# Miscibility, crystallization and melting behaviour, and morphology of binary blends of polycaprolactone with styrene-*co*-maleic anhydride copolymers

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Blends of polycaprolactone (PCL) and random copolymers of styrene and maleic anhydride (SMA) with different maleic anhydride contents were prepared by the coprecipitation technique. The miscibility of both polymers in the melt and in the solid state was studied by means of optical microscopy, light transmission measurements and dynamic mechanical analysis. The crystallization behaviour of PCL in the miscible blends was examined using optical microscopy and the morphology of the semicrystalline PCL/SMA blends was investigated by means of small-angle X-ray diffraction measurements. Their melting behaviour was studied by differential scanning calorimetry. SMA containing 14 and 25 wt% MA was found to be miscible with PCL over the entire composition and temperature range (up to 200°C). SMA appears to segregate interlamellarly during the isothermal crystallization of PCL. The double melting behaviour of PCL in the blends was attributed to a secondary crystallization process and not to a partial melting–recrystallization–remelting process.

**(Keywords: crystallization; semicrystalline morphology; polymer blends)**

## INTRODUCTION

There is an increasing interest in the use of polymer blends for technological applications and many fundamental studies have been devoted to the melt miscibility of polymers. A restricted number of studies deal with the semicrystalline morphology of blends involving a crystallizable and an amorphous component[1–10].

In our laboratory, basic research was started on the diffusion and segregation processes occurring during the crystallization of one of the components of a binary miscible blend. The semicrystalline morphology after isothermal crystallization of polycaprolactone (PCL) in chlorinated polyethylene (CPE)/PCL and poly(hydroxy ether of bisphenol A) (Phenoxy)/PCL blends has already been reported in the previous papers of the present series[8–10]. In both blends, the amorphous diluents are rather mobile and it has been shown that the CPE or Phenoxy molecules can diffuse over rather large distances during the lamellar growth process of PCL. This long-range diffusion results in an interfibrillar as well as interspherulitic segregation of the amorphous polymers at low PCL concentrations and high crystallization temperatures.

In the present study, a glassy rigid-chain polymer (poly(styrene-*co*-maleic anhydride) (SMA)) was blended with PCL and the segregation of the amorphous SMA during the crystallization of PCL was investigated in detail.

## EXPERIMENTAL

### *Materials*

Styrene-*co*-maleic anhydrides, synthesized by radical copolymerization, were kindly supplied by DSM Central Research, Geleen, The Netherlands.

Polycaprolactone was a commercial product obtained from Aldrich Chemicals. Average molecular weights as determined by g.p.c. analysis relative to polystyrene standards at 25°C using tetrahydrofuran (THF) as a solvent are given in *Table 1*. Blends of different compositions were prepared by coprecipitation from a 3% THF (w/v) solution in hexane.

**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 |
| SMA14 | 134 000 | 58 900 | 2.26 |
| SMA25 | 118 000 | 50 200 | 2.35 |

### *Techniques*

Dynamic mechanical analysis, differential scanning calorimetry, small-angle X-ray diffraction and optical microscopy have been used to characterize the phase behaviour and semicrystalline morphology of the binary polymer blends. Experimental details and sample preparation have been reported in previous papers in this journal[9,10].

## RESULTS AND DISCUSSION

### *Miscibility of SMA with PCL*

It is well known that oligomeric polystyrene is miscible with PCL and that such blends exhibit a composition-dependent upper critical solution temperature

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behaviour[11]. For higher-molecular-weight polystyrene, however, the contribution of the entropy of mixing is too low to compensate for the positive enthalpy of mixing involving immiscibility.

In order to enhance miscibility in such binary blends, specific interacting groups have to be incorporated in the polymer backbone by copolymerization or chemical modification to increase the degree of mutual interaction[12]. Copolymerization of styrene with acrylonitrile[13–19] as well as with allyl alcohol[20] has proved to be an effective way to introduce interacting groups and to 'miscibilize' styrenic polymers with polycaprolactone.

In this work, samples of polystyrene randomly copolymerized with maleic anhydride have been used to achieve miscible SMA/PCL blends. There is a two-fold reason for the selection of this comonomer: (i) maleic anhydride has a strong dipole moment, and (ii) introduces stiff links (five-membered rings) into the polymeric chain. Both effects contribute to realize a high glass transition temperature ($T_g$) of SMA copolymers. Consequently, if miscible blends can be obtained for a given MA content, the crystallization process of PCL can be studied in the presence of a rather immobile amorphous diluent.

