Miscibility, crystallization and melting behaviour, and semicrystalline morphology of binary blends of polycaprolactone with poly(hydroxy ether of bisphenol A)

G. Defieuw, G. Groeninckx* and H. Reynaers
Laboratory of Macromolecular Structural Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan, 200F, 3030 Heverlee, Belgium
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Blends of poly(hydroxy ether of bisphenol A) (Phenoxy) with polycaprolactone (PCL) were prepared by the coprecipitation technique. The melt miscibility of the polymers was studied by optical microscopy, light transmission measurements and dynamic mechanical analysis. The crystallization kinetics of PCL in the miscible Phenoxy/PCL blends were studied using optical microscopy and the segregation behaviour of Phenoxy due to the crystallization of PCL was examined by means of optical microscopy and small-angle X-ray diffraction, while the melting behaviour of PCL in the blend was explored by differential scanning calorimetry. The polymers were found to be miscible over the entire composition and temperature range (up to 200°C), while Phenoxy is segregated interlamellarly as well as interfibrillarly and interspherulitically during the crystallization process of PCL.

(Keywords: miscibility; semicrystalline morphology; polymer blends)

INTRODUCTION

Interest in the development of new multicomponent polymeric materials based on mixtures of polymers arises from their growing technological importance. Many fundamental studies have been devoted to the melt miscibility of polymers. In this area, however, we still have a long way to go as far as the prediction of the miscibility behaviour and structure–property relations of polymer blends is concerned. The degree of miscibility of the components in the blend is of crucial importance with respect to its morphology and physical properties. A limited number of studies deal with the semicrystalline morphology of blends of crystallizable and amorphous polymers[1–9].

The miscibility of the binary blend, poly(hydroxy ether of bisphenol A)/polycaprolactone (Phenoxy/PCL), has been investigated previously by torsion pendulum measurements[10]; on the basis of these observations, the authors concluded that the blend is fully miscible. In the present work, the melt miscibility as well as the semicrystalline morphology and the melting behaviour of this system will be studied by a broad experimental approach. The results of this study will be compared with experimental data on other binary blends of semicrystalline and amorphous polymers obtained in this laboratory and reported by other authors.

EXPERIMENTAL

Materials

Both Phenoxy and PCL were commercial products obtained from Aldrich Chemicals. Their average molecular weights were determined relative to polystyrene standards by g.p.c. analysis at 25°C using tetrahydrofuran (THF) as a solvent; they are reported in *Table 1*. Binary blends were prepared by coprecipitation of a 3% THF solution (w/v) in hexane.

Techniques

For the miscibility study, dynamical mechanical analysis (d.m.a.) was performed on specimens compression moulded at 120°C and subsequently quenched in liquid nitrogen. This procedure allows one to obtain amorphous blends at PCL concentrations below 90 wt% and, as a consequence, the state of miscibility in the melt can be evaluated. A Polymer Labs DMTA (bending head) was used at a scanning rate of 2°C min^{-1} and a frequency of 1 Hz.

The spherulitic growth rate of PCL in the PCL-rich blends was determined using optical microscopy; powdered blends were molten in a Mettler FP82 hot stage at 180°C for 5 min, immediately followed by isothermal crystallization in the temperature range between 25 and 45°C.

Samples for SAXS measurements of approximately 1 mm thickness were prepared by compression moulding of the powdered blends at 120°C. SAXS patterns were recorded photographically using an Anton Paar-type Kratky camera provided with a 60 μm entrance slit. The Philips PW1130 X-ray generator was operated at 45 kV and 30 mA; a Kratky-type Cu target in conjunction with

Table 1 Molecular-weight characteristics of the blend components as obtained by g.p.c. analysis relative to polystyrene standards

Sample	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
PCL	22 500	14 000	1.60
Phenoxy	48 600	22 500	2.17

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* To whom correspondence should be addressed

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a Ni β filter was used throughout. Typical irradiation times were of the order of 3 to 10 h depending on sample composition and thickness. All small-angle scattering experiments were performed at room temperature and obtained as slit-smeared data in the infinite-slit approach. Other experimental details with respect to the experimental set-up and data treatment have been reported in a previous paper in this journal[9].

