Vectra B950 and poly(ethylene terephthalate). Based on these results, we propose a new strategy, *in situ* compatibilization, to improve the interfacial adhesion between an LCP and an isotropic polymer.

2. Experimental procedure

2.1. Materials

The LCP used in this research was Vectra B950 (Hoechst Celanese). It is a random liquid crystalline copoly(ester amide) of three components: 60 mol % 2,6-hydroxynaphthoic acid, 20 mol % terephthalic acid and 20 mol % *para*-aminophenol. The isotropic polymers were a bisphenol-A polycarbonate (PC) (Lexan 151) and a bottle-grade poly(ethylene terephthalate) (PET). Lexan 151 is a phenol-terminated polycarbonate. The PC and PET were kindly provided by GE Plastics and Goodyear Company, respectively. To reduce thermal degradation, the materials were dried at 120 °C for at least 24 h before melt mixing.

2.2. Processing

Blends of the LCP and the isotropic polymers were prepared by melt mixing with a ZSK-30 twin-screw extruder (Werner and Pfleiderer). The extruder barrel temperature zones were set at (from up-stream to down-stream): 150, 260, 280, 280 and 280 °C for the Vectra/polycarbonate blends and 145, 260, 270, 280 and 270 °C for the Vectra/PET blends.

2.3. DSC

Differential scanning calorimetry measurements were conducted on a Perkin–Elmer thermal analysis system (DSC-7) under a nitrogen atmosphere. Sample weights ranged from 10–20 mg. . Unless specified, the scanning rate was 20 °C min^{-1}. The temperature was calibrated with an indium standard. The midpoint of a glass transition was taken as the glass transition temperature, and the peak temperature as the crystal–nematic transition temperature or melting temperature. In cases of Vectra/polycarbonate blend samples, the heat of fusion of the LCP was obtained by normalizing the measured value over the LCP fraction in the blend.

Three sets of thermal experiments were performed on the Vectra/polycarbonate blends: isothermal crystallization at 280 °C, non-isothermal crystallization from 300 °C, and annealing at 260 and 280 °C. For a 50/50 Vectra/PET blend, annealing was carried out at different temperatures for various periods of time.

3. Results and discussion

3.1. Miscibility between Vectra LCP and polycarbonate

Fig. 1 shows the DSC traces of the virgin samples of the three polymers used in this study. We see that both the Vectra LCP and PET are semi-crystalline polymers. They display a melting transition and a glass transition in the DSC heating runs. PET also exhibits cold crystallization during heating. Polycarbonate is an amorphous polymer. It only shows, a glass transition during the heating run. Thermal properties of the three polymers used in the study are summarized in Table I. We notice that the change of heat capacity at the glass transition of the LCP is very small compared with the two isotropic polymers. This is because the structure of the LCP glass is a "frozen nematic" glass. It is structurally similar to the nematic mesophase.

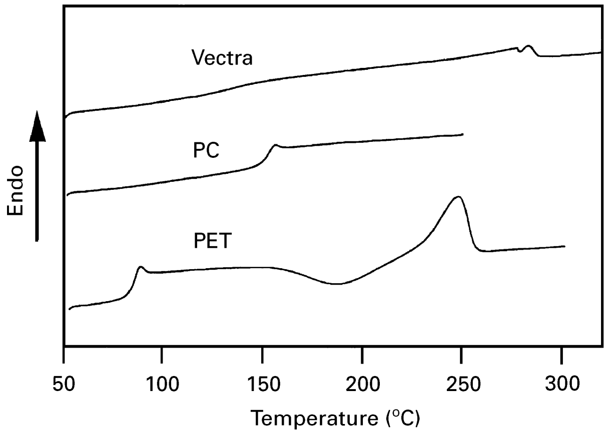

Figure 1 DSC traces of the three polymers used in this study: Vectra B950, polycarbonate, and poly(ethylene terephthalate). The polymers were heated to high temperatures to erase previous thermal history prior to the DSC runs.

TABLE I Thermal properties of the three polymers used in this study

Polymer	T_g(°C)	ΔC_p (J g^{-1}°C^{-1})	T_c(°C)	ΔH_c (J g^{-1})	T_m(°C)	ΔH_m (J g^{-1})
Vectra B950	140	0.08			285	4.0
PC	149	0.25				
PET	81	0.31	186	6.4	247	12.9

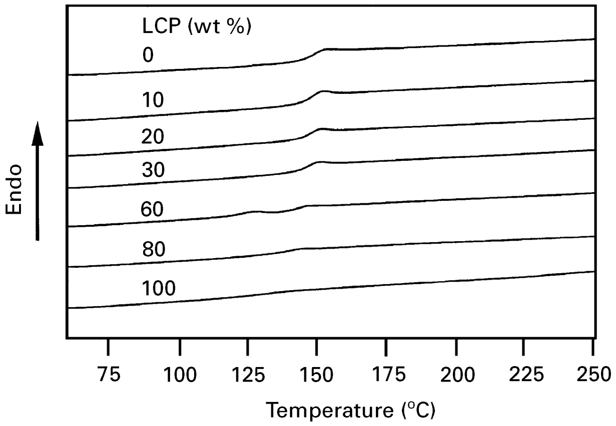

Figure 2 DSC traces of blends of Vectra B950 LCP with polycarbonate.

Blending of the Vectra LCP with the amorphous polycarbonate causes a progressive decrease in the glass transition temperature, T_g, of polycarbonate, while the melting temperature of the LCP remains practically unchanged. DSC traces of the Vectra/polycarbonate blends are shown in Fig. 2. We see that the blends show two distinct thermal transitions: a single glass transition at around 150 °C and a melting transition at about 285 °C. Apparently the glass transition is that of polycarbonate, and the melting transition is that of the Vectra LCP. The glass transition of the LCP is not detectable in the blends probably because of the small change in heat capacity, ΔC_p, at its glass transition. The transition temperatures as functions of the LCP concentration are plotted in Figs 3 and 4, respectively. The invariance of the melting temperature of the LCP with the LCP concentration clearly indicates that the crystalline part of the Vectra LCP is immiscible with the amorphous polycarbonate. The decrease in the glass transition temperature of polycarbonate can be interpreted in three ways: (1) the amorphous polycarbonate is miscible with the amorphous part of the Vectra LCP; (2) the decrease in the T_g of polycarbonate is caused by the plasticization effect of the low molecular weight fraction of the LCP; (3) the decrease in the T_g of polycarbonate is purely a surface effect. Addition of the Vectra LCP into polycarbonate increases the surface area (per unit volume) for polycarbonate. Because polycarbonate molecules at the interface regions have higher mobility than those in the bulk due to less constraint, the increased surface area should lead to a decrease in the T_g of polycarbonate.

