Miscibility of blends of poly(ε-caprolactone) with aromatic polyesters containing mesogenic biphenyl units

P. Van Ende, G. Groeninckx*, H. Reynaers and C. Samyn†
Laboratory of Macromolecular Structural Chemistry and †Laboratory of Macromolecular and Physical Organic Chemistry, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium
(Received 19 July 1991; revised 8 November 1991; accepted 18 November 1991)

Blends of the aliphatic polyester poly(ε-caprolactone) with two biphenyl-containing polyesters have been investigated. The aromatic polyesters differed in the number of phenyl groups incorporated in the repeating unit; in this way a semi-rigid liquid crystalline and a semicrystalline polyester were obtained. Blends of the aromatic polyesters with poly(ε-caprolactone) were prepared by the dissolution/precipitation method and characterized by optical microscopy, d.s.c., small-angle laser light scattering and X-ray diffraction. A marked difference in crystallization behaviour and crystallinity was observed, although melting and crystallization temperatures were not influenced by changing the composition of the blends. The experimental results indicate the occurrence of miscibility phenomena in the isotropic state of blends of poly(ε-caprolactone) with the most flexible biphenyl-containing polyester.

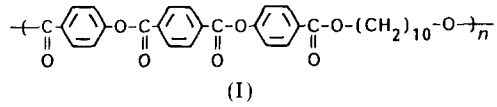
(Keywords: liquid crystalline polyesters; biphenyl mesogens; blend miscibility behaviour; UCST behaviour)

INTRODUCTION

Polymer blends containing liquid crystalline (LC) components have attracted both scientific and industrial interest, especially since the work of Takayanagi and Ogata[1] who used a lyotropic liquid crystalline polymer (LCP) as a reinforcing agent. These blends were found to exhibit unique morphologies strongly depending on the composition of the blend and the processing conditions. The advantage of the use of LCPs is their relatively low viscosity and their ability to reinforce thermoplastic matrices. Amongst the LCPs, poly(ethylene terephthalate)/*p*-hydroxybenzoate [PET/PHB (40/60)] and Vectra (hydroxybenzoic acid/hydroxynapthoic acid, HBA/HNA) are the most widely used in combination with both amorphous and crystallizable matrix polymers.

Some blends of Vectra and PET/PHB with amorphous matrices have been investigated: Vectra with polycarbonate (PC)[2,3], polyamide (PA)[4] and poly(phenylene oxide)/polystyrene (PPO/PS)[5] and PET/PHB with PC[6,7] and poly(ether sulphone) (PES)[8]. All blends were two-phase systems; their viscosity was significantly lower than that of the amorphous matrix polymers and better mechanical properties were realized. In the case where the thermoplastic component was crystallizable, blends with poly(butylene terephthalate) (PBT) and PET were examined[9,10]. A PET/PHB (40/60) copolymer in combination with PBT resulted in a two-phase system for the blend: a PET-rich phase being miscible and a PHB-phase being immiscible with PBT[11].

From the literature results, it became obvious that the combination of rigid-rod liquid crystals with conventional thermoplastic polymers yields two-phase systems, for which interesting morphologies could be obtained concomitant with low viscosities. Only few authors studied blends of semi-rigid LCPs with thermoplastics. Therefore, flexible methylene units were introduced in the polymer backbone of the LC component in order to reduce its rigidity and to obtain better compatibility with the thermoplastic component. The miscibility of a semi-rigid LC polyester (I) with PBT at different compositions was studied by Pracella *et al.*[12]:

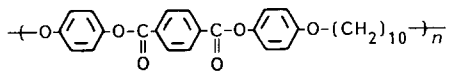


(I)

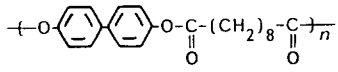
These blends only exhibit one glass transition temperature (T_g) after cooling from the isotropic melt. Also a single crystallization exotherm was found for both components. Shin and Chung[13] studied a flexible LCP (II) in a blend with a crystallizable PET matrix; in this case the crystallization exotherm of PET is shifted towards higher temperatures during cooling because the LCP phase acts as a nucleating agent. The same LCP component was also used in combination with an amorphous PC matrix, resulting in better ultimate mechanical properties[14]. The T_gs of both components, however, were not affected. A semi-rigid LCP (III) in combination with PBT had a major influence on both the transition temperatures and the crystallinity of the PBT phase[10].

* To whom correspondence should be addressed

0032-3861/92/173598-09

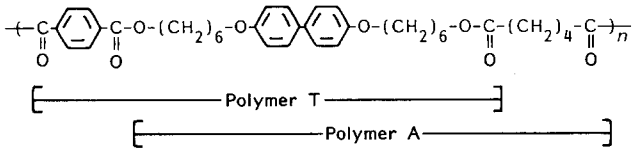


(II)



(III)

It is the aim of this paper to investigate the miscibility behaviour of a semi-rigid LCP (polymer T) and a semicrystalline polymer (polymer A) with a coil-like polymer, poly(ε-caprolactone) (PCL). Through this change in the rigidity of the polymer chain, a variation of the blend miscibility behaviour is expected.



EXPERIMENTAL

Polymer synthesis and characterization

Polymers T and A were prepared by solution polycondensation of a biphenyl-containing diol with the appropriate diacid chloride (terephthaloyl- or adipoyl-chloride)[15]. The synthesis of these polymers is part of an extended study of the relationship between the main chain microstructure and the thermotropic properties, i.e. the type of mesophase and their transition temperatures[16]. The reduced viscosity of these products, determined for 0.2% solutions in *p*-chlorophenol at 45°C, is 0.22 dl g^{-1} for polymer T and 0.21 dl g^{-1} for polymer A.

D.s.c. heating runs performed on both polymers A and T resulted in double melting peaks, with maximum temperatures of 126 and 164°C, respectively. Additional experiments were performed in order to find out if the double melting behaviour was due to a recrystallization process or to the formation of a LC phase. Therefore both polymer samples were cooled from the isotropic melt at a cooling rate of 10°C min^{-1} and heating runs were subsequently recorded for different heating rates. In the case of polymer A, the relative height of the first endotherm as compared to the second one increases as the heating rate increases. At a heating rate of 40°C min^{-1}, the first endotherm even becomes more pronounced than the second one. For polymer T, the size of both peaks becomes equal at a scanning rate of 80°C min^{-1}. At lower heating rates, the effects are significantly smaller. When polymer T is slowly cooled from the melt (-1°C min^{-1}) under the optical microscope, the formation of a LC phase was observed.

Based on the above-mentioned experiments, polymer A was considered to be a semicrystalline polymer without mesophase formation and polymer T a semi-rigid polymer with the possibility of forming a LC phase under slow-cooling conditions.