The melting behaviour of the semicrystalline samples was studied by d.s.c. scans, run on a Perkin–Elmer DSC 2C equipped with a Thermal Analysis Data Station (TADS). The sample weight was approximately 5 mg.

RESULTS AND DISCUSSION

Miscibility and crystallization behaviour of Phenoxy/PCL blends

Previous to the study of the segregation processes and the semicrystalline morphology in Phenoxy/PCL blends, the miscibility of both components in the melt was investigated. Indeed, the study of segregation processes during the liquid–solid phase separation (crystallization of PCL) only make sense if miscible blends are obtained above and below the equilibrium melting point of PCL ($T_{\mathrm{m}}^{\circ}=63^{\circ}\mathrm{C}$).

D.m.a. experiments on quenched amorphous blends involving different contents of Phenoxy reveal the presence of a miscible blend on the molecular level as manifested by the narrow tan δ peak, intermediate between those of the pure components (*Figure 1*). These experimental glass transition temperatures fit rather well with the T_g values predicted by the Fox equation (*Figure 2*). All the binary blends were transparent at 100°C and no lower critical solution temperature behaviour could be detected below 200°C for all compositions by light transmission measurements.

Another proof of the melt miscibility can be obtained by studying the spherulitic growth rate of PCL in crystallizable Phenoxy/PCL blends. The spherulitic growth rate of PCL as measured by optical microscopy is substantially decreased in the presence of the amorphous diluent and this decrease in growth rate is a function of the overall concentration of Phenoxy in the blends (*Figure 3*). The latter dependences of the spherulitic growth rates and the glass transition temperatures on the composition indicate the presence of a miscible melt above the equilibrium melting temperature of PCL, and are strong evidence for the melt miscibility of both polymers. Other indications will be obtained from the study of the semicrystalline morphology and the melting behaviour of the Phenoxy/PCL blends.

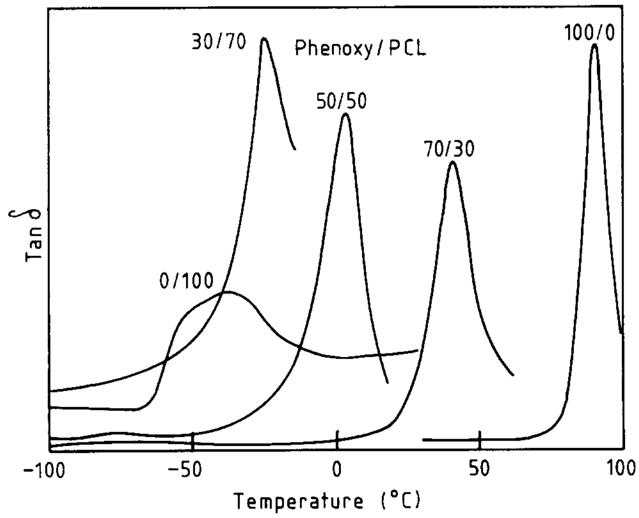

Figure 1 D.m.a. of quenched amorphous Phenoxy/PCL blends

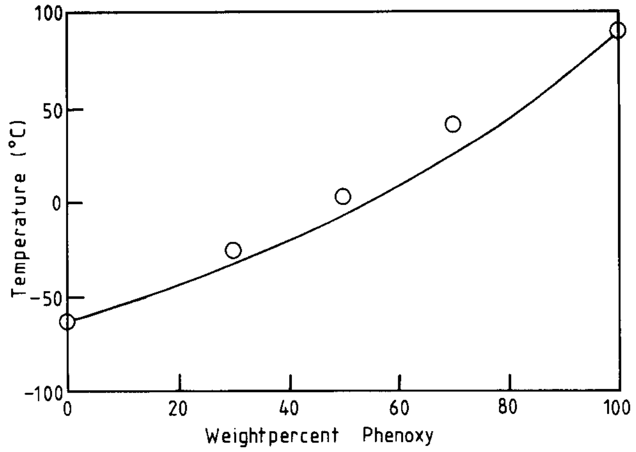

Figure 2 Glass transition temperatures *versus* composition for amorphous Phenoxy/PCL blends. ○, Experimental; ——, Fox equation