We are inclined to the first interpretation of the DSC results, i.e. the amorphous polycarbonate is miscible with the amorphous part of the LCP. Although statistical thermodynamic analysis concludes

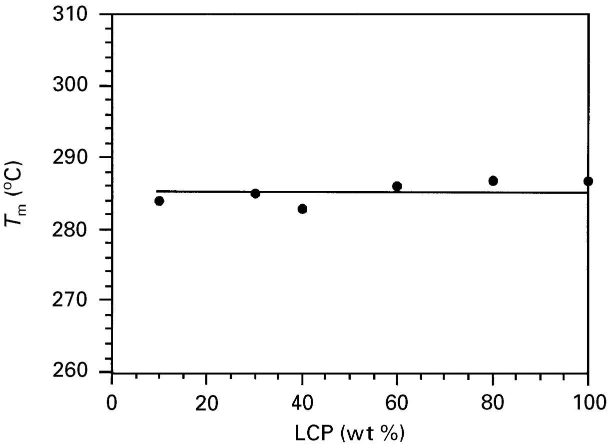

Figure 3 Melting temperature of Vectra B950 LCP as a function of the LCP concentration in the Vectra/polycarbonate blends.

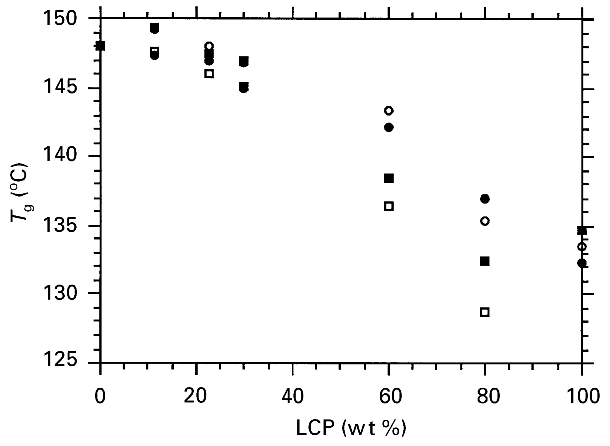

Figure 4 Glass transition temperature of polycarbonate as a function of the LCP concentration in the Vectra/polycarbonate blends. (●) untreated samples; (○) heat treated in the solid state at 260 °C for 60 min; (■) heat treated in the solid state at 280 °C for 60 min; (□) heat treated in the melt at 280 °C for 60 min.

that blends of perfectly rigid rod LCPs are immiscible with flexible coil polymers [31], more recent theoretical analyses show that reducing chain rigidity and/or increasing the molecular weight of LCPs favour the miscibility between LCPs and flexible isotropic polymers [32, 33]. Owing to the incorporation of naphthalene units into its backbone, Vectra B950 LCP is not a perfectly rigid rod polymer. This reduced rigidity opens up possibilities for it to be miscible with isotropic polymers. Furthermore, the possibility for miscibility is enhanced by the compatibilization effect of the copolymers formed through exchange reactions (transesterification and transamidation) between polycarbonate and Vectra B950, which is a liquid crystalline copoly(ester amide). This enhanced miscibility is manifested in the additional decrease in the T_g of polycarbonate after the blends have been heat treated in the melt state at 280 °C for 60 min (isothermal crystallization) (Fig. 4). The crystallinity of the LCP is also reduced or destroyed by the heat treatment at this elevated temperature. The Vectra/ polycarbonate blends do not show any detectable melting exotherm after the heat treatment except those with higher LCP contents (60 and 80 wt % LCP) (Fig. 5). Even in samples where crystallinity is present, the degree of crystallinity is lower than that before the heat treatment. For example, the heat of fusion of the LCP for the heat-treated blend with 60 wt % LCP is 0.54 J g^{-1}, whereas that of the non-isothermally crystallized sample is 2.77 J g^{-1}. The much reduced crystallinity lends further support to the conclusion about the exchange reactions.

In fact, it has been well-documented that exchange reactions, mostly transesterification, can occur in many condensation polymer blends processed in the melt state (for a recent review, see [34]). Polycarbonate has been known to undergo transesterification with many polyesters, such as poly(ethylene terephtha late), poly(butylene terephthalate), poly(ε-caprolactone), and polyarylate [34]. The exchange reactions first produce copolymers with blocky chain structures and then proceed to more random chain structures [35].

In the present case, the incorporation of polycarbonate segments into the LCP backbone makes the crystallization of the LCP more difficult. The Vectra LCPs are known to crystallize to form non-periodic layer crystallites through a sequence matching mechanism. Chain segments with the same sequence structure aggregate together in the melt to form the crystallites [36, 37]. The introduction of polycarbonate segments into the LCP backbone reduces (or eliminates) the probability of finding LCP segments with the same sequence structure, thus lowering the crystallinity.

3.2. Crystallization of the Vectra LCP in the presence of the amorphous polycarbonate

It has been widely reported that an LCP can accelerate the crystallization process of a crystallizable isotropic polymer by functioning as a nucleating agent [28–30]. Here we are interested in the opposite effect, namely, how an amorphous polymer affects the crystallization of an LCP. We again use the Vectra/ polycarbonate blend as a model system to investigate this effect.

Because polycarbonate is very difficult to crystallize from its melt, it was expected that polycarbonate would retard the crystallization of the Vectra LCP due to the partial miscibility of polycarbonate with the LCP. To test this hypothesis, isothermal and non-isothermal crystallization experiments of the LCP in the presence of polycarbonate were carried out. These results are then compared with the crystallization of the LCP in its neat form, and conclusions about the effects of polycarbonate are drawn.