The PCL used in this study was a commercial Union Carbide product (UC 700) with $\bar{M}_w = 94000$ and $\bar{M}_n = 34000$; it was chosen because of its intrinsic flexibility in contrast with polymers T and A.

Blend preparation and characterization techniques

PCL/polymer T and PCL/polymer A blends were prepared by solution mixing; 5 wt% solutions in *p*-chlorophenol were prepared at 45°C and coprecipitated in methanol, filtered and washed with acetone and refluxed with petroleum ether to remove all phenolic residues. The blends were dried at 45°C under vacuum for 72 h.

The thermal behaviour of the semicrystalline samples was studied by d.s.c. using a Perkin–Elmer DSC 7 (δ-series), at a scanning rate of 5°C min^{-1}. The sample weight was between 5 and 10 mg. Due to baseline curvature, the exact determination of the heat of melting and crystallization was rather difficult and the reported values should only be compared to each other with caution.

The spherulitic growth rate of PCL in the blends was determined using optical microscopy. Powdered blends, pressed between glass slides, were molten in a Mettler FP 82 hot stage at 180°C for 3 min and subsequently quenched to a preset crystallization temperature. An optical microscope coupled with a CCD camera was used to follow the growth rate of the PCL spherulites in real time.

For the small-angle X-ray scattering (SAXS) experiments, samples (~1 mm thick) were prepared by compression moulding of the powdered blends at 180°C. SAXS patterns were recorded photographically using an Anton-Paar-type Kratky camera with a 60 μm entrance slit. The Philips PW 1130 X-ray generator was operated at 45 kV and 30 mA; a Kratky-type Cu target in conjunction with a Ni β filter was used throughout. All SAXS experiments were performed at room temperature and obtained as infinite slit-smeared data. The optical density of the recorded films was obtained through microdensitometry. After baseline correction and desmearing, long spacings were obtained from Lorentz-corrected data. Correlation functions were calculated directly from the slit-smeared data. All data processing was done using the program FFSAXS[17].

Polymer films (25–50 μm thick) were prepared for small-angle laser light scattering (SALLS) by compression moulding of the powdered blends in a hot press using Al foil spacers in order to obtain a uniform sample thickness. The SALLS device was designed according to the principles formulated by Stein *et al.*[18,19]. Calibration of the scattering angles was performed with a diffraction grating of 100 lines mm^{-1}.

RESULTS AND DISCUSSION

Blends of PCL with polymer T

D.s.c. study of the crystallization and melting of the blends. During d.s.c. cooling runs, the maximum of the crystallization temperature of PCL and polymer T appears to be shifted towards lower temperatures in all blends, when compared with pure PCL and pure polymer T, respectively. The heat of crystallization of PCL in the blends is only influenced when the amount of polymer T exceeds 30 wt% (*Figure 1*). The same is true for the polymer T phase when the content of PCL exceeds 70 wt% (*Table 1*). A T_g analysis could not be used to probe the degree of miscibility in the isotropic state, as it appeared to be impossible to obtain fully amorphous samples after quenching from the melt. This is attributed to the low T_g of PCL and to the low molecular weight of polymer T. However, it has been shown in the literature for blends with two crystallizable components, that both a decrease of the heat of fusion and of the crystallization

Table 1 D.s.c. results for the PCL/polymer T blends during crystallization and melting experiments (5°C min^{-1})

Blend composition (PCL/T)[a]	Heating run (melting)				Cooling run (crystallization)			
	T_{mPCL} (°C)	$\Delta H_{PCL}{}^{b}$ ($J\,g^{-1}$)	T_{mT} (°C)	$\Delta H_T{}^{b}$ ($J\,g^{-1}$)	T_{cPCL} (°C)	$\Delta H_{PCL}{}^{b}$ ($J\,g^{-1}$)	T_{cT} (°C)	$\Delta H_T{}^{b}$ ($J\,g^{-1}$)
100/0	58 ± 1	84 ± 2	–	–	31 ± 1	66 ± 2	–	–
90/10	59 ± 1	84 ± 2	165 ± 1	29 ± 2	26 ± 1	65 ± 2	133 ± 1	24 ± 2
80/20	58 ± 1	85 ± 2	164 ± 1	31 ± 2	26 ± 1	65 ± 2	134 ± 1	24 ± 2
70/30	58 ± 1	70 ± 2	164 ± 1	35 ± 2	26 ± 1	63 ± 2	133 ± 1	30 ± 2
50/50	59 ± 1	69 ± 2	164 ± 1	37 ± 2	26 ± 1	49 ± 2	134 ± 1	31 ± 2
30/70	58 ± 1	61 ± 2	164 ± 1	36 ± 2	26 ± 1	46 ± 2	134 ± 1	32 ± 2
0/100	–	–	164 ± 1	36 ± 2	–	–	138 ± 1	31 ± 2

[a] Samples crystallized at $T_c = 35$°C for 72 h
[b] Normalized to the amount of PCL or polymer T in the blends

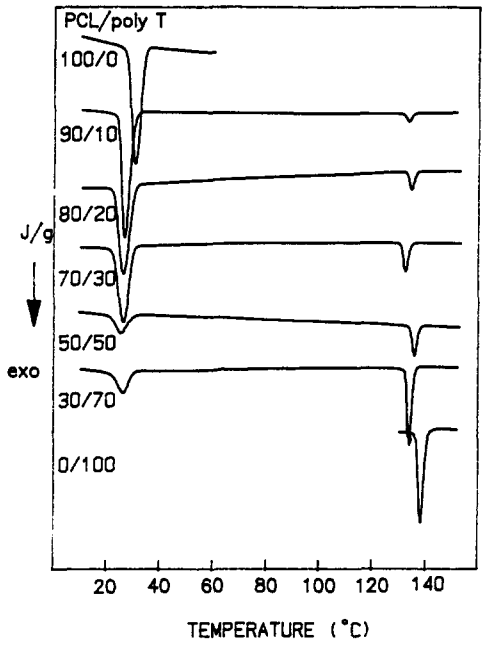


Figure 1 D.s.c. cooling curves of PCL/polymer T blends (−5°C min^{-1}) for different compositions

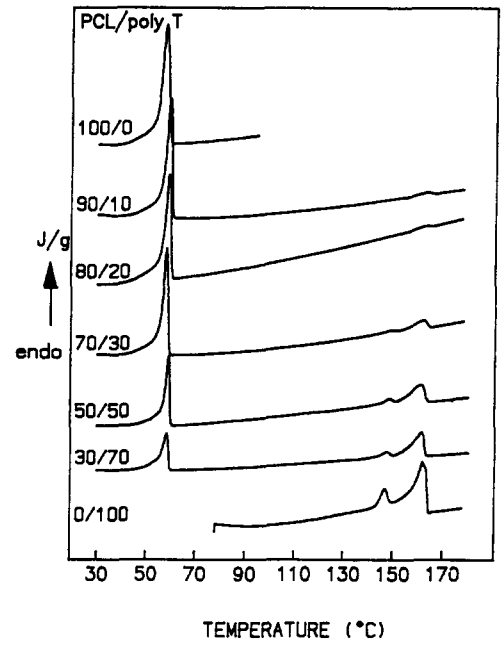


Figure 2 D.s.c. melting curves of PCL/polymer T blends ($T_c = 35$°C, 5°C min^{-1}) for different compositions

rate are indicative of miscibility phenomena in the isotropic state[20].