Binary blends of PCL and SMA were prepared from the two types of SMA reported in the 'Experimental' part. Their glass transition behaviour was studied on quenched amorphous samples, since crystallization of PCL in a miscible polymer blend changes the composition of the amorphous phase (solid–liquid phase separation). Copolymers of styrene with 14 wt% MA form miscible blends with PCL, as evident from a single narrow tan $\delta$ peak, intermediate between those of the pure polymers (*Figure 1*). A similar behaviour is observed for SMA25/PCL blends (*Figure 2*); these blends however show higher $T_g$ values than the SMA14/PCL blends with the same composition. This difference in blend $T_g$ values can be ascribed to the rather pronounced difference in $T_g$ between pure SMA14 and SMA25. Incorporation of more MA rings in the polystyrene backbone results in an increase in the number of intermolecular interactions and in a decrease in chain flexibility.

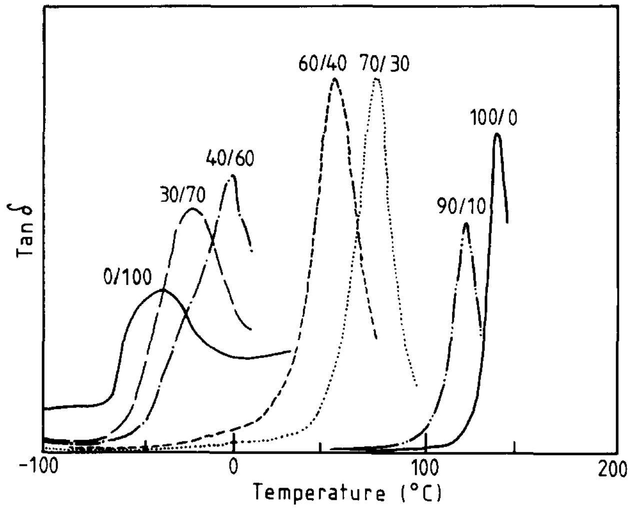

Figure 1 D.m.a. of quenched amorphous SMA14/PCL blends

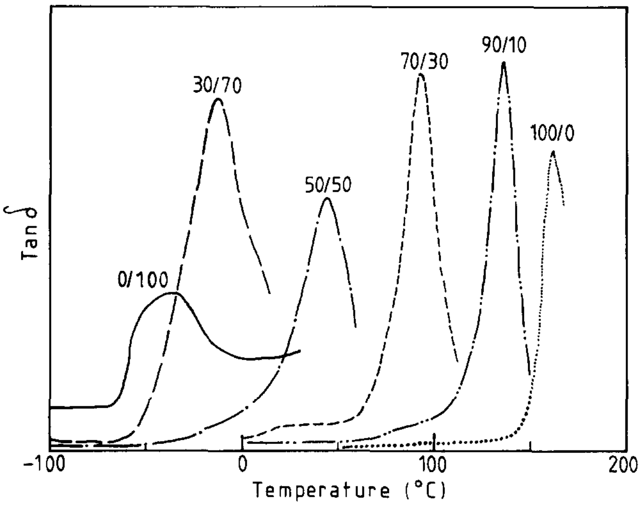

Figure 2 D.m.a. of quenched amorphous SMA25/PCL blends

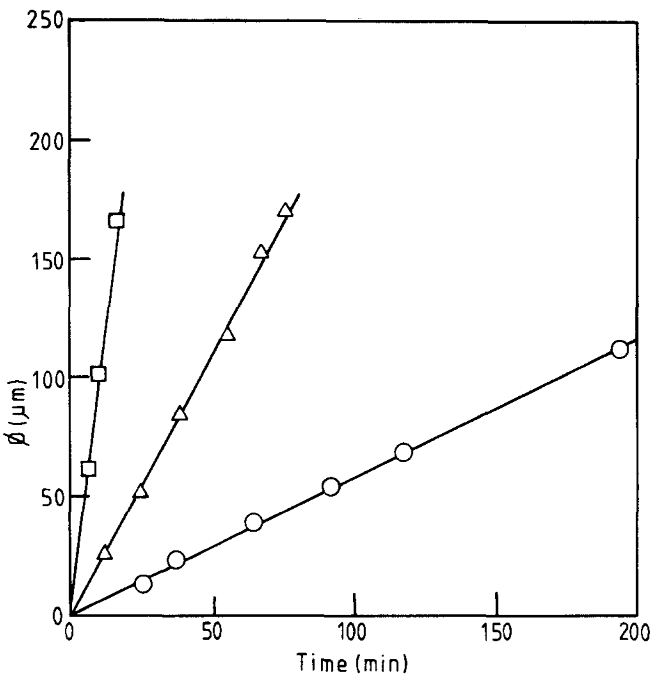

Figure 3 Spherulite growth in SMA14/PCL blends isothermally crystallized at 45°C. Blends: □, 0/100; △, 10/90; ○, 20/80