Non-isothermal crystallization of the blends was carried out by cooling the blends in the melt state from 300 °C to 40 °C at a cooling rate of 20 °C min^{-1}. Results of the crystallization temperature and heat of crystallization of the LCP in the blends are presented in Figs 6 and 7. It is seen that the crystallization temperature is virtually unaltered by the variation of the LCP concentration, while the heat of

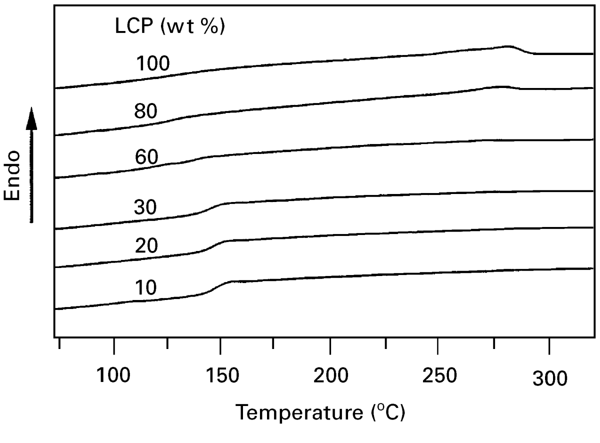

Figure 5 DSC traces of the Vectra/polycarbonate blends after isothermal crystallization at 280 °C for 60 min. The samples were heated to 300 °C and held for 2 min to erase previous thermal history. They were then cooled to 280 °C at 50 °C min^{-1}.

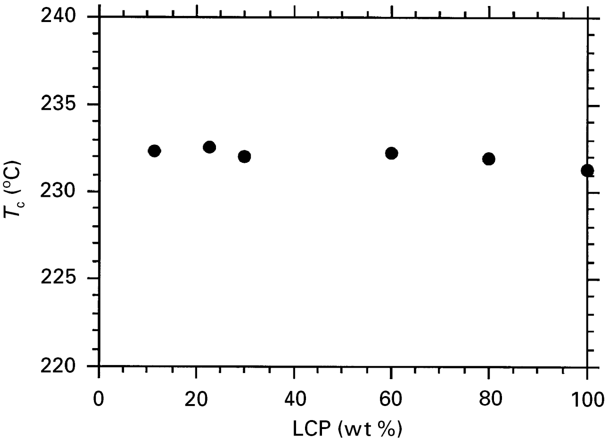

Figure 6 Crystallization temperature of Vectra B950 LCP during non-isothermal crystallization. The blend melts were cooled from 300 °C to 40 °C at a cooling rate of 20 °C min^{-1}.

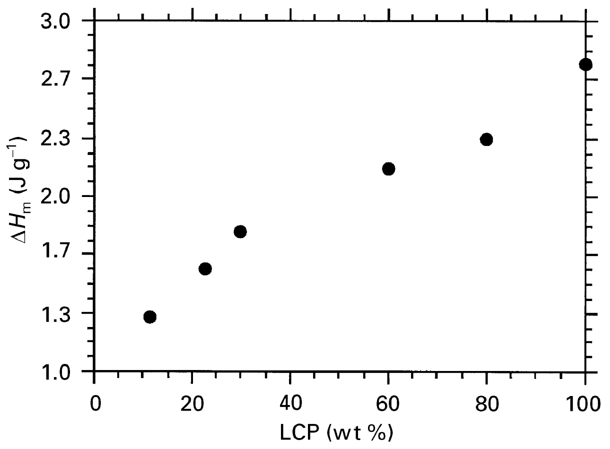

Figure 7 Heat of crystallization of Vectra B950 LCP during the non-isothermal crystallization. The blend melts were cooled from 300 °C to 40 °C at a cooling rate of 20 °C min^{-1}.

crystallization, ΔH_c, of the LCP (normalized over LCP fraction in the blends) increases monotonically with the LCP content. For example, ΔH_c is 1.3 J g^{-1} for the LCP in the blend with 11.5 wt % LCP. The ΔH_c value is more than doubled (2.7 J g^{-1}) for the neat LCP under the same crystallization conditions. Owing to the supercooling effect, the crystallization temperature (232 °C) of LCP is about 50 °C lower than its melting temperature (285 °C). The constancy of the crystallization temperature indicates that the nature of the LCP crystallites that are formed is not changed by the presence of polycarbonate; however, the amount of the LCP which crystallizes during cooling is affected by the presence of polycarbonate. The steady increase in the heat of crystallization with the LCP concentration suggests that the effect of polycarbonate on the crystallization of the LCP occurs in the interfacial regions. The less the amount of LCP in contact with the polycarbonate, the greater is the amount of its crystallinity.

This finding is in agreement with our previous conclusion, based on T_g depression, about the partial miscibility of the Vectra LCP and polycarbonate. Because the amorphous part of the LCP is miscible with polycarbonate, it is conceivable that as the contact area between the LCP and polycarbonate is decreased due to the increased LCP concentration, the amount of the amorphous LCP that can dissolve into polycarbonate decreases. Therefore, the amount of the LCP available for crystallization, and hence the LCP crystallinity increases.

Isothermal crystallization at a temperature (280 °C) close to the melting temperature of the LCP causes exchange reaction(s) between Vectra B950 LCP and polycarbonate. The exchange reactions disrupt the crystallinity of the LCP, making the crystallization of the LCP more difficult, even impossible. These results have been discussed in the previous section.

3.3. Annealing of the Vectra LCP/PC blends

To investigate further the effect of polycarbonate on the crystallization of Vectra B950 LCP, annealing experiments were conducted. Two annealing temperatures were used: one at 260 °C, and the other at 280 °C. Annealing at these two temperatures is expected to give rise to different annealing behaviours because 260 °C is well below the melting temperature and 280 °C is close to it. In the annealing experiments, the samples were heated to about 15 °C above the melting temperature (300 °C), and held for 2 min to erase the previous thermal history. The samples were then cooled down to 40 °C and then heated again to the annealing temperature, and kept at that temperature for 60 min. DSC heating traces of the samples annealed at 260 °C are displayed in Fig. 8, and the results of the annealing experiments are shown in Figs 9 and 10. It is seen in Fig. 8 that annealing at 260 °C for 60 min enhances the LCP melting transition peak. The annealing reduces the melting temperature range and shifts the melting transition to higher temperatures. The heat of fusion of the LCP initially increases with the LCP content, then levels off (Fig. 9). The increment in the heat of fusion agrees with the non-isothermal crystallization results. These results again indicate a suppression of the crystallization of the LCP by polycarbonate owing to the partial miscibility of the two polymers.