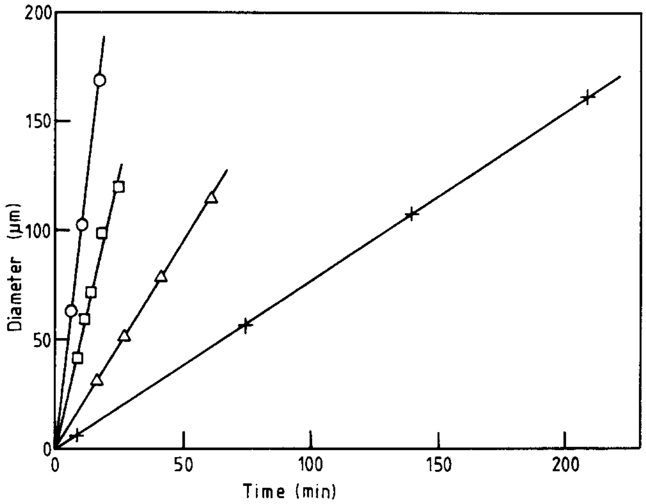

Figure 3 Spherulite growth in Phenoxy/PCL blends isothermally crystallized at 45°C. Blends: ○, 0/100; □, 10/90; △, 20/80; +, 30/70

Segregation phenomena in and semicrystalline morphology of Phenoxy/PCL blends

During the crystallization of PCL in the miscible Phenoxy/PCL blends, a liquid–solid phase separation process occurs, and Phenoxy is segregated in the amorphous phase as in the case of all miscible blends of semicrystalline and amorphous components. Three types of segregation processes can occur in such systems. The amorphous blend component can be rejected in the amorphous regions between the crystalline lamellae during the crystallization of the crystallizable component. This type of segregation is referred to as interlamellar segregation and is found in blends of poly(vinyl chloride) (PVC) with PCL[1–4], styrene–acrylonitrile (SAN) with PCL[11] and poly(vinylidene fluoride) (PVDF) with poly(methyl methacrylate) (PMMA)[5,6]. Interfibrillar segregation has been considered in those cases where the amorphous component is segregated within the spherulites between stacks of lamellae, as experimentally found in isotactic/atactic polystyrene (iPS/aPS)[12] and chlorinated polyethylene (CPE)/PCL[8,9] blends. Finally, interspherulitic segregation has to be considered for those cases where the amorphous component is rejected at the border of the growing spherulites during the crystallization process. Such a type of segregation has been observed in CPE/PCL blends at high CPE contents and high crystallization temperatures[8,9].

With respect to the present blend, a constant spherulitic growth rate during the lamellar growth process of the PCL crystals in blends containing at least 70 wt% PCL was already reported in *Figure 3*, indicating that Phenoxy is segregated intraspherulitically. A similar situation was also encountered in the case of CPE/PCL blends at high PCL concentrations[8,9]. The spherulitic morphology of crystallized Phenoxy/PCL blends, as obtained by optical microscopy, shows a superstructure analogous to that reported for CPE/PCL blends[9] (*Figure 4*). Again, a fibrillar fine texture of the spherulites is observed and Phenoxy is segregated interspherulitically at low PCL concentrations. At high PCL concentrations (>60 wt%), a volume-filling spherulitic network is formed, while interspherulitic segregation occurs at higher Phenoxy concentrations.

The next problem to be faced refers to the localization of the amorphous Phenoxy component within the spherulites of the PCL-rich blends. SAXS experiments might provide an answer with respect to the occurrence of interlamellar segregation of Phenoxy during the crystallization process of PCL (*Figure 5*). As can be seen from these curves, the angle where a maximum in the scattered intensity is observed initially decreases with

