A comparison between the morphology of semicrystalline polymer blends of poly(ε-caprolactone)/poly(vinyl methyl ether) and poly(ε-caprolactone)/(styrene–acrylonitrile)

A. A. C. M. Oudhuis*, H. J. Thiewes, P. F. van Hutten and G. ten Brinke
Laboratory of Polymer Chemistry, University of Groningen, Nijenborgh 4,
9747 AG Groningen, The Netherlands

(Received 17 September 1993; revised 28 February 1994)

The morphology of polymer blends of poly(ε-caprolactone) (PCL) and poly(vinyl methyl ether) (PVME) is compared with that of PCL and a random copolymer of styrene and acrylonitrile (SAN). The main objective is to determine the influence of the glass transition temperature of the amorphous component ($T_{g,a}$) on the morphology of the semicrystalline polymer blends. These blends represent the two extreme cases corresponding to $T_c < T_{g,a}$ and $T_c > T_{g,a}$, where T_c is the crystallization temperature. The morphology of these blends, with PVME and SAN representing the amorphous components, have been studied by small angle X-ray scattering. For both blends the long period increases with the addition of amorphous polymer, which is a strong indication for an interlamellar morphology. D.s.c. experiments, including enthalpy relaxation, are used to investigate the crystallinity and the interphases. The overall amount of crystallinity in both blends decreases with increasing content of amorphous polymer. However, the fraction of PCL that crystallizes decreases in PCL/SAN and increases slightly in PCL/PVME. Apparently, the addition of the low $T_{g,a}$ PVME improves the crystallization of PCL in accordance with a simple Gamblers Ruin Model type argument. The high $T_{g,a}$ of SAN means this does not occur in PCL/SAN blends. Conventional d.s.c. experiments show an interphase of pure amorphous PCL in PCL/SAN blends and enthalpy relaxation experiments demonstrate its presence in PCL/PVME blends as well.

(Keywords: semicrystalline blends; morphology; SAXS)

INTRODUCTION

In the last decades the understanding of phase behaviour in polymer blends has greatly improved and the motivation for continuing research in this field remains, as before, the possibility of changing properties in a simple way[1]. One class of interesting polymer systems is formed by semicrystalline polymer blends. The morphology of these blends is complex and many problems remain unresolved. The kind of blend considered in this paper contains an amorphous and a semicrystalline polymer, which are completely miscible in the melt, but start to phase separate upon cooling due to crystallization of the crystallizable component. In all cases the blend separates into several distinguishable phases: a crystalline phase containing the crystallizable polymer only, an amorphous phase that is either a more or less homogeneous mixture of both polymers in the interlamellar region [poly(vinylidene fluoride)/poly(methyl methacrylate), PVDF/PMMA][2–4] or the pure phase of the amorphous polymer in the interfibrillar (isotactic polystyrene/atactic polystyrene, iPS/aPS)[5] or interspherulitic [chlorinated polyethylene/poly(ε-caprolactone), CPE/PCL][6] regions and finally, an interphase between the two phases whose presence and composition is not always clear. The reasons for the existence of the three different morphologies are not completely understood yet. Kumar and Yoon[7] suggest that the value of the Flory–Huggins interaction parameter χ is of prime importance, a sufficiently negative value of χ being the prerequisite for a lamellar structure with the amorphous component residing in the interlamellar region.

Flory[8] was the first to propose a crystal–amorphous interphase as a transition region in which the order from the chains proceeding from the crystallites dissipates. It is believed that a similar interphase exists in a melt miscible semicrystalline polymer blend. Such regions were discovered experimentally in various blends like PVDF/PMMA[9] and poly(ethylene oxide) (PEO)/PMMA[10]. Kumar and Yoon[11,12] investigated numerically, using a lattice model, this interphase assuming a lamellar morphology. They also found that the thickness of the concentration gradient layer is inversely proportional to the square root of the absolute value of the Flory–Huggins interaction parameter χ_{AB}. If $|\chi_{AB}| \rightarrow 0$, this thickness diverges signalling the exclusion of the amorphous polymer from the interlamellar regions, which would explain the iPS/aPS case. If the interaction parameter becomes less negative or the stiffness of the

---

* To whom correspondence should be addressed

0032-3861/94/18/3936–07

chains increases, the interphase becomes broader. On the other hand, if the interaction parameter becomes more negative, the interphase seems to diminish because the amorphous polymer, due to the favourable interactions, diffuses into it and an interphase of pure amorphous material of the crystallizable component can no longer be observed. The conclusions of this numerical work are partly confirmed by experiments of Runt *et al.*[13,14] using polymer systems with different known interaction parameters. Another polymer system with a strongly negative interaction parameter, PVDF/poly(vinyl pyrrolidone) (PVP) has been investigated by Alfonso *et al.*[15] Despite the strong favourable interactions, the blend contained an interphase of pure amorphous PVDF. The explanation given is the presence of head to head and tail to tail defects in the crystallizable polymer. This is conceptually a very important issue, because the presence of small defects in the polymer chains may influence strongly the perfectness of the crystallites and the thickness of the interphase.