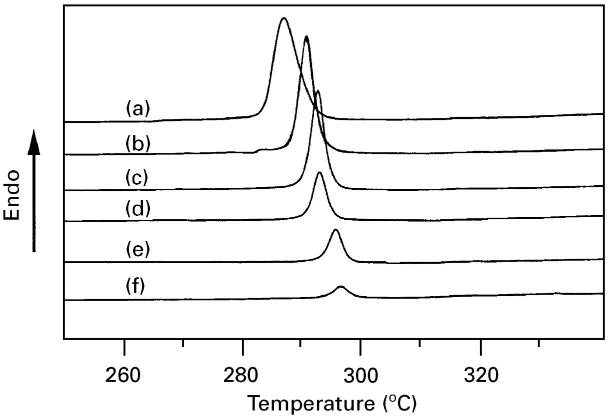

Figure 8 DSC traces of the Vectra/polycarbonate blends after annealed at 260 °C for 60 min. LCP concentration: (a) 100 vol %, (b) 77.4 vol %, (c) 57.3 vol %, (d) 26.9 vol %, (e) 20 vol %, (f) 10 vol %.

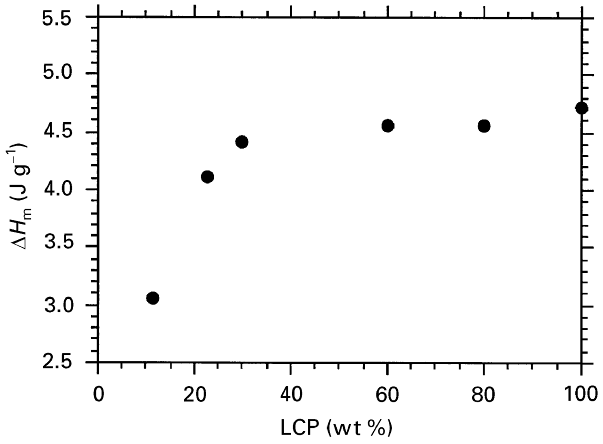

Figure 9 Heat of fusion of Vectra B950 LCP after the Vectra/polycarbonate blends have been annealed at 260 °C for 60 min.

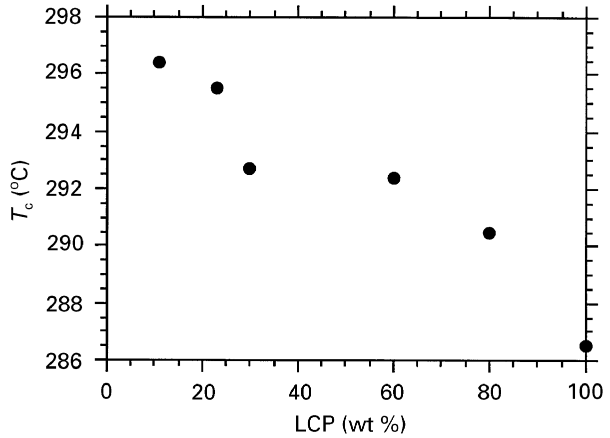

Figure 10 Melting temperature of Vectra B950 LCP after the Vectra/polycarbonate blends have been annealed at 260 °C for 60 min.

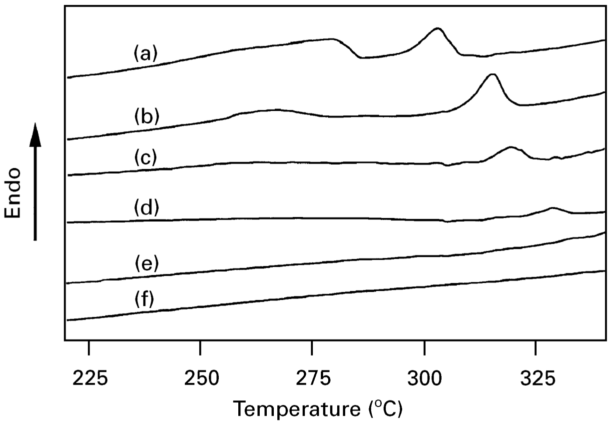

Figure 11 DSC traces of the Vectra/polycarbonate blends after annealed at 280 °C for 60 min. LCP concentration: (a) 100 vol %, (b) 77.4 vol %, (c) 57.3 vol %, (d) 26.9 vol %, (e) 20 vol %, (f) 10 vol %.

Surprisingly, the melting temperature of the LCP decreases with increasing LCP content in the annealed Vectra/polycarbonate blends (Fig. 10). In contrast, the melting temperature of the LCP in the as-prepared samples does not change appreciably with LCP concentration [4]. In general, the melting temperature of a crystalline polymer is mainly determined by its crystallite size and perfection, in addition to the chemical structure of the polymer. In view of the sequence matching crystallization mechanism, annealing of the blends most likely causes perfection of the LCP crystallites by reducing defect density. This results in a sharpening of the melting peak and enhancement of the heat of fusion. An increase in the crystallite size would be impossible because this process would require the translational motion of an entire LCP chain. This is highly unlikely at a temperature some 25 °C below the melting temperature. Therefore, it is still unclear why the melting temperature of the Vectra LCP decreases with the LCP concentration after annealing.

Annealing of the LCP at 280 °C leads to an additional melting peak at around 300 °C. This higher melting crystallite has also been observed in the annealing of a Vectra liquid crystalline copolyester (Vectra A900) [38]. However, its origin is still unclear. Annealing of the Vectra/polycarbonate blends at 280 °C gives similar results to the isothermal crystallization at this temperature. Blends with higher LCP contents show both the low and high LCP melting peaks. However, blends with low LCP contents do not exhibit any detectable melting peak in the subsequent DSC heating runs (Fig. 11). This result again suggests that exchange reactions have occurred, thus destroying the crystallinity of the LCP in the blends. It appears that the exchange reactions are promoted by the partial melting of the Vectra LCP at 280 °C.