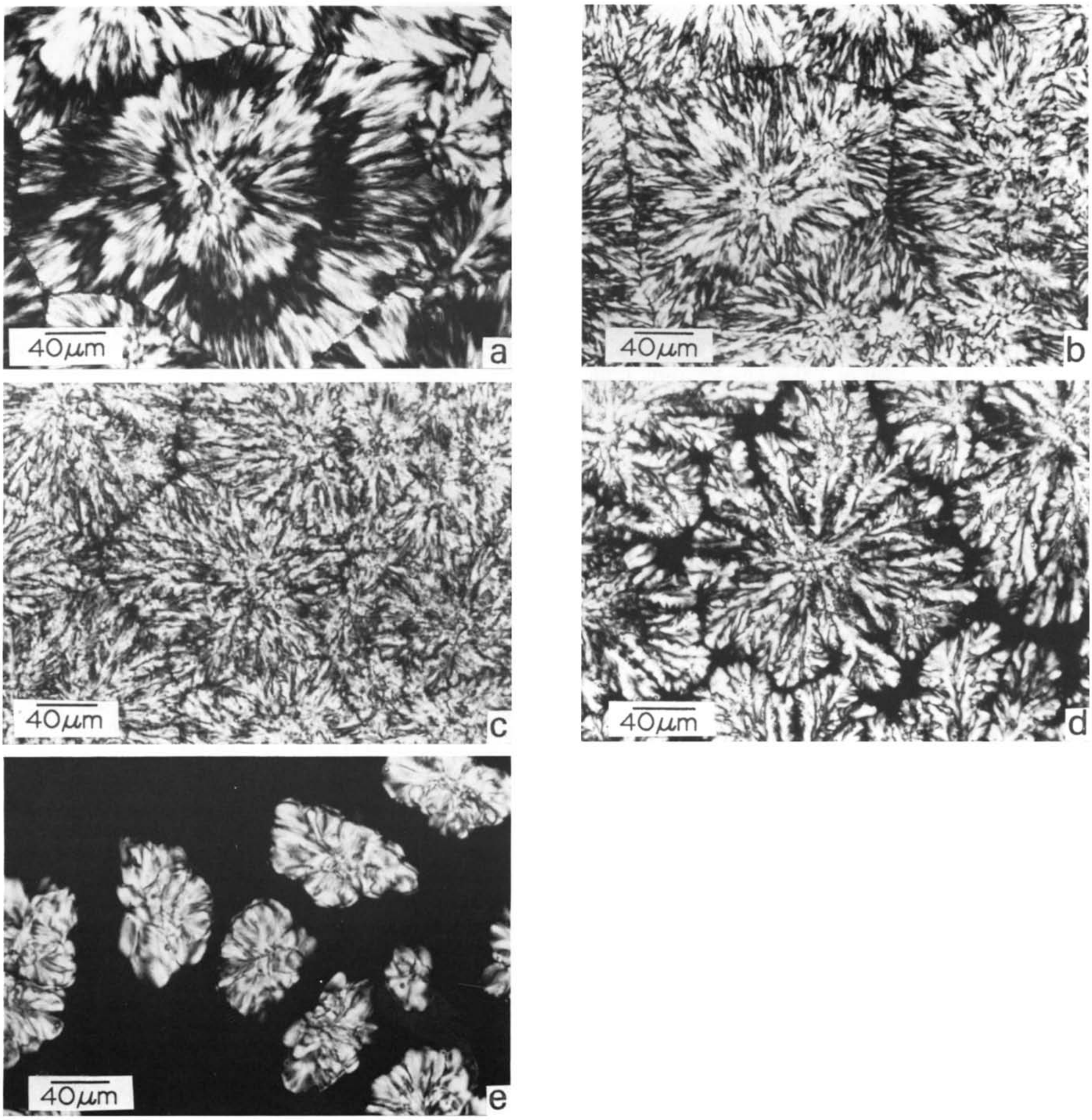

Figure 4 Spherulitic morphology of Phenoxy/PCL blends isothermally crystallized at 45°C for 14 days. Blends are: (a) 10/90; (b) 20/80; (c) 30/70; (d) 40/60; (e) 50/50