Guttman *et al.*[16] modelled the amorphous part of a semicrystalline polymer in between the crystalline lamellae on the basis of the Gamblers Ruin Model[17]. Taking a simple cubic lattice and some simplifying assumptions, they found that at most 1/3 of the chains emanating from the crystalline lamellae can proceed as a random walk into the amorphous region either in the form of a loop or a tie molecule, otherwise overcrowding would occur. Hence they concluded that an amount of tight folding for the chains on the surface of the crystal of at least 70% has to occur. The random walk exit takes the same amount of space as three crystal-like stems, as long as the latter are perpendicular to the interphase. The addition of a second amorphous polymer in a semicrystalline polymer blend makes the constraint even more severe and more chains must form tight folds to avoid density problems. Theoretically for a cubic lattice, the amount of tight folds has to increase from 2/3 to $(2/3+1/3\varphi_a)$, where φ_a is the volume fraction of the amorphous component in the interlamellar region, which is obviously much larger than the overall volume fraction. Thus, in principle, addition of an amorphous melt miscible polymer could lead to more perfect crystallites. Better properties are not necessarily obtained, however, since the amount of tie molecules will be reduced as well.

The crystallization of a polymer is governed by three important processes. First, the formation of a critical nucleus on the front of the growing spherulite. Second, the diffusion of the polymer chain through the matrix of other chains near the growing spherulite. And finally, the diffusion of the centre of mass of other crystallizable polymer chains towards the growing front. The diffusion of the crystallizable polymer chain through a polymer matrix can be described by reptation theory[18–20]. The diffusion of polymer chains depends on various quantities such as the molecular weights of the polymers, the composition of the blend, interactions between the dissimilar polymers and the glass transition temperature of the polymers[21]. The effect of the glass transition temperature of the polymers will be the main topic of this paper. The glass transition temperature near the growing front of the spherulite in a semicrystalline blend is related to the local composition of the polymer blend and the local glass transition temperature will be higher (or lower) than that of the pure crystallizable polymer depending on the glass transition temperature of the amorphous polymer. The reeling-in rate of the crystallizable polymer can be depressed or enhanced in relation to the glass transition temperature at the growing front of the spherulite. The crystallization of a polymer chain depresses the amount of crystallizable polymer near the growing front and enhances the local amorphous polymer concentration. The concentration difference induces a diffusion of amorphous and crystallizable polymers towards regions of lower concentrations. The diffusion distance and the extent to which the amorphous polymers are captured by the growing spherulite will be determined by growth and diffusion processes and in practice the amorphous polymers can be found between lamellae, fibrils or spherulites.

Therefore, the glass transition temperature of the amorphous polymer is of prime importance for the crystallization of the semicrystalline polymer. For a blend containing a crystallizable polymer with a glass transition temperature that is much lower than the glass transition temperature of the amorphous component $T_{g,a}$, crystallization at a temperature T_c considerably below $T_{g,a}$, accompanied by an increase in the concentration of the amorphous component, may locally lead to vitrification making the expulsion of the amorphous component from the interlamellar regions almost impossible. This effect is obviously more pronounced if the overall concentration of the amorphous component is higher. It is not unreasonable to expect that its presence may disrupt the forming of lamellae resulting in defective, lower melting point crystallites. On the other hand, if the $T_{g,a}$ of the amorphous component is much lower than T_c the amorphous regions remain mobile throughout and locally near the growing front there could even be a glass transition temperature depression. In this case the formation of lamellae is not disturbed at all and more perfect crystallites may be expected.

Our main objective is to study the role of amorphous polymers with different glass transition temperatures on the morphology of semicrystalline polymer blends. The systems chosen were PCL with poly(vinyl methyl ether) (PVME) and with a copolymer of styrene and acrylonitrile (SAN, 24 wt% AN), where the latter two are both amorphous. The glass transition temperatures are 213, 248 and 381 K for PCL, PVME and SAN, respectively. The morphology of these blends is studied by optical microscopy, small angle X-ray scattering (SAXS) and d.s.c. (including enthalpy relaxation).

EXPERIMENTAL

Materials

The materials used were a semicrystalline polymer (PCL) and amorphous polymers (PVME) and a copolymer of styrene and acrylonitrile (SAN, 24 wt% AN). PCL was prepared in our laboratory. PVME was obtained from Janssen Chemica and SAN from DOW Chemicals. The polymers were purified by a precipitation procedure and dried under vacuum at 313 K for at least 24 h. Their average molecular weights were determined by g.p.c. using chloroform (PVME) and tetrahydrofuran (PCL, SAN) as eluent at 298 K. The weight and number average molecular weights (M_w and M_n, respectively) were calculated relative to polystyrene standards. Characteristics of the polymers are reported in *Table 1*. Blends of PCL/PVME and PCL/SAN were prepared by solvent casting using toluene as a mutual solvent. The

Table 1 Sample characterization

Polymer	T_g (K)[a]	T_m (K)[b]	M_w	M_w/M_n	%AN
PCL	213	352	168 000	1.9	
SAN	381		185 000	2.4	24.1
PVME	248		114 000	2.0	

[a] Glass transition temperature
[b] Melting temperature

initial concentration of the solutions was 4 wt% and the solvent was evaporated under vacuum at 308 K for several days. The compositions of the blends were 100/0, 90/10, 80/20, etc. wt% PCL/SAN and PCL/PVME.