D.s.c. melting experiments were performed on samples isothermally crystallized at 35°C for 72 h (*Figure 2*). The melting temperature of the PCL phase in the blends is the same as that of pure PCL. However when the amount of polymer T in the blends is >20 wt%, a significant lowering of the melting enthalpy of the PCL is noticed (*Figure 3*). For the polymer T phase, no melting point depression as a function of the blend composition was observed. The melting enthalpy of the polymer T phase decreases when the blends contain <30 wt% polymer T.

Spherulitic crystallization of PCL and texture of the blends. Prior to the crystallization, all blends were heated up to 180°C. At this temperature both components are isotropic, but thin films are opaque, even up to 300°C. All blends were subsequently quenched to the crystallization temperature ($T_c = 35$°C). The addition of polymer T to pure PCL clearly reduces the spherulitic growth rate as evidenced by the results in *Figure 4*, which points to the presence of a miscible melt above the equilibrium melting temperature of PCL (59°C)[21]. Moreover, for all blends studied, a reduction of the

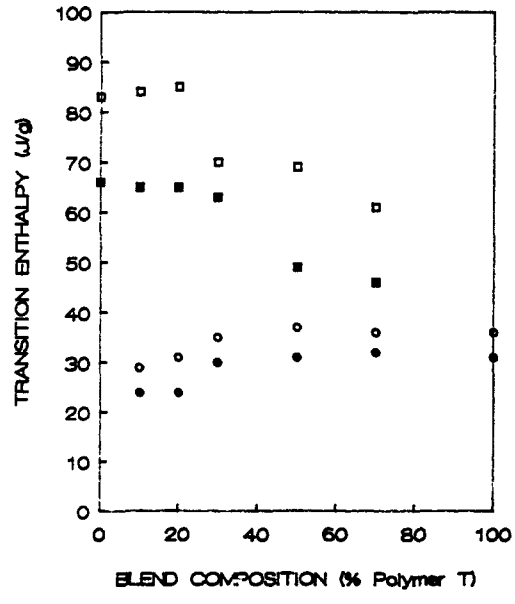


Figure 3 Heat of transition of the PCL/polymer T blends ($T_c = 35$°C). Heating run: (□) PCL phase; (○) polymer T phase. Heat of crystallization during cooling: (■) PCL phase; (●) polymer T phase

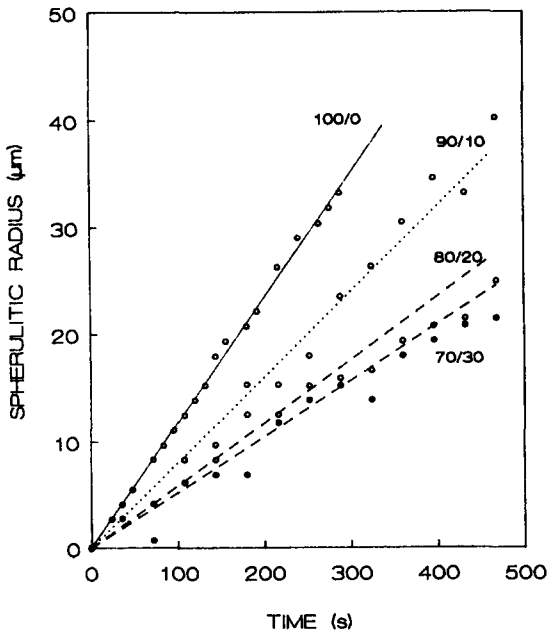


Figure 4 Spherulitic growth rate for different blend compositions of PCL/polymer T (T_c = 35°C)

primary nucleation density was noticed, resulting in larger spherulites. The spherulitic growth rate of PCL in the 50/50 and 30/70 blends could not be measured because of the disturbed spherulitic structures.

In the literature, similar effects on the crystallization rate have been noticed for binary blends of nylon 6 with LC poly(biphenyl-4,4'-ylene sebacate)[22]; these blends did not show a melting point depression, although a rather strong interaction between the two polymers caused the nylon to crystallize in a different manner.

For our blends, a marked change is observed in the semicrystalline morphology of the spherulites; the addition of the semi-rigid T component to PCL results in the formation of banded spherulitic structures indicating lamellar twisting (*Figure 5*). For all blends, small droplets can be observed in the spherulites. When these crystallized samples are heated above the melting point of PCL, these small droplets remain observable between crossed polarizers and even above the melting point of polymer T (*Figures 5h* and *i*). Hence, it is clear that these droplets are segregated polymer T domains.

The phenomenon of spherulitic banding has been studied as a function of the T_c and the composition of the blends using SALLS.

For the study of the effect of the blend composition on the spherulitic texture, pure PCL and blends of PCL/polymer T with compositions 90/10, 80/20, 70/30 and 50/50 were crystallized at 35°C. The results are reported in *Figure 6*. The lamellar twisting periodicity initially decreases with increasing polymer T content and then remains constant above 20 wt% polymer T in the blends. For the 50/50 and 30/70 blends, the spherulites exhibit a disordered structure in the presence of large polymer T domains; the lamellar twisting however can still be noticed.

A 80/20 blend was used to study the dependence of the periodicity of lamellar twisting of PCL on the T_c ranging from 32 to 42°C (*Figure 7*). An increase of the lamellar periodicity was observed for PCL as T_c was increased. At T_cs above 45°C, banded spherulites are transformed into unbanded ones with polymer T domains within the PCL spherulites (*Figure 8*). When such unbanded spherulitic samples are heated above the melting point of PCL, but below the melting region of polymer T, a ring of segregated polymer T can also be observed around the previous spherulitic structures. On the other hand, following a similar thermal treatment, banded spherulites obtained below a T_c of 45°C did not exhibit polymer T regions surrounding the PCL spherulites.