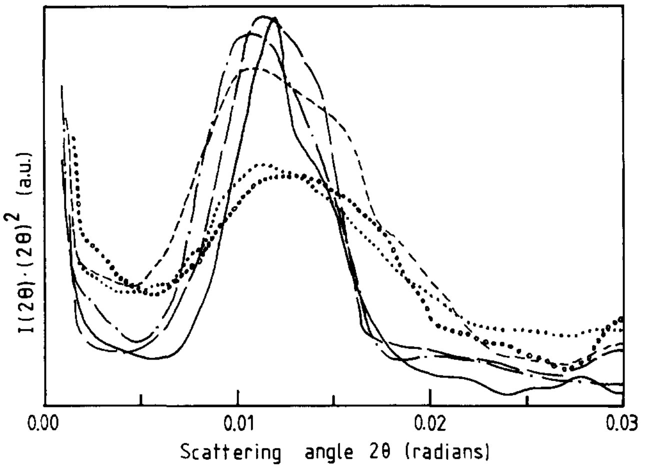

Figure 5 Desmeared and Lorentz-corrected SAXS curves for Phenoxy/PCL blends isothermally crystallized at 40°C for 14 days. Blends: ——, 0/100; — —, 10/90; —·—, 20/80; ----, 30/70; ●●●●●, 40/60; ○○○○, 50/50

increasing Phenoxy content up to 20 wt%, and subsequently increases at higher Phenoxy concentrations. A better morphological appreciation of this observation follows from inspection of the experimental one-dimensional correlation functions obtained by Fourier transformation of the scattered data (*Figure 6*). All correlation functions exhibit a linear decrease of the self-correlating triangle, typical of the presence of a well defined core of the lamellar crystals. A distinct maximum is observed for all the correlation functions corresponding with the long spacing L. The values of the structural long spacing as obtained from the desmeared Lorentz-corrected scattering curves are represented in *Figure 7*; the shape of this long-spacing curve is similar to that for CPE/PCL blends[9]. The higher tendency to segregate Phenoxy interlamellarly can be understood in terms of the lower mobility of Phenoxy as compared with CPE in blends with PCL. In spite of the fact that Phenoxy has roughly the same glass transition temperature as PVC, it only segregates partially between the crystalline lamellae, while PVC is reported to be rejected in the interlamellar zones during the crystallization of PCL in PVC/PCL blends, even at high PVC contents[3]. This clearly indicates that, apart from the effect of T_g on the mobility of the amorphous diluent in the blend, other effects have to be taken into account, such as for example the mutual friction as a result of the degree of interaction between the blended macromolecules[13,14]. The latter statement could be one of the possible reasons for the dissimilar segregation behaviour of PCL in Phenoxy/PCL and PVC/PCL blends.

Melting behaviour of semicrystalline Phenoxy/PCL blends

Isothermally crystallized Phenoxy/PCL blends containing at least 50 wt% PCL exhibit a double melting behaviour (*Figure 8*), similar to that usually observed in miscible blends of crystallizable and amorphous polymers[8,9]. The maximum of the second melting endotherm decreases with increasing Phenoxy content (*Figure 9*), a phenomenon that can be explained in two ways. One can argue that the thickness of the crystalline lamellae will be decreased in the presence of Phenoxy (morphological effect) or that the melting-point depression points to a negative value of the χ parameter (thermodynamic effect). The melting enthalpy of PCL in the blend is substantially lowered and tends to zero at about 70 wt% Phenoxy (*Figure 10*). The absence of crystallization in Phenoxy-rich blends has to be ascribed to the high glass transition temperature of the blend as compared to the isothermal crystallization temperature. Lack of segmental mobility below T_g of the blends blocks the diffusion of PCL and, as a consequence, the development of crystallinity.