All binary blends of the types SMA14/PCL and SMA25/PCL are transparent in the temperature range 60–200°C and no lower critical solution temperature behaviour could be detected by light transmission measurements.

Dipole–dipole interactions as well as the 'repulsion effect' were believed to be responsible for the observed degree of miscibility.

### *Crystallization behaviour of PCL in miscible SMA/PCL blends*

It has long been shown that the determination of the spherulitic growth rate of a crystallizable polymer in a blend of a crystallizable and an amorphous polymer provides information on the degree of miscibility in the blends[21]. A study of the spherulitic growth rate of PCL in the binary SMA/PCL blends at low SMA concentration revealed a substantial decrease of the growth rate in both SMA14/PCL (*Figure 3*) and SMA25/PCL (*Figure 4*) blends with increasing SMA content. Moreover, a pronounced difference in spherulitic growth rate is found between the SMA14/PCL 10/90 and the SMA25/PCL 10/90 blends (*Figure 5*), although the $T_g$ of the blends is roughly the same. This observation clearly indicates the involvement of local diffusion effects during the lamellar

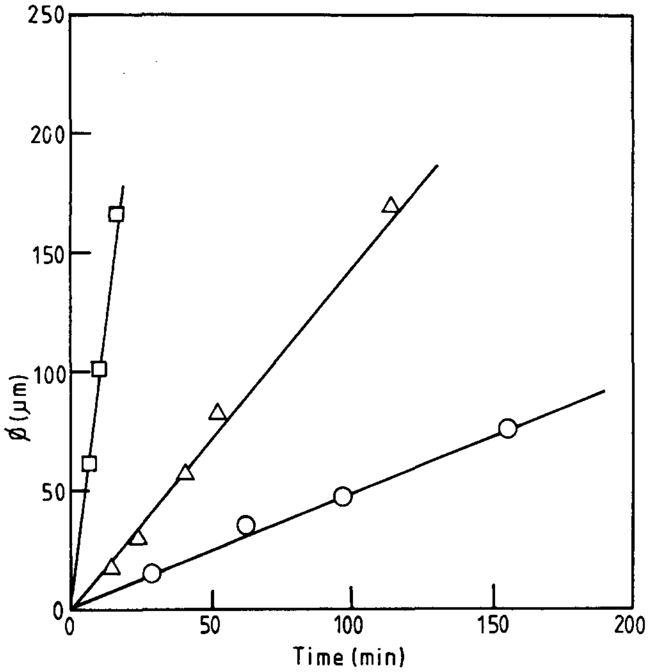

**Figure 4** Spherulite growth in SMA25/PCL blends isothermally crystallized at 45°C. Blends: □, 0/100; △, 10/90; ○, 20/80