3.4. Annealing of a Vectra LCP/PET blend at low temperatures

Heat treatment of a 50/50 (wt) Vectra/PET blend was conducted in three temperature regimes: temperatures below the melting temperature of PET (regime I), temperatures between the melting temperatures of PET and the Vectra LCP (regime II), and temperatures above the melting temperature of the Vectra LCP (regime III). The two components exist in different states in these three regimes. In regime I, both polymers are in the solid state. In regime II, PET melts, while the LCP remains in the solid state. In regime III, both polymers are in the liquid state, although the LCP is in its anisotropic state, while PET is in the isotropic liquid state. We have found that heat treatment in these three different regimes leads to distinctly different thermal behaviour of the resulting samples.

Annealing the Vectra/PET blend in the temperature regime I gives rise to a new endothermic peak in the subsequent DSC heating runs. Moreover, the annealing eliminates the cool crystallization peak of PET which appears in the DSC heating runs of the virgin PET sample. Typical DSC heating traces of the annealed samples are shown in Fig. 12. Three endothermic peaks can be identified in these DSC traces. The highest temperature peak occurs at 288 °C, which is close to the T_m of the neat LCP. Obviously, this is the melting peak of the LCP. The peak temperature and the heat of fusion do not change appreciably with the annealing temperature, indicating that annealing

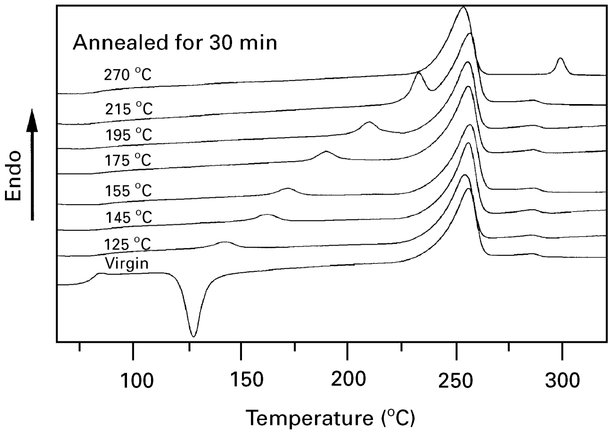

Figure 12 DSC traces of the 50/50 Vectra/PET blend after annealing at different temperatures for 30 min.

in regime I does not affect the crystallite structure and crystallinity of the Vectra LCP.

The two low-temperature endothermic peaks are apparently due to the melting of the crystalline PET. The higher temperature peak ($T_m = 250\,^\circ\mathrm{C}$) does not change with the annealing temperature in terms of the peak position and the heat of fusion. The peak temperature of the other peak, however, increases linearly with the annealing temperature (Fig. 13). Its temperature is always located 15 °C above the annealing temperature. The heat of fusion of this low-temperature peak also increases at higher annealing temperatures (Fig. 14). This double-peak melting phenomenon has been widely reported for PET [39, 40] and a number of other polymers [41–44]. Two mechanisms have been proposed to explain this phenomenon. One is the melting and recrystallization mechanism. The other is the two crystallite population mechanism. The former mechanism postulates that the low-temperature endotherm peak is the melting of the crystallite formed in the previous thermal history. The melted polymer then undergoes a recrystallization process and re-melts at the higher temperature [39, 41]. The latter mechanism attributes the double melting peaks to two distinctly different crystallite populations in the polymer: one with a large crystallite size (or lamellar thickness), the other with a smaller crystallite size. The smaller crystallites melt at the lower temperature, while the larger ones melt at the higher temperature [45].

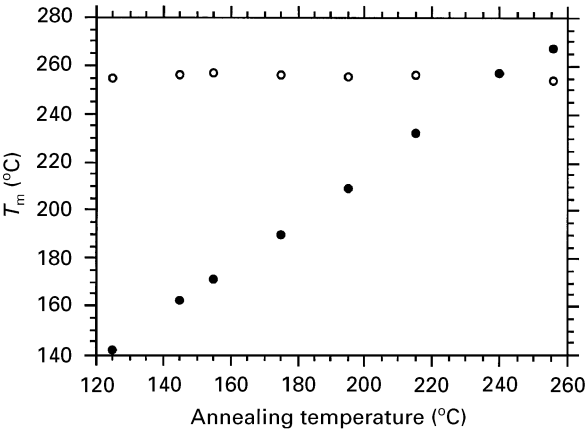

Figure 13 Variation of the melting temperatures of PET with annealing temperature in regime I for the 50/50 Vectra/PET blend. The samples were annealed for 30 min.

We are more inclined to the double crystallite population mechanism because we have not detected any recrystallization exothermic peaks in between the two PET melting peaks for the annealed samples. Moreover, from a thermodynamic point of view, it is difficult to imagine that a crystal which melts at a lower temperature will re-crystallize at a higher temperature. It is clear that annealing the samples at the intermediate temperatures between the T_g and T_m of the PET mobilizes the amorphous PET to crystallize into the smaller crystallites. The melting of these smaller crystallites gives rise to the lower temperature endotherm. The higher endotherm apparently results from the melting of the pre-existing larger PET crystallites. Therefore, its peak position is unaffected by the annealing process. In fact, recent X-ray scattering and transmission electron microscopy studies of the crystallization process of semi-crystalline polymers have provided strong evidence to support the two distinct crystallite population mechanism [46, 47]. The most convincing experimental evidence has been obtained from TEM studies of thin PEEK films. It was observed that there is only one crystal population for the sample with one melting peak, while there are two crystal populations with widely differing lamellar thicknesses for samples with two melting peaks. Furthermore, on heating the samples with two melting peaks to any temperature between the two melting peak temperatures, the thinner crystals melt. However, the thicker crystals are unaffected.