The double melting behaviour can be attributed to a secondary crystallization process, as demonstrated in

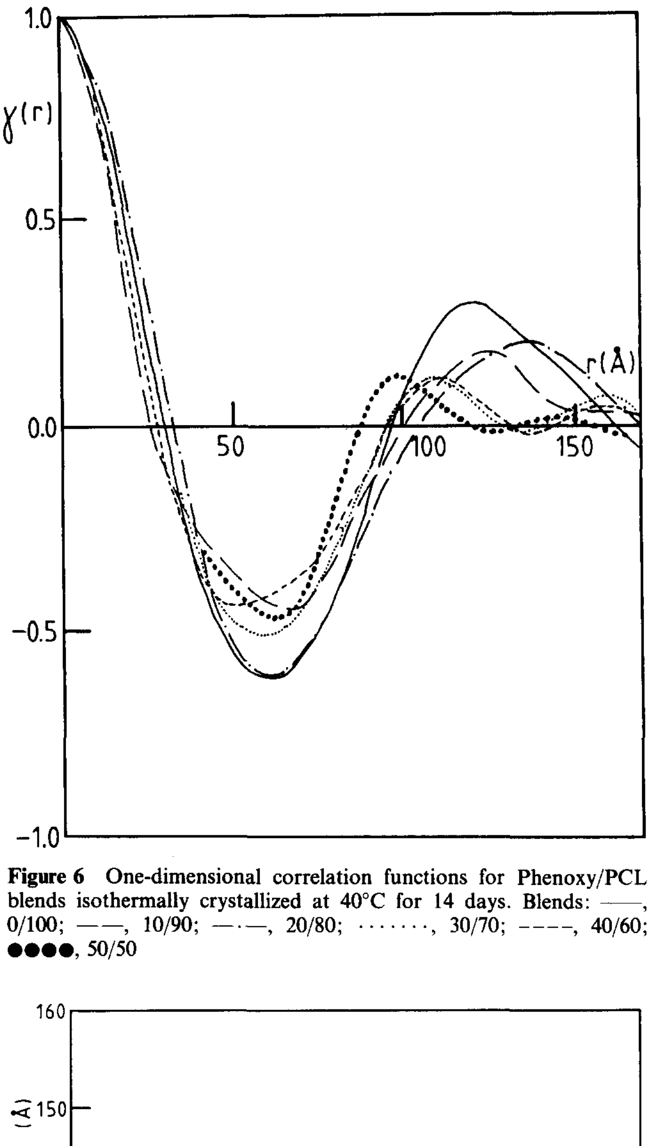

Figure 6 One-dimensional correlation functions for Phenoxy/PCL blends isothermally crystallized at 40°C for 14 days. Blends: ——, 0/100; — —, 10/90; —·—, 20/80; ·······, 30/70; ----, 40/60; ●●●●, 50/50

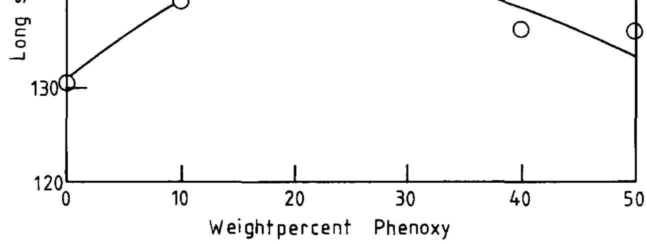

Figure 7 Structural long spacing L as a function of the Phenoxy content for Phenoxy/PCL blends isothermally crystallized at 40°C for 14 days