Optical microscopy

Phase contrast microscopy was used to determine the phase behaviour of PCL/PVME. Blends with different compositions were heated at several temperatures above the melting temperature of PCL and crystallized at $T_c = 308$ K. The formation of different spherulites was determined and compared.

SAXS experiments

Samples for SAXS experiments were prepared by compression moulding of the powdered blends at 373 K, which was above the melting temperature of PCL. The samples were 1 mm thick. The samples were kept at 373 K for at least 30 min to destroy any trace of crystallinity. Then the temperature was lowered to the crystallization temperature ($T_c = 308$ K). The blends were isothermally crystallized in a temperature-controlled stage for at least 1 month.

SAXS experiments were conducted with an Anton-Paar-type Kratky camera using monochromatized Cu Kα radiation with a Ni-β filter. All SAXS experiments were performed at room temperature (293 K). After baseline corrections and desmearing, long spacings were obtained from Lorentz-corrected data. Correlation functions were calculated directly from slit-measured data. All data processing was performed using the program FFSAXS3[22].

Crystallinity

Crystallinity in the blends was determined by d.s.c. using a Perkin–Elmer DSC-7. The blends used were treated with the same temperature procedure as for the SAXS measurements. After isothermal crystallization the blends were cooled to $T_0 = 173$ K and heated with a heating rate of 20 K min^{-1} to 20–60° above the melting temperature. The area of the melting peak is a measure of the amount of crystalline material. The crystallinity is determined using:

$$X_c = \frac{\Delta H_{\text{exp}}}{\Delta H_u^0} \tag{1}$$

where ΔH_u^0 is the melting enthalpy of 100% crystalline PCL, i.e. $\Delta H_u^0 = 136.08$ J g^{-1} (ref. 23).

Enthalpy relaxation experiments

For the enthalpy relaxation experiments the blend PCL/PVME 70/30 was kept at a temperature $T_0 = 373$ K for 10 min. The blend was cooled to the crystallization temperature ($T_c = 308$ K) with a cooling rate of 10 K min^{-1} and kept there for 20 h. After the isothermal crystallization the sample was cooled to the annealing temperatures ($T_a = 198$ or 203 K) and annealed at these temperatures for various amounts of time ($t_a = 1$, 5 and 25 h). After the annealing procedure the sample was cooled to 173 K and reheated to 373 K with a heating rate of 20 K min^{-1}. After keeping the sample at 373 K for 5 min, a second scan was taken over the same temperature range. The first and second scans were subtracted to determine the amount of relaxation in the blends.

RESULTS AND DISCUSSION

The melt miscibility of SAN and PCL is discussed extensively in the literature[24–26]. If SAN contains >6 wt% or <28 wt% AN, it forms miscible blends with PCL across the entire range of blend compositions. Blends of SAN with 28 wt% AN and PCL phase separate for >70 wt% PCL. Polymer blends of PCL and SAN containing 24 wt% AN, studied in this paper, are therefore miscible in all blend compositions. Lower critical solution temperature (*LCST*) behaviour was found to occur above 510 K. The miscibility of PCL/PVME has been briefly discussed before[27]. For the particular sample used we established it again by optical microscopy. If in the melt the blend is phase separated it is possible to observe the phase separation as illustrated by *Figure 1a*, which is a phase contrast photograph of the blend PCL/PVME 50/50 annealed at 483 K for 10 min and quenched in liquid N_2. The blend clearly shows a phase separated morphology. *Figure 1b* is an optical photograph with crossed polarizers of the blend

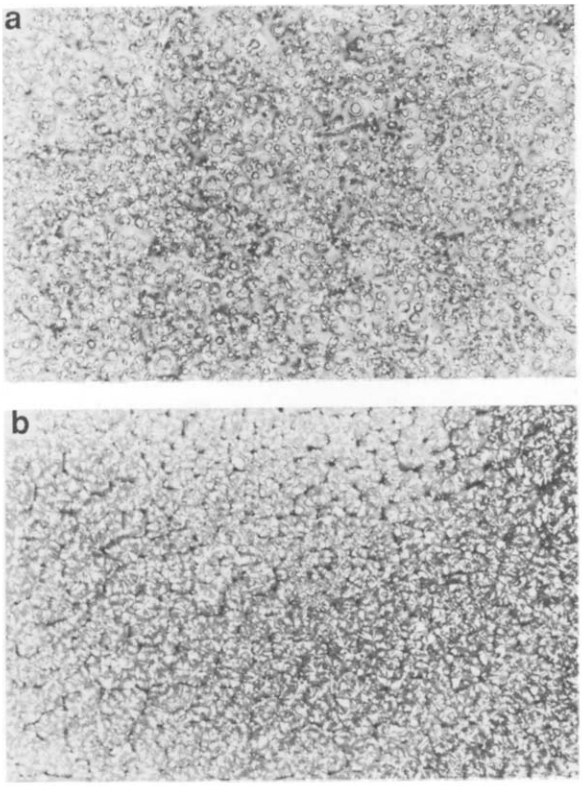

Figure 1 (a) Phase contrast photograph of the blend PCL/PVME = 50/50, $T_0 = 483$ K, quenched in liquid N_2. (b) Optical photograph with crossed polarizers of the blend PCL/PVME = 20/80, $T_0 = 353$ K, isothermally crystallized at $T_c = 308$ K for $t_c = 130$ min