Increasing annealing time in regime I causes a steady increase in the melting temperature and the heat of fusion of the lower temperature peak of PET (Figs 15 and 16). Again the high melting peak of PET and the melting peak of the LCP are unaffected. Annealing the 50/50 Vectra/PET blend at a temperature between the two melting temperatures of the PET and the Vectra LCP gives a sharper and more prominent

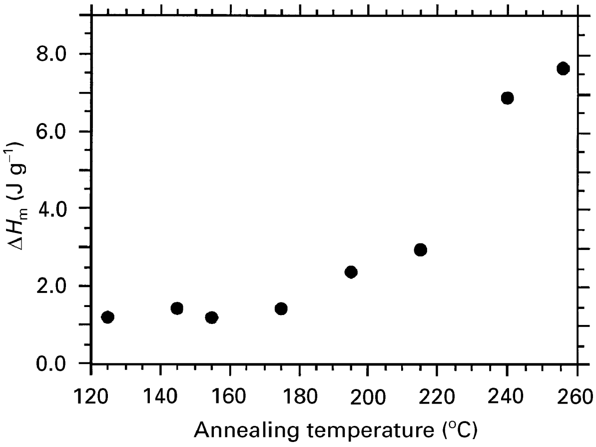

Figure 14 Variation of the heat of fusion of the low-temperature melting peak of PET with annealing temperature in regime I for the 50/50 Vectra/PET blend.

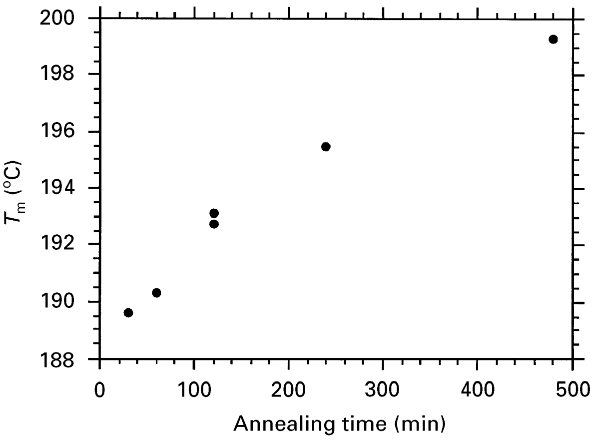

Figure 15 Variation of the low melting temperature of PET with annealing time at 175 °C for the 50/50 Vectra/PET blend.

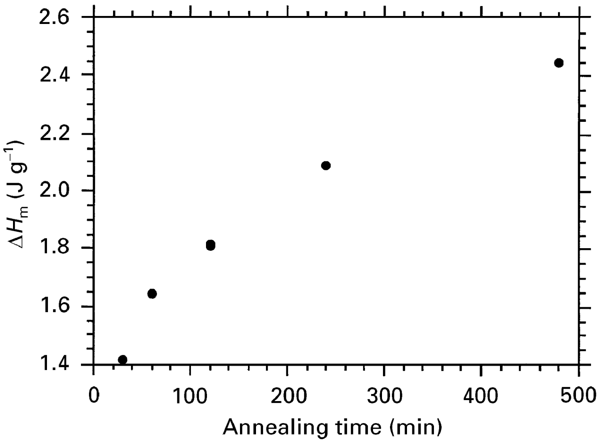

Figure 16 Variation of the heat of fusion of PET with annealing time at 175 °C for the 50/50 Vectra/PET blend.

LCP melting endotherm (Fig. 12) near 300 °C. However, this annealing does not change the melting behaviour of the PET appreciably as compared with the untreated PET sample. The formation of the high melting crystallite of the LCP with annealing at temperatures close to the T_m of the LCP is similar to what has been observed in the Vectra/polycarbonate blends. However, it seems that, in the Vectra/PET blend, the annealing does not allow exchange reactions to take place, because the crystallinity of the LCP is still highly visible in the subsequent DSC runs.

3.5. Exchange reactions between the Vectra LCP and PET

Heat treatment at temperatures above the melting temperature of the Vectra LCP (regime III) causes exchange reactions between the Vectra LCP and PET. The exchange reactions have tremendous effects on the thermal behaviour of both the LCP and PET. DSC traces of the 50/50 Vectra/PET blend heat treated at 300 °C for various periods of time are shown in Fig. 17. Major results of the heat treatment of the Vectra/PET blend are summarized as follows.

1. The melting transition of the LCP becomes less prominent after the heat treatment at 300 °C for 15 min, and eventually vanishes for 30 min. The melting temperature of the LCP also decreases with the heat treatment (Fig. 17). These results suggest that the LCP crystallites have been completely destroyed after 30 min heat treatment at 300 °C due to the exchange reactions. As in the Vectra/polycarbonate blends, it appears that the exchange reactions between the Vectra LCP and PET produce copolymers which significantly reduce (and eventually eliminate) the possibility of the sequence matching process for the crystallization of the LCP.

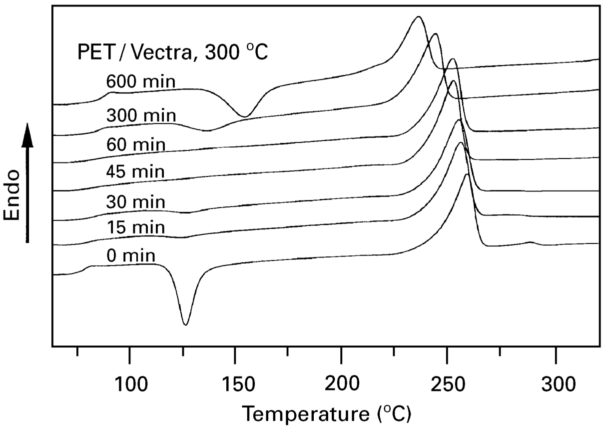

Figure 17 DSC traces of the 50/50 Vectra/PET blend heat treated at 300 °C for various periods of time as indicated.

2. The melting temperature of PET drops steadily with the heat-treatment time (Fig. 18). Similar results have been reported for the blends of Vectra A900 and PET, and were attributed to exchange reactions [26, 27]. The heat of fusion of PET increases initially with time, then falls as the heat treatment proceeds. The maximum value is located at 45 min of the heat treatment (Fig. 19).

3. The glass transition temperature of PET increases sharply within the first 45 min of heat treatment, then increases more gradually (Fig. 20). This trend has been observed in the heat treatment of other binary polymer blends, and was attributed to exchange reactions [48, 49].