In the literature, similar effects have been described for PCL to which small quantities (<5 wt%) of interacting material have been added[23]. Such segregation phenomena have been described by Keith and Padden using a δ-parameter, defined as follows[24]:

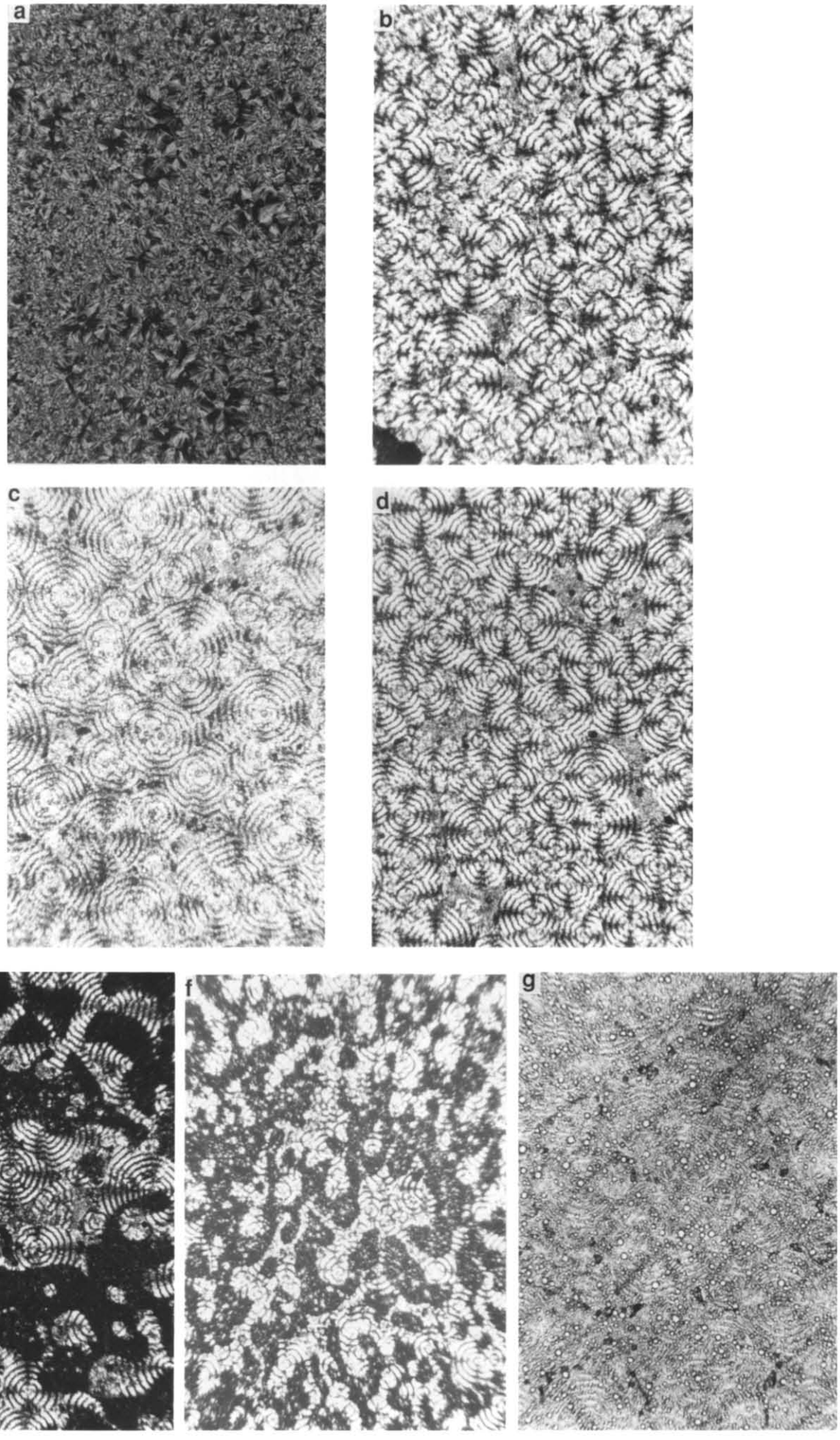
$$\delta = \frac{D}{G}$$

where D is the diffusion coefficient of the non-crystallizable component and G is the spherulitic growth rate of the crystallizable component. δ can thus be visualized as the 'impurity layer thickness' surrounding the growing lamellae. When the T_c is raised, the diffusion of non-crystallizable material will increase, while the spherulitic growth rate at low degrees of supercooling will decrease, resulting in a net increase in the δ parameter, which means that relatively more non-crystallizable material is rejected. Under such thermal conditions, the growing lamellae are able to push 'impurities' away; normal spherulites are then formed with segregated material surrounding them. At lower temperatures, the impurity layer thickness is smaller and therefore more polymer T material is incorporated into the spherulites. It is probable that these incorporated impurities are the reason for the observation of banded spherulitic structures.

Level of segregation of polymer T. SAXS measurements were performed on the blend samples exhibiting banded spherulitic structures in order to determine if a fraction of the polymer T component is incorporated between the crystalline PCL lamellae for T_cs below 45°C. If this segregation occurs between the lamellae (interlamellar), an increase of the long spacing L has to be found[25]. On the other hand, segregation into the interfibrillar regions of the spherulites (i.e. between stacks of lamellae) will not affect L.

Blend compositions of PCL/polymer T 100/0, 90/10, 80/20 and 70/30, crystallized at T_c = 35°C, exhibit well-behaved one-dimensional correlation functions (*Figure 9*). The position of the first maximum in the correlation function corresponds to L and the following values are found for the different PCL/polymer T blend compositions: 100/0; L = 136 Å; 90/10, L = 132 Å; 80/20, L = 128 Å; 70/30, L = 132 Å. A distinct maximum is no longer observed for the 50/50 blend, pointing to the absence of a one-dimensional superstructure. From optical microscopic observations, we know that there is no interspherulitic segregation of the polymer T component when the blends are crystallized below 45°C. Therefore one has to conclude that segregation occurs within the spherulites and on an interfibrillar level.

From all the reported experimental data, it is obvious that the addition of polymer T to PCL has a significant effect on the melting enthalpy and crystallization behaviour. The crystallization behaviour of PCL in the blends is affected in two ways: the morphology of the