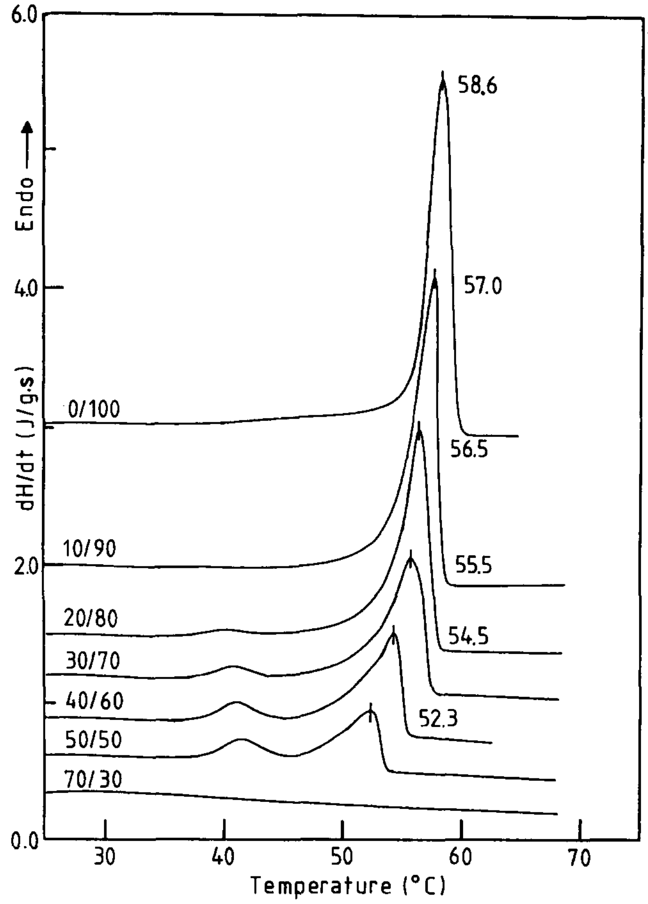

Figure 8 D.s.c. melting traces at Phenoxy/PCL blends isothermally crystallized at 25°C for 14 days

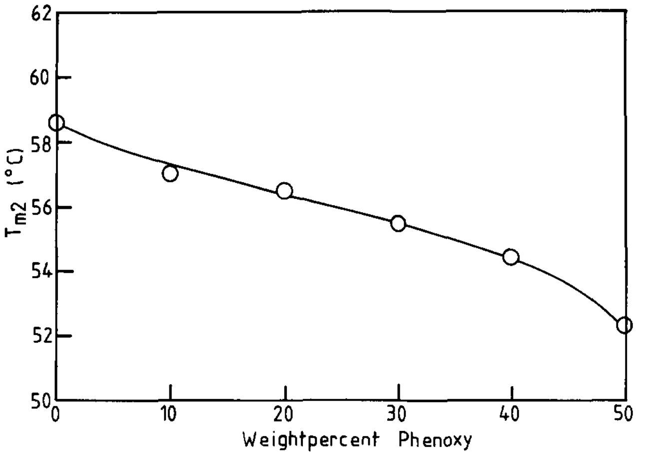

Figure 9 Influence of Phenoxy content on the position of the second melting peak of PCL in Phenoxy/PCL blends isothermally crystallized at 25°C for 14 days

Figure 11. A similar crystallization experiment as previously described for CPE/PCL[9] blends was carried out on Phenoxy/PCL blends. The isothermal crystallization process was interrupted after different time intervals and the d.s.c. melting trace was immediately recorded. As can be seen from *Figure 11*, the highest melting endotherm reaches a constant area and position on the temperature scale after short isothermal crystallization times (primary crystallization), while the lower melting peak only appears after much longer crystallization times (secondary crystallization). The secondary crystallization is supposed to occur in the amorphous phase segregated during the primary crystallization of PCL, resulting in a slower crystallization process as this happens in the presence of a higher Phenoxy concentration. A second consequence of this crystallization in a more diluted environment is the lower melting point of the secondary crystallized PCL (morphological as well as thermodynamic effects). It should be emphasized that the observed melting behaviour of PCL in Phenoxy/PCL blends also proves the molecular miscibility of both mixed polymers in the molten state.

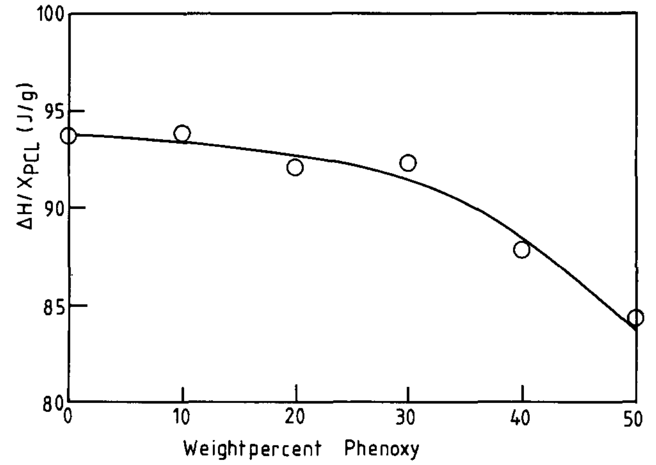

Figure 10 Influence of Phenoxy content on the melt enthalpy of PCL in Phenoxy/PCL blends isothermally crystallized at 25°C for 14 days