The above three observations lead us to conclude tentatively that the changes in thermal properties have

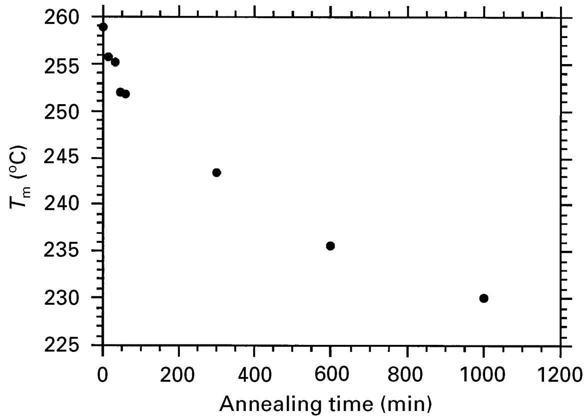

Figure 18 Melting temperature of PET as a function of heat treatment time at 300 °C in the 50/50 Vectra/PET blend.

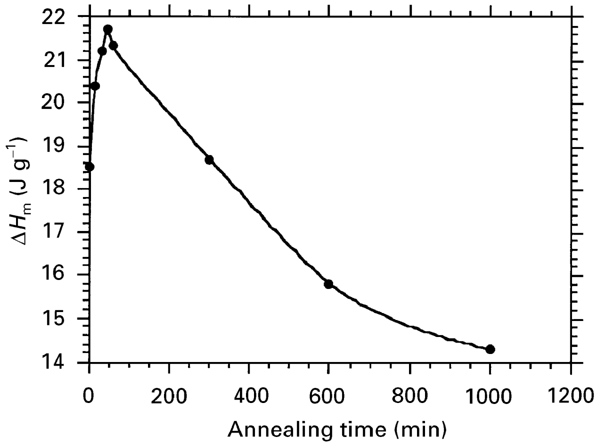

Figure 19 Heat of fusion of PET as a function of heat treatment time at 300 °C in the 50/50 Vectra/PET blend.

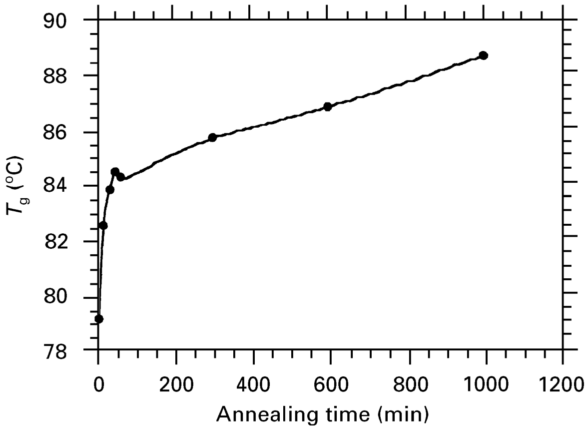

Figure 20 Glass transition temperature of PET as a function of heat treatment time at 300 °C in the 50/50 Vectra/PET blend.

been brought about by the exchange reactions between the Vectra LCP and PET. The exchange reactions randomize the chain sequence structures of both the LCP and PET. This prohibits crystallization of the LCP and suppresses the crystallization of PET. The incorporation of LCP segments into PET chains results in the increase in the glass transition temperature and the drop in the melting temperature of PET.

One may argue that the changes in the thermal properties reported above are not due to the exchange reactions, rather, they are the results of the decomposition of PET at elevated temperatures, because PET is known to be vulnerable to hydrolysis in the presence of moisture. However, the following results, along with parallel experiments on neat PET, in fact, demonstrate that thermal degradation, if any, is not severe.

1. The glass transition temperature of PET increases as heat-treatment time is prolonged. If thermal degradation had been severe, the T_g would have fallen because glass transition temperature decreases with molecular weight.
2. The decomposition temperature of the Vectra/PET blend was determined to be around 400 °C by DSC. This decomposition temperature is 100 °C higher than the heat-treatment temperature.
3. Parallel heat-treatment experiments at 300 °C on neat PET shows little or no deterioration in the glass transition temperature and the melting temperature of PET. The results are summarized in Table II.

As shown in Table II, the glass transition temperature of neat PET is essentially the same as that in the blend, and remains practically constant throughout the heat treatment. Only the sample exposed to 300 °C for as long as 800 min exhibits a slight decrease in the melting temperature (3 °C), presumably due to thermal degradation. Compared with blend samples subjected to the same thermal exposure, it is reasonable to conclude that the increase in the T_g and the additional decrease in the T_m are due to the exchange reactions between PET and Vectra B950 at 300 °C.

TABLE II Thermal properties of neat PET heat treated at 300 °C

Time (min)	T_g(°C)	T_c(°C)	ΔH_c (J g^{-1})	T_m(°C)	ΔH_m (J g^{-1})
0	80.2	133.9	25.0	254.3	38.2
30	82.2	138.0	9.6	255.0	17.6
200	79.3	133.4	4.9	254.8	41.0
800	80.8	140.8	18.0	251.5	40.7

To summarize, the thermal treatment results suggest that it is possible thermally to induce exchange reactions between the liquid crystalline poly(ester-amide) and polycarbonate and PET. This points to a new strategy of improving the interfacial adhesion between the otherwise generally immiscible LCP/isotropic polymer blends through processing, namely *in situ* compatibilization. In *in situ* compatibilization, copolymers of the LCP and the isotropic polymer are generated by the thermally induced exchange reactions during processing. These copolymers then act as compatibilizers for the otherwise immiscible polymer blends [50, 51]. The compatibilization effect is expected to improve the interfacial adhesion, and therefore mechanical properties of the blends. The exchange reactions appear to be slow in the systems studied. These reactions can be accelerated by adding an appropriate catalyst [52].