a
b
c
d
e
f
g

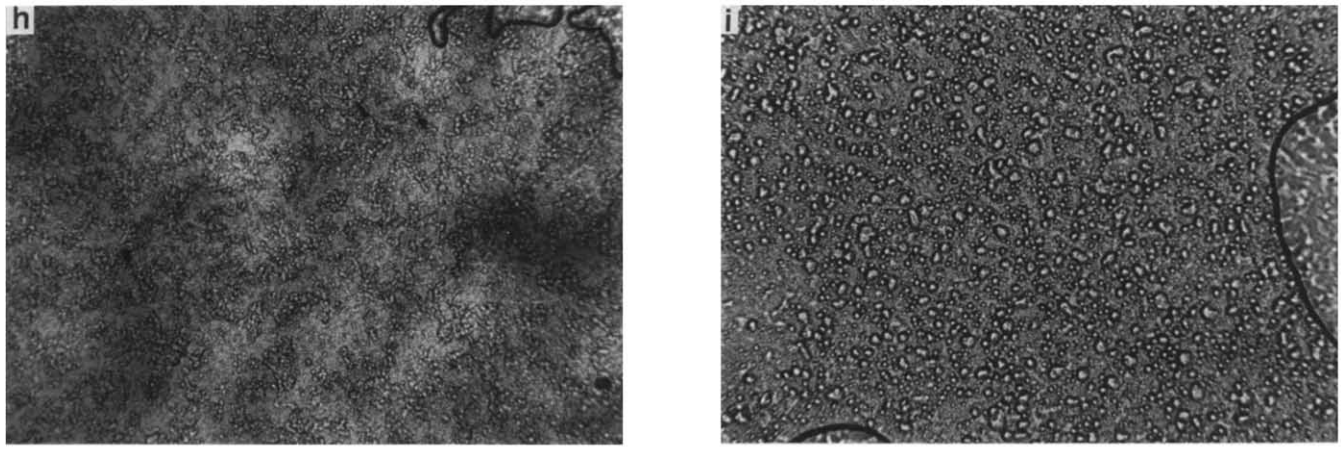


Figure 5 Optical micrographs of crystallized PCL/polymer T blends, $T_c = 35°C$: (a) 100/0; (b) 90/10; (c) 80/20; (d) 70/30; (e) 50/50; (f) 30/70; (g) 80/20; (h) 70/30 blend at 145°C; (i) 70/30 at 180°C. (a)–(f) With crossed polarizers; (g)–(i) with parallel polarizers. Magnification × 130

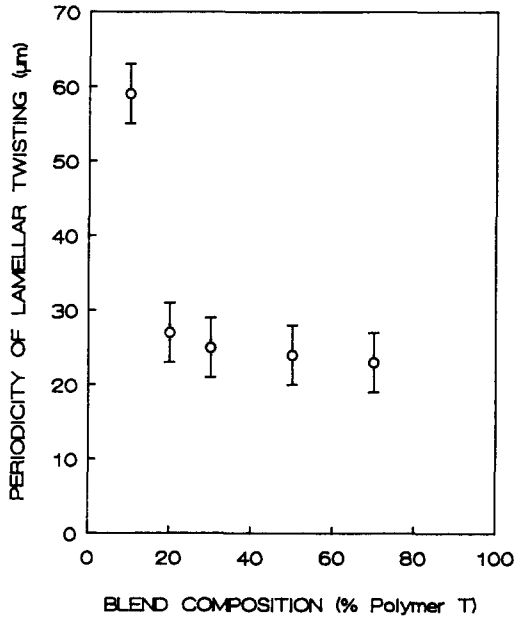


Figure 6 Periodicity of lamellar twisting for PCL/polymer T blends as a function of composition ($T_c = 35°C$)

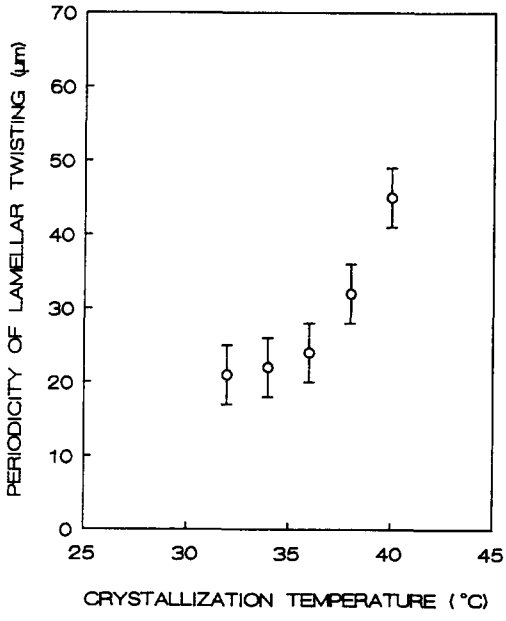


Figure 7 Periodicity of lamellar twisting of the 80/20 blend at different crystallization temperatures

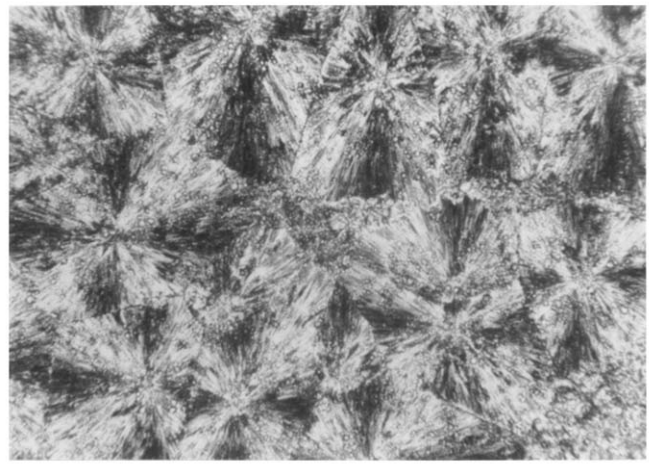


Figure 8 Spherulitic structures of the 80/20 blend crystallized above 45°C

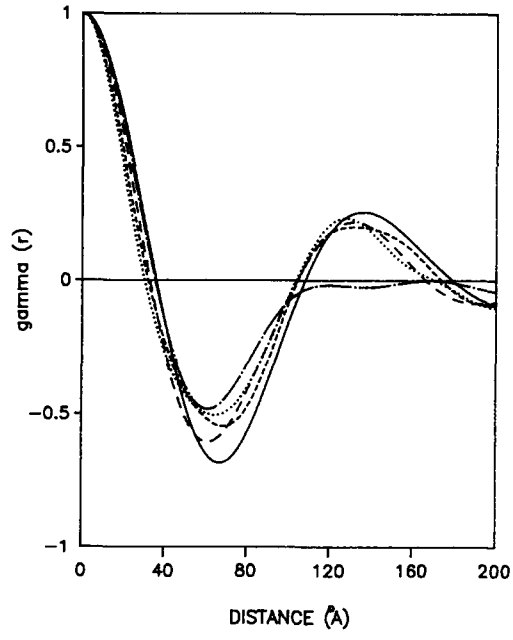


Figure 9 One-dimensional correlation functions of PCL/polymer T blends for different compositions ($T_c = 35°C$): (——) 100/0; (– – –) 90/10; (· · · · ·) 80/20; (— —) 70/30; (—·) 50/50