PCL/PVME 20/80 annealed at 353 K, cooled rapidly to the crystallization temperature ($T_c = 308$ K) and isothermally crystallized for at least 130 min. The spherulites have the same average size; a clear indication of miscibility in the melt. Crystallization from a phase separated blend gives rise to spherulites of different sizes in the regions of different composition[28]. The PCL/PVME blends used in this study exhibit *LCST* behaviour with the *LCST* estimated to be around 473 K in good agreement with the literature data[27].

The *LCST*s of both blends used, PCL/SAN and PCL/PVME, are in the same temperature range suggesting that the interactions between the two polymers in both blends are comparable and that the Flory–Huggins χ parameters are very similar. Since this implies that the equilibrium melting point depression of PCL by SAN or PVME will be nearly identical, the isothermal crystallization in both blends was performed at the same temperature. The amount of crystallinity in PCL/SAN and PCL/PVME blends isothermally crystallized at 308 K for at least 1 month, was determined by d.s.c. experiments. *Figure 2* shows the results of these crystallization experiments where the crystallinity of PCL in PCL/SAN and PCL/PVME is expressed in wt% of the blend and in wt% of PCL as a function of the concentration of the amorphous component. The two series of data of SAN and PVME do not converge at 0 wt% of amorphous polymer due to slightly different thermal histories. The overall amount of crystallinity decreases linearly with increasing content of amorphous polymer from 59 to 36% in PCL/SAN and from 56 to 43% in PCL/PVME blends. The decrease is not surprising, since the amount of crystallizable polymer is reduced. The overall amount of crystallinity in the blend PCL/SAN is smaller than in the blend PCL/PVME for nearly all blend compositions. This indicates, that in the blend with PVME more PCL is able to crystallize. *Figure 2* also shows the fraction of crystallized PCL relative to its own weight in the blend. The addition of SAN reduces this fraction from 59 to 55%, whereas the addition of PVME results in a considerable increase from 56 to 68%. Apparently, the addition of PVME improves the crystallization of PCL in agreement with the glass transition temperature argument given. During the isothermal crystallization of PCL the composition of the amorphous mixed phase changes, which in the case of PCL/SAN implies that the glass transition temperature of the polymer matrix may even reach the crystallization temperature locally. The system starts to vitrify and the crystallization process becomes strongly hampered inhibiting lamellar growth. In the case of PVME, the mixed amorphous phase remains mobile throughout and the crystallization process is not interrupted.

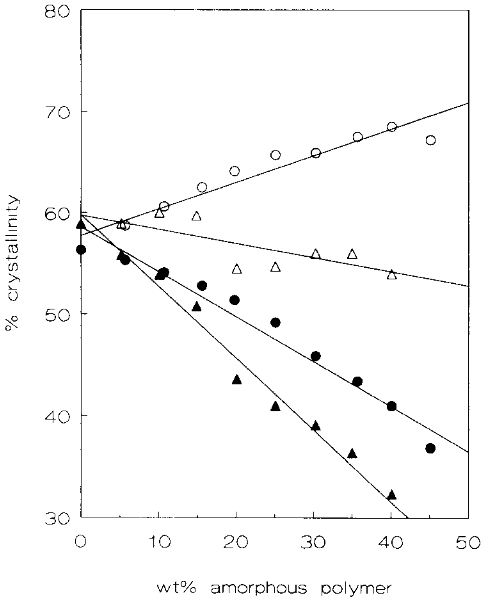

Figure 2 Crystallinity of PCL in the blends: PCL/SAN expressed in wt% of the blend (▲) and wt% of PCL(△); PCL/PVME expressed in wt% of the blend (●) and wt% of PCL(○)

The next issue to address is the influence of the glass transition temperature of the amorphous polymer on the thickness of the crystalline lamellae and the morphology of the above-mentioned blends. The thickness of the crystalline lamellae, l_c, is known to be inversely proportional to the supercooling, $\Delta T \equiv T_m^0 - T_c$, $l_c \sim 1/\Delta T$, where T_m^0 is the equilibrium melting temperature[29]. A decrease in ΔT results in an increase of the lamellar thickness. The presence of an amorphous melt miscible polymer decreases the equilibrium melting temperature of the crystallizable polymer (melting point depression). If the crystallization temperature is the same for all blend compositions, as is the case in our study, the supercooling decreases by addition of the amorphous component. According to this simple argument, the thickness of the lamellae obtained by isothermal crystallization is expected to increase as the amount of amorphous polymer increases. This behaviour has indeed been observed in PCL/PVC blends, which show a small increase in the thickness of PCL lamellae with increasing PVC content[30].