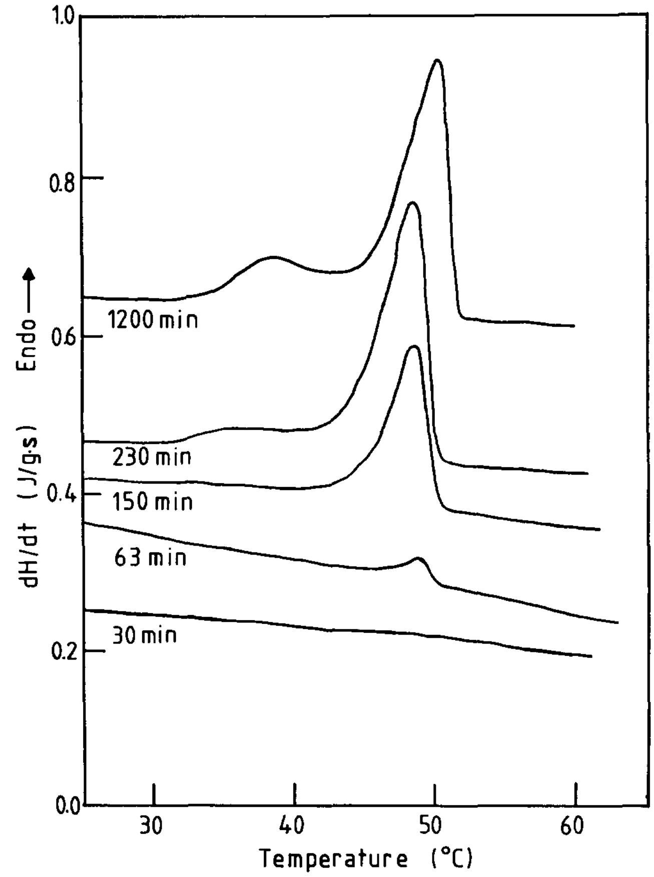

Figure 11 Double melting behaviour of the Phenoxy/PCL 40/60 blend isothermally crystallized at 25°C for different time intervals

CONCLUSIONS

It has been shown that Phenoxy and PCL are miscible over the entire composition and temperature range. The segregation behaviour of Phenoxy during the crystallization of PCL in the blends is similar to that observed for CPE/PCL blends, but the diffusion of Phenoxy is more restricted and consequently a higher amount of interlamellar segregation of Phenoxy is found, especially at low Phenoxy contents. Interspherulitic segregation of Phenoxy has been observed in blends containing 40 to 50 wt% Phenoxy at high crystallization temperatures. The double melting behaviour in the semicrystalline Phenoxy/PCL blends has been attributed to a secondary crystallization process.

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REFERENCES

1 Khambatta, F. H., Warner, F. P., Russell, T. and Stein, R. S. *J. Polym. Sci. (A-2)* 1976, **14**, 1391

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

3 Russell, T. P. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 999

4 Ong, C. J. and Price, F. P. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 45

5 Morra, B. S. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 2261

6 Morra, B. S. and Stein, R. S. *Polym. Eng. Sci.* 1984, **24** (5), 311

7 Wenig, W., Karasz, F. E. and MacKnight, W. J. *J. Appl. Phys.* 1975, **46** (10), 4194

8 Defieuw, G., Groeninckx, G. and Reynaers, H. in 'Integration of Polymer Science and Technology' (Eds P. J. Lemstra and L. A. Kleintjens), Elsevier Applied Science, London, 1988, Vol. 2, pp. 238–42

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

10 Brode, G. L. and Koleske, J. V. *J. Macromol. Sci.–Chem. (A)* 1972, **6** (6), 1109

11 Vandermarliere, M., PhD Thesis, KU Leuven, 1986

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

13 Brochard, F., Jouffroy, J. and Levinson, P. *Macromolecules* 1983, **16**, 1638

14 Brochard, F., Jouffroy, J. and Levinson, P. *Macromolecules* 1984, **17**, 2925