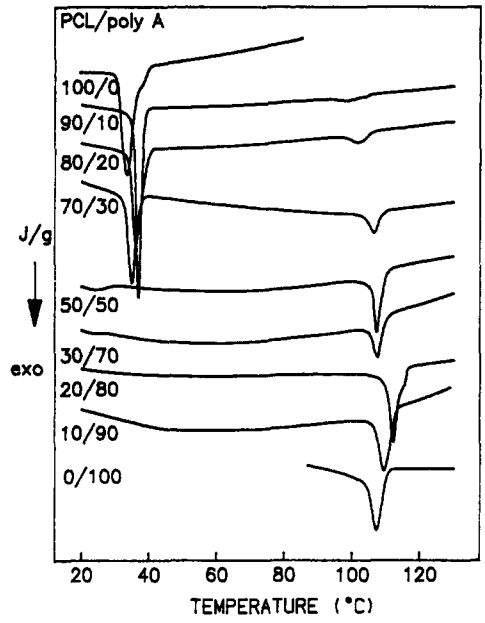


Figure 10 D.s.c. cooling curves of PCL/polymer A blends ($-5°C\ min^{-1}$) for different compositions

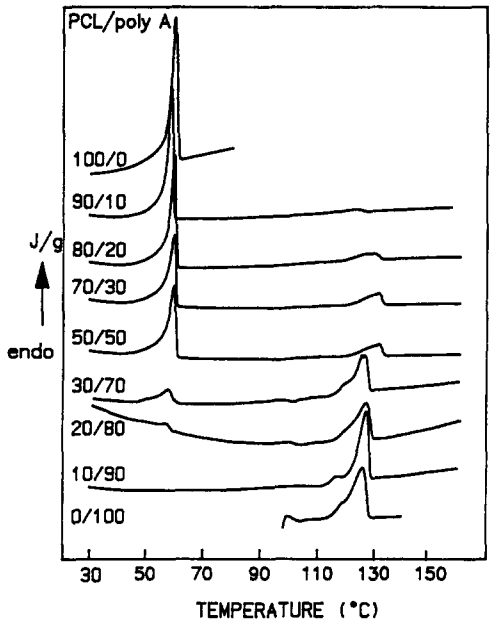


Figure 11 Heat of transition for the blend PCL/polymer A ($T_c = 35°C$). Heating run: (□) PCL phase; (○) polymer A phase. Heat of crystallization during cooling: (■) PCL phase; (●) polymer A phase

spherulites is altered into banded ones for sufficiently low T_cs and the spherulitic growth rate is reduced depending on the amount of polymer T in the blend. The presence of the semi-rigid component induces a T_c-dependent ring structure in the spherulites; the semi-rigid component being incorporated in ($T_c < 45°C$) or rejected from ($T_c > 45°C$) the growing stacks of lamellae. Spherulitic banding here appears to be due to interfibrillar instead of interlamellar segregation.

These observations force us to conclude that crystallization occurs from a partially miscible blend melt because at temperatures up to 300°C thin films of these mixtures are opaque. In our opinion, small amounts of polymer T remain dissolved in the PCL isotropic phase when the blend is cooled below the T_c of polymer T (138°C). Probably only small amounts (<5 wt%) of polymer T induce spherulitic ringing and this could be a reason for the absence of a detectable decrease in the heat of crystallization of polymer T in the different blends during a cooling experiment from the melt.

Blends of PCL with polymer A

Polymer A exhibits a lower chain rigidity than polymer T. Therefore it is interesting to investigate the influence of the chain rigidity on the miscibility behaviour of PCL with this component.

Crystallization and melting behaviour of the blends. For the PCL/polymer A blends, the peak T_cs for PCL obtained in d.s.c. cooling runs increase at first by incorporating polymer A, indicative of a higher nucleation density, which was also observed using optical microscopy. When the amount of polymer A in the blends is $\geqslant 50$ wt%, the PCL fraction can hardly crystallize as can be seen from the low T_cs and the broad crystallization exotherms. For the 20/80 and 10/90 PCL/polymer A blends, the PCL fraction could not crystallize during cooling at $5°C\ min^{-1}$ (*Figures 10* and *11*, *Table 2*). A marked reduction in the heat of fusion was found for the PCL phase in blends with polymer A contents >20%. For polymer A contents below 50%, the crystallization enthalpy of polymer A also decreases. Care should be taken however when evaluating these data because of the difficulty in determining small enthalpic changes for polymer A in blends with high amounts of PCL. When a heating run is performed on isothermally crystallized samples ($T_c = 35°C$, 72 h), a reduction of 5°C of the melting point of the PCL phase can be noticed, while

Table 2 D.s.c. results for the PCL/polymer A blends during crystallization and melting experiments ($5°C\ min^{-1}$)

Blend composition (PCL/A)[a]	Heating run (melting)				Cooling run (crystallization)			
	$T_{m_{PCL}}$ (°C)	$\Delta H_{PCL}{}^b$ ($J\ g^{-1}$)	T_{m_A} (°C)	$\Delta H_A{}^b$ ($J\ g^{-1}$)	$T_{c_{PCL}}$ (°C)	$\Delta H_{PCL}{}^b$ ($J\ g^{-1}$)	T_{c_A} (°C)	$\Delta H_A{}^b$ ($J\ g^{-1}$)
100/0	58 ± 1	84 ± 2	–	–	31 ± 1	66 ± 2	–	–
90/10	57 ± 1	82 ± 2	122 ± 1	44 ± 2	36 ± 1	65 ± 2	97 ± 1	45 ± 2
80/20	57 ± 1	82 ± 2	122 ± 1	49 ± 2	35 ± 1	56 ± 2	101 ± 1	43 ± 2
70/30	56 ± 1	75 ± 2	124 ± 1	43 ± 2	34 ± 1	51 ± 2	103 ± 1	46 ± 2
50/50	54 ± 1	35 ± 2	123 ± 1	60 ± 2	23 ± 1	35 ± 2	103 ± 1	57 ± 2
30/70	54 ± 1	12 ± 2	123 ± 1	59 ± 2	22 ± 1	15 ± 2	103 ± 1	54 ± 2
20/80	56 ± 1	–	124 ± 1	57 ± 2	–	–	108 ± 1	57 ± 2
10/90	53 ± 1	–	124 ± 1	58 ± 2	–	–	105 ± 1	59 ± 2
0/100	–	–	124 ± 1	58 ± 2	–	–	104 ± 1	57 ± 2

[a] Samples crystallized at $T_c = 35°C$ for 72 h
[b] Normalized to the amount of PCL or polymer A in the blends

the melting point of the polymer A phase remains nearly constant (*Figure 12*). On the basis of the melting enthalpies, it can be seen that 30 wt% polymer A is needed to decrease the crystallinity of the PCL phase, while 70 wt% PCL is needed in order to reduce the crystallinity of the polymer A phase.