The morphology and the thickness of the lamellae of PCL/SAN and PCL/PVME were investigated by SAXS experiments. After isothermal crystallization there are several distinguishable phases in the semicrystalline polymer blend as mentioned before. The difference in density between the amorphous and crystalline phases can be used to determine the thickness of the different phases. Information about the morphology is obtained using a two-phase model translating the scattering data via a one-dimensional correlation function, $\gamma(x)$ (ref. 31). The fully backgound corrected scattering intensity $I(q)$ is related to $\gamma(x)$ by

$$\gamma(x) = \int_0^\infty I(q) q^2 \cos(xq)\, dq \qquad (2)$$

where q is the scattering vector. *Figures 3a* and *b* show the one-dimensional correlation functions of PCL/SAN and PCL/PVME, respectively, for three different blend compositions obtained from the scattering data. The x-axis value at the position of the first maximum corresponds to the long period or interlamellar spacing. In both figures, a substantial increase of the long period by addition of the amorphous polymer is observed. In the case of PCL/SAN the long period increases from 14.8 to 19.2 nm and in the blend PCL/PVME from 15.8 to 20.9 nm for a 65/35 blend composition. These increases are still small compared to other systems like PEO/PMMA where the long period increases by a factor of 3 or more depending on the blend composition[10], but for blends containing PCL this seems quite normal[23]. The long period value for PCL/PVC blends increases from 16.1 to 32.2 nm for a 50/50 blend[23]. For melt miscible blends the increase of long period with the addition of an amorphous component is considered to be a strong

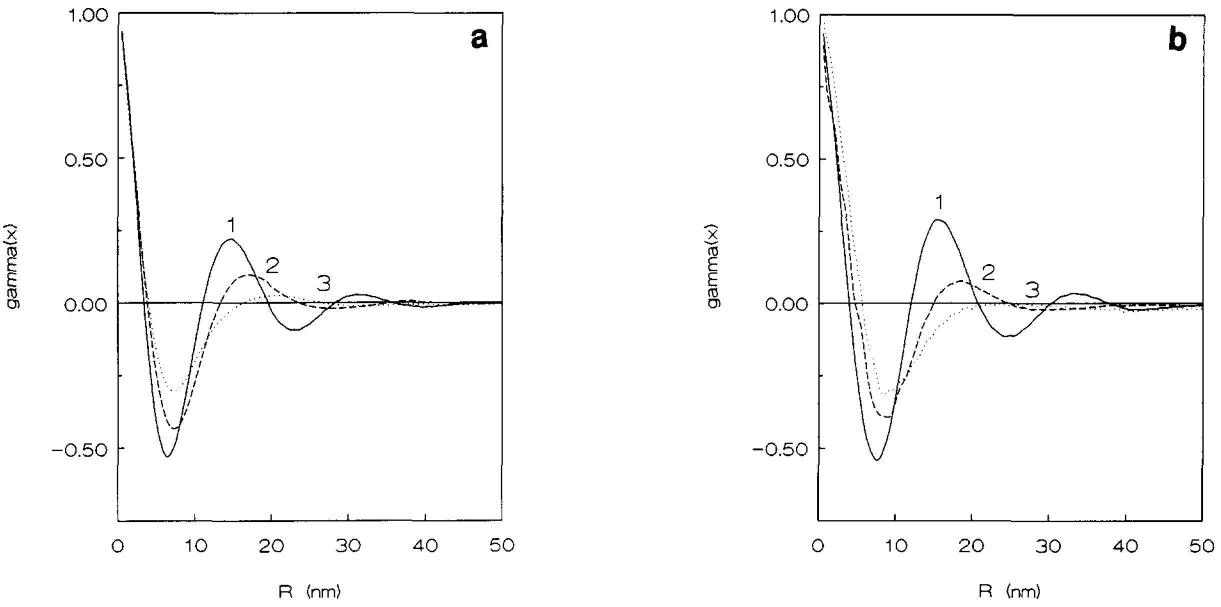

Figure 3 One-dimensional correlation function of (a) PCL/SAN and (b) PCL/PVME blends crystallized at $T_c = 308$ K for at least 1 month. Blends: (1) 100/0; (2) 75/25; (3) 60/40