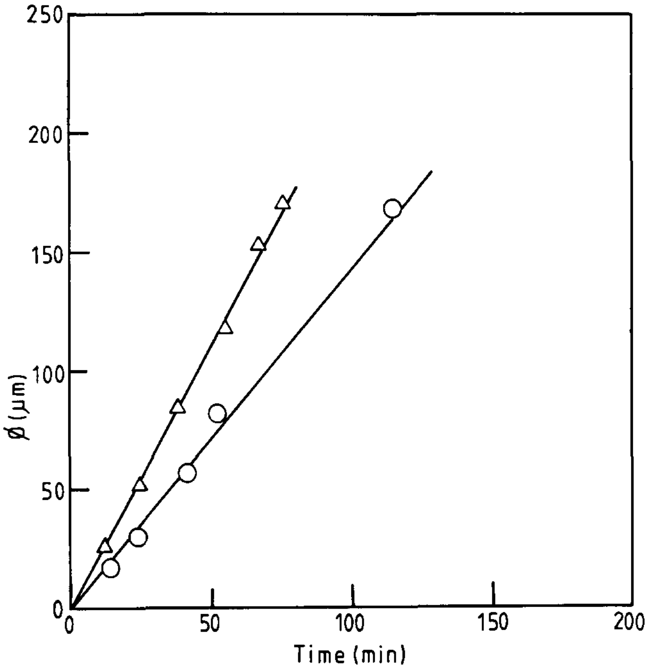

**Figure 5** Spherulite growth in SMA/PCL 10/90 blends isothermally crystallized at 45°C. △, 14% MA; ○, 25% MA

growth process of PCL. Both the lower chain flexibility of SMA25 and possibly the higher degree of mutual friction[22,23] with PCL result in a much more restricted diffusion process of the amorphous diluent for SMA25/PCL blends than for the SMA14/PCL blends.

The spherulitic growth rate of PCL in blends containing more than 20 wt% SMA could not be determined by optical microscopy due to the increasing nucleation density as a function of increasing SMA content. Theoretically, small angle laser light scattering could be of use; however, attempts to measure $H_v$ scattering patterns during crystallization remained unsuccessful since no way was found to prepare unoriented thin films (±20 μm) of the polymer blends in the melt.

Apart from the present evidence, other indications for the molecular miscibility on the molecular level of SMA14 and SMA25 with PCL will be given in the following sections where the semicrystalline morphology and the melting behaviour of PCL in the blends is presented.

### *Segregation phenomena in and semicrystalline morphology of SMA/PCL blends*

The liquid–solid phase separation occurring during the crystallization process of PCL in miscible SMA/PCL blends requires the segregation and diffusion of SMA away from the crystalline nucleus. As already mentioned in the previous section, the stiff, high-$T_g$ SMA molecules display a rather limited mobility as compared with amorphous diluents such as CPE and Phenoxy described in previous papers in this series[8–10].

No interspherulitic segregation of SMA could be detected at any SMA content, not even at high crystallization temperatures (*Figure 6*). In contrast to the spherulitic superstructure of CPE/PCL and Phenoxy/PCL blends, volume-filling spherulitic textures are always observed. Consequently, amorphous SMA molecules have to be segregated interlamellarly or interfibrillarly during the crystallization process of PCL. With respect to this point, measurements of SAXS patterns can provide experimental evidence on the presence or absence of interlamellar incorporation of SMA during the lamellar growth process in crystallizable SMA/PCL blends. The scattering angle at maximum intensity, after desmearing and subsequent Lorentz correction, decreases with increasing SMA content in SMA14/PCL as well as in SMA25/PCL (*Figures 7* and *8*) blends. This is a first indication for the interlamellar incorporation of SMA during isothermal crystallization in SMA/PCL blends. The long spacing $L$ increases drastically with increasing SMA content for both blends (*Figure 9*). Similar observations have been made in the literature for styrene–acrylonitrile (SAN)/PCL[18], poly(vinylidene fluoride (PVDF)/atactic poly(methyl methacrylate) (aPMMA)[6,24], poly(ethylene oxide) (PEO)/aPMMA[25–31], PEO/syndiotactic PMMA[31] and poly(vinyl chloride) (PVC)/PCL[1–4] blends. A better morphological appreciation of this observation follows from inspection of the experimental one-dimensional correlation functions obtained by Fourier transformation of the scattering data[9] (*Figure*