When the blends are investigated with the polarizing microscope, it can be seen that the crystalline morphology is clearly influenced. The nucleation density is very high, resulting in high crystallization rates even at high T_c (>45°C); this could not be followed by optical microscopy or SALLS. The long spacing L of isothermally crystallized samples ($T_c = 35$°C) was determined from the correlation functions using SAXS data (*Figure 13*), and resulted in the following values for the different PCL/polymer A blend compositions: 100/0, $L = 140$ Å; 90/10, $L = 132$ Å; 80/20, $L = 132$ Å; 70/30, $L = 136$ Å. As can be seen from these results, a very slight decrease of the lamellar spacing of PCL in the blends compared to pure PCL occurs. Polymer A is not segregated into interlamellar regions during the crystallization of PCL and no clear distinction could be made between interspherulitic and interfibrillar segregation. It was also not possible to observe whether banded or unbanded spherulites were formed depending on the T_c because of the very small crystalline entities. In any case spherulitic patterns (banded or unbanded) were not found when these systems were studied with SALLS.

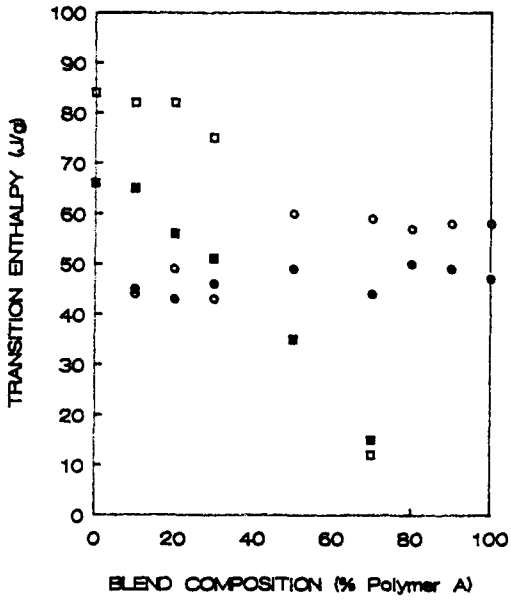


Figure 12 D.s.c. melting curves ($T_c = 35$°C, 5°C min^{-1}) for different blend compositions of PCL/polymer A

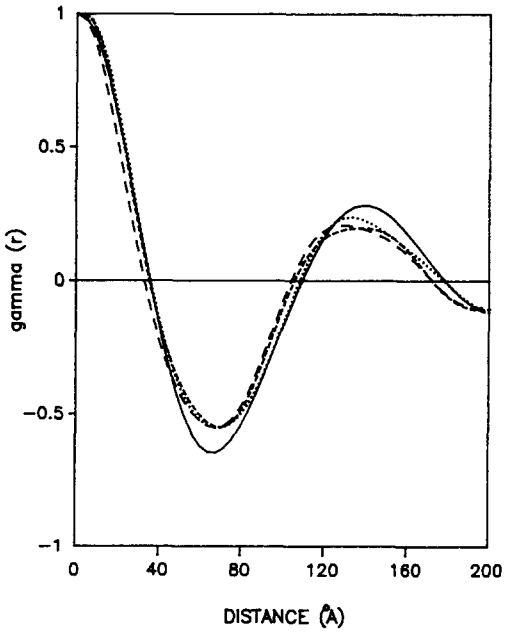


Figure 13 One-dimensional correlation functions of PCL/polymer A blends for different compositions ($T_c = 35$°C): (——) 100/0; (– – –) 90/10; (· · · · · ·) 80/20; (— —) 70/30

It has been observed that the presence of a LC polyester increases the crystallization rate and influences the crystalline morphology of a crystallizable flexible polymer[26,27]. The LC component appears to act as a nucleating agent, resulting in a significant enhancement of the crystallization rate[12,14].

The phase diagram of the PCL/polymer A system was determined by light transmission measurements through the polymer samples at a heating rate of 0.2°C min. In this way a lower critical solution temperature (*LCST*) behaviour can be detected for miscible systems when a blend becomes opaque on phase separating. A polymer film which becomes transparent, hence miscible, above a certain temperature, exhibits upper critical solution temperature (*UCST*) behaviour. The phase diagram for the PCL/polymer A blend is given in *Figure 14*. Above 170°C the blend is miscible for all compositions which indicates *UCST* behaviour. In the literature, similar light transmission measurements on oligomeric and low molecular weight blend systems revealed an *UCST*; examples are poly(isobutylene)/poly(dimethylsiloxane) and polystyrene/polyisoprene blends[28]. Such *UCST* behaviour is often due to the low molecular weight of one of the components in the blend, which is the case for polymer A; the low molecular weight A component acts as a 'solvent' for the high molecular weight PCL component.

The phase mixing process could also be studied by optical microscopy, following the gradual disappearance of polymer A droplets as a function of time at a preset temperature above the *UCST* (*Figure 15*).