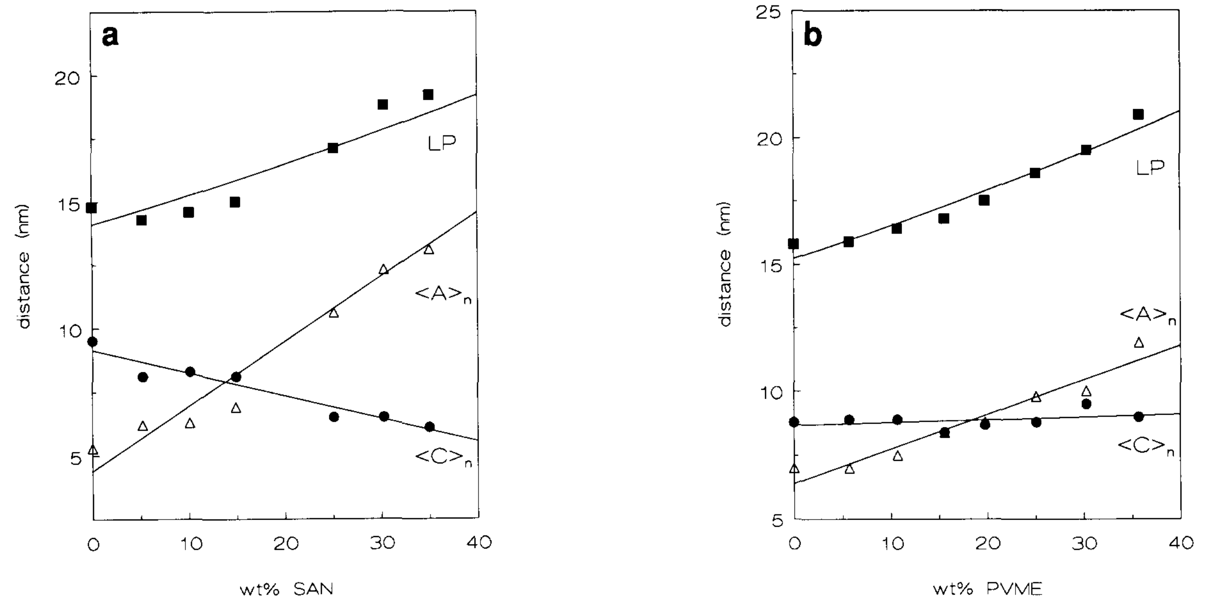

Figure 4 SAXS data of (a) PCL/SAN and (b) PCL/PVME as a function of the wt% amorphous component: long period, LP (■); thickness of the crystalline phase $\langle C \rangle_n$ (●); thickness of amorphous phase, $\langle A \rangle_n$ (△)

indication for the incorporation of the amorphous polymer within the lamellae[10,23,33]. Despite the large difference in glass transition temperatures between both amorphous polymers, SAN and PVME, both blends apparently show an interlamellar morphology. So far only a few studies concerning the influence of the amorphous polymer with a glass transition temperature lower than the crystallization temperature on the blend morphology have appeared[6,32,33]. Defieuw *et al.*[6] found an interfibrillar morphology for the blend PCL/CPE (49.1% CL) with $T_{g,a} = 292$ K and $T_c = 298$ K, if the blend contains 10–30 wt% CPE; for other compositions an interspherulitic structure is found. In the case of nylon 6 and 66 blended with an amorphous polyamide nylon 3Me6T ($T_{g,a} = 420$ K and $T_c = 428$ or 473 K) the amorphous polymer is rejected from the interlamellar regions[33]. In both cases the glass transition temperatures of the amorphous components are below the crystallization temperature, allowing its rejection from the interlamellar regions if this is somehow thermodynamically favoured (for instance, small positive χ parameter). From the calculated long period the average thicknesses of the crystalline ($\langle C \rangle_n$) and amorphous ($\langle A \rangle_n$) phases are determined using the crystallinity data obtained by d.s.c. In *Figures 4a* and *b* the long period, $\langle C \rangle_n$ and $\langle A \rangle_n$ of the PCL/SAN and PCL/PVME blends, respectively, are shown. The addition of SAN leads to a decrease of $\langle C \rangle_n$ from 9.5 to 6.1 nm, whereas the addition of PVME leaves $\langle C \rangle_n$ essentially unaltered. Clearly, the amorphous polymer with a glass transition temperature far below the crystallization temperature influences the crystallization in a favourable way leading to more perfect crystallites.