References

1. B. R. BASSETT and A. F. YEE, *Polym. Compos.* **11** (1990) 10.
2. R. J. AMUNDSEN and A. F. YEE, in "Proceedings of the American Society for Composites", Fifth Technical Conference, E. Lansing, MI, 12–14, June 1990, p. 209.
3. Q. H. LIN and A. F. YEE, *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **33** (1) (1992) 298.
4. Q. H. LIN, J. Y. JHO and A. F. YEE, *Polym. Eng. Sci.* **33** (1993) 789.
5. Q. H. LIN and A. F. YEE, *Polym. Compos.* **15** (1994) 156.
6. *Idem*, *Polymer* **35** (1994) 2646.
7. A. DATTA, H. H. CHEN and D. G. BAIRD, *ibid.* **34** (1993) 759.
8. R. A. WEISS, W. HUH and L. NICOLAIS, *Polym. Eng Sci.* **27** (1987) 684.
9. B. S. HSIAO, R. S. STEIN, N. WEEKS and R. GAUDIANA, *Macromolecules* **24** (1991) 1299.
10. C. U. KO, G. L. WILKES and C. P. WONG, *J. Appl. Polym. Sci.* **37** (1989) 3063.
11. H. FRIEDRICH, M. HESS and R. KOSFELD, *Makromol. Chem. Macromol. Symp.* **16** (1988) 251.
12. M. KIMURA and R. S. PORTER, *J. Polym. Sci. Polym. Phys. Ed.* **22** (1984) 1697.
13. L. -H. WANG and R. S. PORTER, *ibid.* **31** (1993) 1067.
14. K. G. BLIZARD and D. G. BAIRD, *Polym. Eng. Sci.* **27** (1987) 653.
15. M. R. NOBILE, E. AMENDOLA and L. NICOLAIS, *ibid.* **29** (1988) 244.
16. S. S. BAFNA, T. SUN and D. G. BAIRD, *Polymer* **34** (1993) 708.
17. R. E. S. BRETAS and D. G. BAIRD, *ibid.* **33** (1992) 5233.
18. A. NAKAI, T. SHIWAKU, H. DASEGAWA and T. HASHIMOTO, *Macromolecules* **19** (1986) 3008.
19. Y. G. LIN, H. W. LEE, H. H. WINTER, S. DASHEVSKY and K. S. KIM, *Polymer* **34** (1993) 4703.
20. P. VAN ENDE, G. GROENINCKX, H. REYNAERS and C. SAMYN, *ibid.* **33** (1992) 3598.
21. T. KYU and P. ZHUANG, *Polym. Commun.* **29** (1988) 99.
22. J. Q. ZHENG and T. KYU, "Liquid Crystalline Polymers", edited by R. A. Weiss and C. K. Ober, ACS symposium series, 435 (American Chemical Society, Washington, DC, 1990) p. 460.

23. H. G. ZACHMANN, D. CHEN, J. NOWACKI, E. OLBRICH and C. SCHULZE, in "Integration of Fundamental Polymer Science and Technology", Vol. 4, edited by P. J. Lemstra and L. A. Kleintjens (Elsevier Applied Science, New York, 1990) p. 242.
24. M. PACI, C. BARONE and P. L. MAGAGNINI, *J. Polym. Sci. Polym. Phys. Ed.* **25** (1987) 1595.
25. G. V. LAIVINS, *Macromolecules* **22** (1989) 3974.
26. W. N. KIM and M. M. DENN, *J. Rheol.* **36** (1992) 1477.
27. P. TANG, J. A. REIMER and M. M. DENN, *Macromolecules* **26** (1993) 4269.
28. A. M. SUKHADIA, D. DONE and D. G. BAIRD, *Polym. Eng. Sci.* **30** (1990) 519.
29. S. K. SHARMA, A. TENDOLKAR and A. MISRA, *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **157** (1988) 597.
30. L. I. MINKOVA, M. PACI, M. PRACELLA and P. L. MAGAGNINI, *Polym. Eng. Sci.* **32** (1992) 57.
31. P. J. FLORY, *Macromolecules* **11** (1978) 1138.
32. D. A. JONAH, W. BROSTOW and M. HESS, *ibid.* **26** (1993) 76.
33. R. HOLYST and M. SCHICK, *J. Chem. Phys.* **96** (1992) 721.
34. R. S. PORTER and L. -H. WANG, *Polymer* **33** (1992) 2019.
35. J. DEVAUX, P. GODARD, J. P. MERCIER, R.TOUILAUX and J. M. DEREPPE, *J. Polym. Sci. Polym. Phys. Ed.* **20** (1982) 1881.
36. A. H. WINDLE, C. VINEY, G. GOLOMBOK, A. M. DONALD and G. R. MITCHELL, *Farad. Discuss. Chem. Soc.* **79** (1985) 55.
37. S. HANNA and A. H. WINDLE, *Polymer* **29** (1988) 207.
38. Y. G. LIN and H. H. WINTER, *Macromolecules* **21** (1988) 2439.
39. P. J. HARDSWORTH and A. TURNER-JONES, *Polymer* **12** (1971) 195.
40. C. ZHOU and S. B. CLOUGH, *Polym. Eng. Sci.* **28** (1988) 65.
41. L. MANDELKERN and A. L. ALLOU Jr, *J. Polym. Sci. Polym. Lett. Ed.* **4** (1966) 447.
42. M. E. NICHOLS and R. E. ROBERTSON, *J. Polym. Sci. Polym. Phys. Ed.* **30** (1992) 755.
43. D. C. BASSETT. R. H. OLLEY and I. A. M. AL RAHEIL, *Polymer* **29** (1988) 1745.
44. T. H. HOU and R. M. REDDY, *SAMPE Q.* January (1991) 38.
45. S. Z. D. CHENG, M. Y. CAO and B. WUNDERLICH, *Macromolecules* **19** (1986) 1868.
46. B. S. HSIAO, K. H. GARDENER, D. Q. WU, B. LIANG, and B. CHU, *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **33** (1992) 265.
47. M. P. LATTIMER, J. K. HOBBS, M. J. HILL and P. J. BARHAM, *Polymer* **33** (1992) 3971.
48. M. KIMURA and R. S. PORTER, *J. Polym. Sci. Polym. Phys. Ed.* **21** (1983) 367.
49. M. KIMURA, G. SALEE and R. S. PORTER, *J. Appl. Polym. Sci.* **29** (1984) 1629.
50. C. DAI, B. J. DAIR, K. H. DAI, C. K. OBER, E. J. KRAMER, C.-Y. HUI and L. W. JELINSKI, *Phys. Rev. Lett.* **73** (1994) 2472.
51. R. KULASEKERE, H. KAISER, J. F. ANKNER, T. P. RUSSELL, H. R. BROWN, C. J. HAWKER and A. M. MAYES, *Macromolecules* **29** (1996) 5493.
52. Q. H. LIN and A. F. YEE, unpublished results.

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