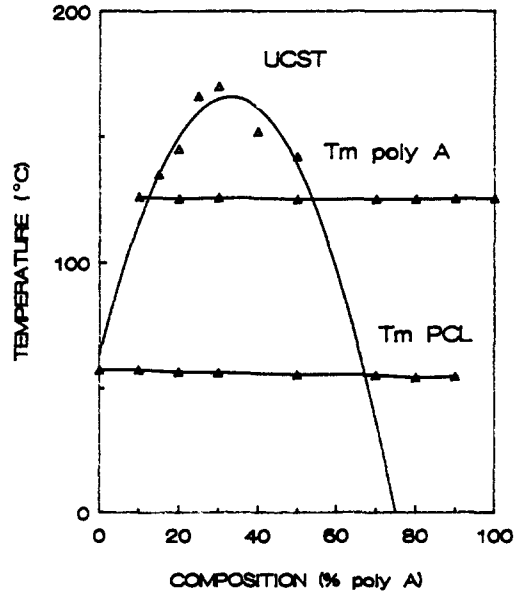


Figure 14 Phase diagram for the PCL/polymer A blend

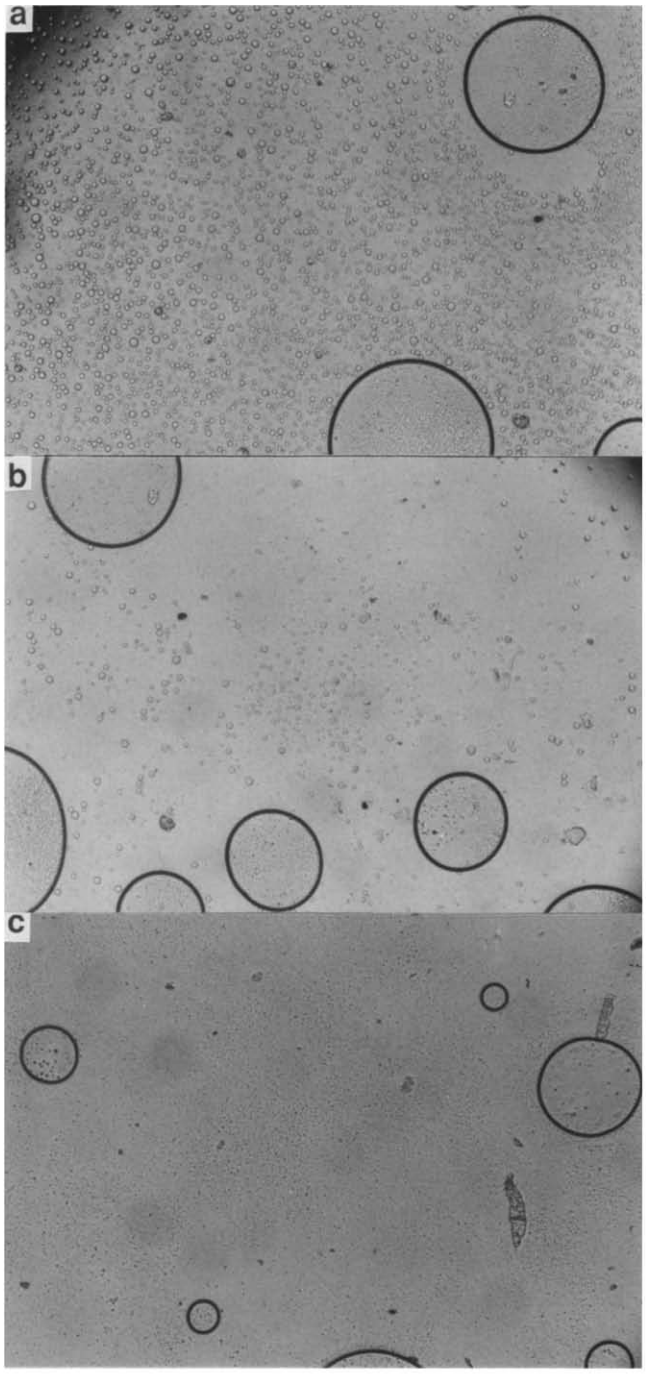


Figure 15 Phase mixing process of a PCL/polymer A blend 70/30 at 180°C: (a) 0 min; (b) 15 min; (c) 30 min

CONCLUSIONS

In this paper binary blends of PCL with two different aromatic polyesters containing mesogenic biphenyl units have been studied with respect to their miscibility behaviour and morphology. Miscibility of PCL with the most flexible biphenyl component (polymer A) was obtained in the isotropic state, above the *UCST* of 170°C. Blends of PCL with a more rigid biphenyl component (polymer T), turned out to be partially miscible in the isotropic state.

A reduction of the rigidity of the biphenyl component clearly affects the crystalline morphology of PCL. In the case of the addition of polymer T, the nucleation density is lowered and the crystallization rates are reduced. When polymer A is added to PCL, a higher nucleation density was found, resulting in an enhanced crystallization.

From the present study it can be concluded that the flexibility of the polymer chain is an important parameter for obtaining miscibility of a LCP and a conventional thermoplastic polymer. However, if the rigidity of a LCP is lowered using flexible moieties in the main chain, care must be taken that the LC behaviour is not lost. A reduction of the rigidity of a LC polyester in our case results in LC (polymer T) and in semi-crystalline (polymer A) behaviour.

ACKNOWLEDGEMENTS

The authors are indebted to the Nationaal Fonds voor Wetenschappelijk Onderzoek for financial support given to the laboratory and to the Instituut voor Wetenschappelijk Onderzoek in Nijverheid en Landbouw for a research grant (P. Van Ende).

REFERENCES

1 Takayanagi, M. and Ogata, T. *J. Macromol. Sci. Phys.* 1980, **B17**, 591
2 Beery, D., Siegmann, A. and Kenig, S. *J. Mater. Sci. Lett.* 1988, **7**, 1071
3 Malik, T. M., Carreau, P. J. and Chapeleau, N. *Polym. Eng. Sci.* 1989, **29**, 600
4 Siegmann, A., Dagan, A. and Kenig, S. *Polymer* 1985, **26**, 1325
5 Crevecoeur, G. and Groeninckx, G. *Polym. Eng. Sci.* 1990, **30**, 532; *Bull. Soc. Chim. Belg.* 1990, **11–12**, 1031
6 Kyu, T. and Zhuang, P. *Polym. Commun.* 1988, **29**, 99
7 Nobile, M. R., Amendola, E. and Nicolais, L. *Polym. Eng. Sci.* 1989, **29**, 244
8 James, S. G., Donald, A. M. and Macdonald, W. A. Abstracts of the Int. Conference on Liquid Crystals, Bordeaux, 1987, 2, p. 8
9 Kimura, M. and Porter, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1697
10 Paci, M., Liu, M., Magagnini, P. L., La Mantia, F. P. and Valenza, A. *Thermochim. Acta* 1988, **137**, 105
11 Porter, R. S. *Thermochim. Acta* 1988, **134**, 251
12 Pracella, M., Danielli, D. and Chiellini, E. *Makromol. Chem.* 1986, **187**, 2387
13 Shin, B. Y. and Chung, I. J. *Polym. Eng. Sci.* 1990, **30**, 13
14 Shin, B. Y. and Chung, I. J. *Polym. J.* 1989, **21**, 851
15 Blumstein, A., Sivaramkrishnan, K. N., Blumstein, R. B. and Clough, S. B. *Polymer* 1982, **23**, 47
16 Darragas, K. *PhD Dissertation*, Katholieke Universiteit Leuven, 1989; Van Ende, P. *PhD Dissertation*, Katholieke Universiteit, Leuven, in preparation
17 Vonk, C. G. *J. Appl. Cryst.* 1973, **6**, 89
18 Stein, R. S. and Rhodes, M. R. *J. Appl. Phys.* 1960, **31**, 1873
19 Defieuw, G. *PhD Dissertation*, Katholieke Universiteit, Leuven, 1989
20 Guo, Q. *Makromol. Chem.* 1990, **191**, 2639
21 Defieuw, G., Groeninckx, G. and Reynaers, H. *Polymer* 1989, **30**, 2164
22 Paci, A., Barone, C. and Magagnini, P. L. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1595
23 Keith, H. D., Padden, F. J. and Russel, T. P. *Macromolecules* 1989, **22**, 666
24 Keith, H. D. and Padden, F. J. *J. Appl. Phys.* 1963, **34**, 2409
25 Russel, T. P. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 999
26 Shama, S. K., Tendolkar, A. and Misra, A. *Polym. Mol. Cryst., Liq. Cryst.* 1988, **157**, 597
27 Bhattacharya, S. K., Tendolkar, A. and Misra, A. *Mol. Cryst.* 1987, **153**, 507
28 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979, Ch. 3, pp. 141–142