One final question remains, whether an interphase of pure amorphous PCL exists between the lamellae and the mixed amorphous phase. It is not possible to determine unambiguously the existence of such an interphase from our SAXS data and we have to recourse to d.s.c. For PCL/SAN, due to the large difference in the glass transition temperatures of PCL and SAN the procedure is straightforward. However, PVME/PCL presents a problem since both glass transition temperatures are very similar, $T_{g,a}$(PCL) = 213 K and $T_{g,a}$(PVME) = 248 K. Recent studies[34,35] summarized in a review article[36] have shown that these limitations are superfluous. It is possible to obtain the necessary information using enthalpy relaxation behaviour experiments. This method has been developed into an analytical tool, which can be applied to reveal phase behaviour and morphology related phenomena based on the fact that heterogeneous mixtures are characterized by multiple relaxation peaks despite nearly identical glass transition temperatures. As discussed, crystallization of semicrystalline polymer blends often leads to a crystalline phase, an amorphous mixed phase and an interphase of amorphous material of the crystalline component. The amount of amorphous material in the interphase is small and sometimes difficult to detect even if both glass transition temperatures are far apart. In this case enthalpy relaxation may also be used to enhance the detecting capabilities of thermal analysis. *Figure 5* shows the results of a conventional d.s.c. experiment on PCL/SAN 90/10 blend. One recognizes immediately a glass transition temperature at 213 K. The presence of the lower transition corresponds to the existence of an interphase of pure amorphous PCL. The broad transition above 273 K, although difficult to detect, is due to the amorphous mixed phase and indicates that a compositional gradient is present. To determine the existence of an interphase in the blend PCL/PVME a blend with 30 wt% PVME was used. Not surprisingly, the blend shows a single glass transition temperature located at 228 K. If there is an interphase of pure PCL, the proximity of the glass transition temperatures of the amorphous mixed phase (213–228 K) and the interphase (213 K) automatically implies single glass transition temperature behaviour. Information about the presence of such an interphase in the blend PCL/PVME can be obtained by the enthalpy relaxation method. The blend PCL/PVME 70/30 is annealed at two different temperatures (T_a = 203 or 198 K) and different annealing times (t_a = 1, 5 and 25 h). The enthalpy relaxation peaks are visible as two shoulders. *Figures 6a* and *b* show the subtracted enthalpy relaxation peaks, annealed at T_a = 198 K and T_a = 203 K, respectively. Both figures show at short annealing times (t_a < 5 h) a double relaxation peak, a strong indication for the existence of two phases: an amorphous mixed phase and an interphase. At longer annealing times the peak at the lowest temperatures shifts to higher temperatures and disappears completely under the second relaxation peak and only one single relaxation peak is observed. The shift of relaxation peaks as a function of annealing time to higher temperatures as well as the increase in the amount of enthalpy relaxation are well known features of enthalpy relaxation experiments. Nevertheless, some care has to be taken in the interpretation of the occurrence of double enthalpy relaxation peaks, since these are known to be sometimes present in homopolymers as well[37]. However, annealing experiments of pure PCL only showed a single enthalpy relaxation peak of the amorphous phase.

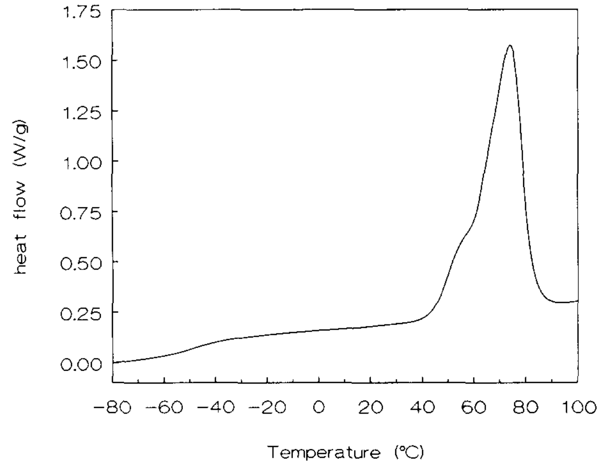

Figure 5 D.s.c. thermogram of PCL/SAN 90/10, isothermally crystallized at T_c = 308 K for 1 month

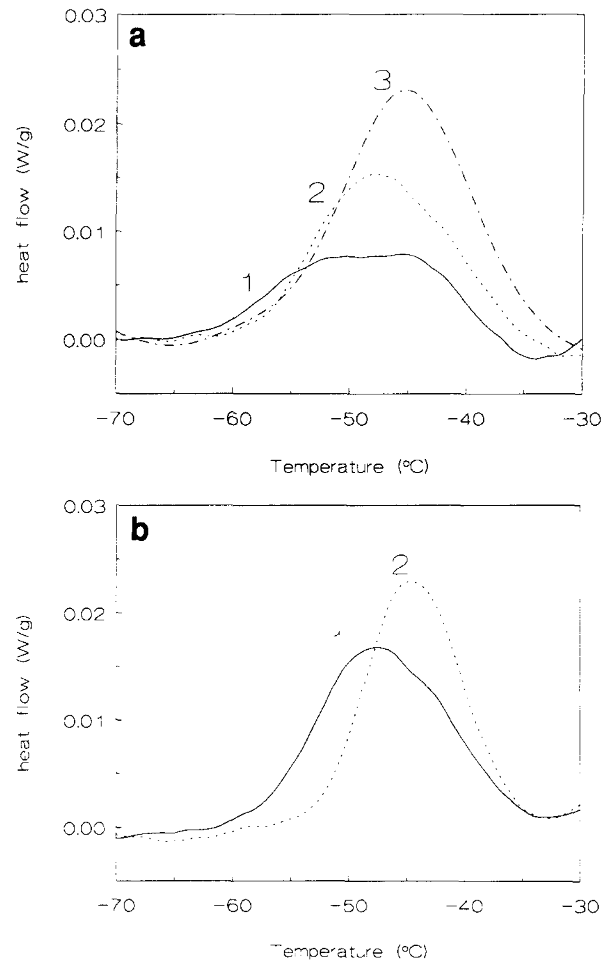

Figure 6 Subtracted enthalpy relaxation peaks of PCL/PVME 70/30, isothermally crystallized at T_c = 308 K and annealed at: (a) T_a = 198 K for t_a = 1 (1), 5 (2) and 25 (3) h; (b) T_a = 203 K for t_a = 1 (1) and 5 (2) h

CONCLUSIONS

The blends PCL/SAN and PCL/PVME both exhibit *LCST* behaviour (510 and 473 K). Below these temperatures these blends are completely miscible in the melt and after crystallization of PCL show an interlamellar morphology. The interphase of pure amorphous PCL in

PCL/SAN is determined by common d.s.c. experiments, whereas in PCL/PVME, it is detected by enthalpy relaxation experiments. In contrast to the high $T_{g,a}$ SAN component, PVME, an amorphous polymer with a glass transition temperature below the crystallization temperature, improves crystallization of PCL as witnessed by SAXS and d.s.c.

REFERENCES

1 Utracki, L. A. 'Polymer Alloys and Blends', Hanser, Munich, 1989

2 Hahn, B. R., Wendorff, J. H. and Yoon, D. Y. *Macromolecules* 1981, **18**, 718

3 Hahn, B. R., Herrmann-Schonherr, O. and Wendorff, J. H. *Polymer* 1987, **28**, 201

4 Ando, Y. and Yoon, D. Y. *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.* 1987, **28**, 26; 1988, **29**, 381

5 Warner, F. P., MacKnight, W. J. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 2113

6 Defieuw, G., Groeninckx, G. and Reynaers, H. *Polymer* 1989, **30**, 595

7 Kumar, S. K. and Yoon, D. Y. *Macromolecules* 1989, **22**, 4098

8 Flory, P. J. *J. Am. Chem. Soc.* 1962, **84**, 2857

9 Ando, Y. and Yoon, D. Y. *Macromolecules* 1989, **22**, 4098

10 Russell, T., Ito, H. and Wignell, G. D. *Macromolecules* 1988, **21**, 1703

11 Kumar, S. K. and Yoon, D. Y. *Macromolecules* 1989, **22**, 3458

12 Kumar, S. K. and Yoon, D. Y. *Macromolecules* 1991, **24**, 5414

13 Barron, C. A., Kumar, S. K. and Runt, J. P. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1992, **33**, 610

14 Runt, J. P., Barron, C. A., Zhang, X. and Kumar, S. K. *Macromolecules* 1991, **24**, 3468

15 Alfonso, G. C., Turturro, A., Scandola, M. and Ceccorulli, G. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 1195

16 Guttman, C. M., DiMarzio, E. A. and Hoffman, J. D. *Polymer* 1981, **22**, 1466

17 Feller, W. 'An Introduction to Probability Theory and Its Applications', Vol. 1, Wiley, New York, 1968, Ch. XIV

18 DiMarzio, E. A., Guttman, C. M. and Hoffman, J. D. *Discuss. Faraday. Soc.* 1979, **68**, 177, 210

19 Hoffman, J. D. *Polymer* 1982, **23**, 656

20 Klein, J. and Ball, R. *Discuss. Faraday Soc.* 1979, **68**, 198

21 Alfonso, G. C. 'Integration of Fundamental Polymer Sciences and Technology' (Eds P. Lemstra and L. Kleintjens), Vol. 5, Elsevier, London, 1991, p. 143

22 Vonk, C. G. and Pijpers, A. P. *J. Appl. Crystallogr.* 1981, **14**, 8

23 Khambatta, F. B., Warner, F., Russell, T. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 1391

24 Chiu, S.-C. and Smith, T. G. *J. Appl. Polym. Sci.* 1984, **29**, 1781

25 Chiu, S.-C. and Smith, T. G. *J. Appl. Polym. Sci.* 1984, **29**, 1797

26 Rim, P. B. and Runt, J. P. *Macromolecules* 1983, **16**, 762

27 Watanabe, T., Fujiwara, T., Sumi, Y. and Nishi, T. *Rep. Prog. Polym. Phys.* 1982, **25**, 285

28 ten Brinke, G., Roerdink, E. and Challa, G. in 'Polymer Compatibility and Incompatibility' (Ed. K. Solc), MMI Press, New York, 1982, pp. 77–89

29 Barham, P. J., Chivers, R. A., Keller, A., Martinez-Salazar, J. and Organ, S. J. *J. Mater. Sci.* 1985, **20**, 1625

30 Stein, R. S., Khambatta, F. B., Warner, F. P., Russell, T., Escala, A. and Balizer, E. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 313

31 Strobl, G. R. and Schneider, M. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 1343

32 Runt, J. P., Zhang, X., Miley, D. M. and Gallagher, K. P. *Macromolecules* 1992, **25**, 3902

33 Myers, M. E., Wims, A. M., Ellis, T. S. and Barnes, J. *Macromolecules* 1990, **23**, 2807

34 Bosma, M., ten Brinke, G. and Ellis, T. S. *Macromolecules* 1988, **21**, 1465

35 ten Brinke, G. and Grooten, R. *Colloid Polym. Sci.* 1989, **267**, 992

36 ten Brinke, G., Oudhuis, A. A. C. M. and Ellis, T. S. *Thermochim. Acta* in press

37 Kovacs, A. J., Akonis, J. J., Hutchinson, J. M. and Ramos, A. R. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 1097