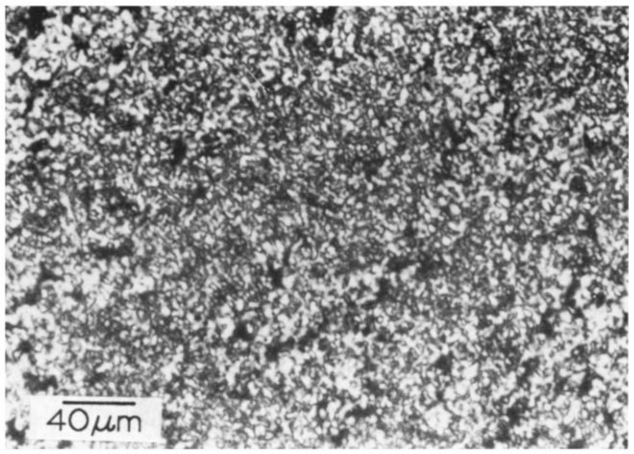

**Figure 6** Spherulitic morphology of SMA14/PCL 50/50 blend isothermally crystallized at 45°C for 14 days

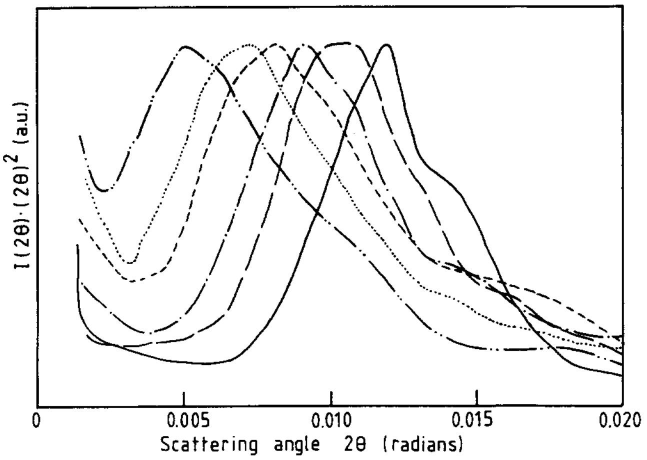

**Figure 7** Desmeared and Lorentz-corrected SAXS curves for SMA14/PCL blends isothermally crystallized at 40°C for 14 days. Blends: ——, 0/100; — —, 10/90; —·—, 20/80; ----, 30/70; ······, 40/60; —··—, 50/50

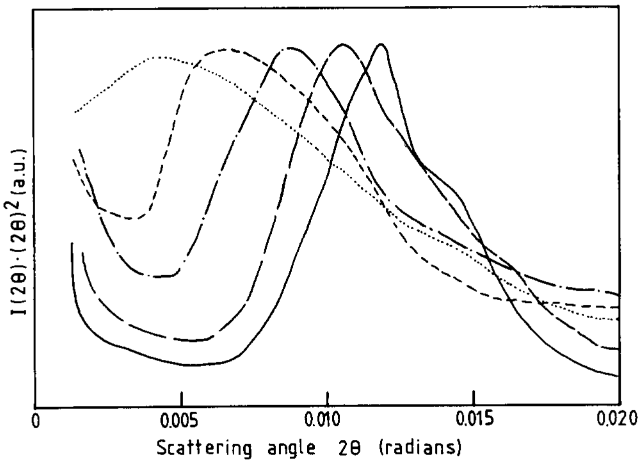

**Figure 8** Desmeared and Lorentz-corrected SAXS curves for SMA25/PCL blends isothermally crystallized at 40°C for 14 days. Blends: ——, 0/100; — —, 10/90; —·—, 20/80; ----, 30/70; ······, 40/60;

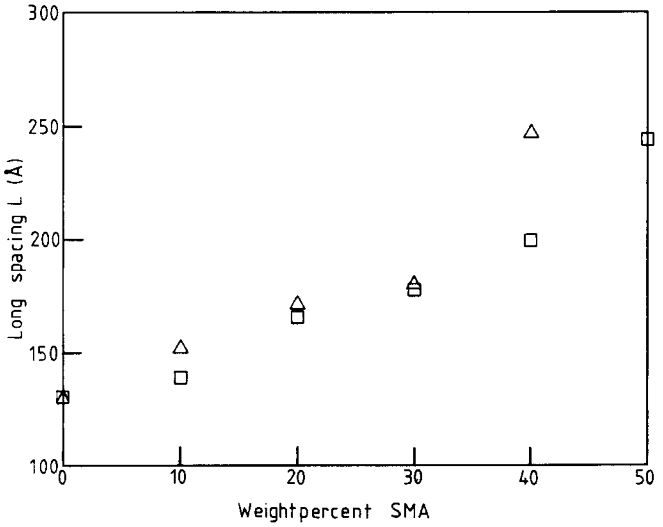

**Figure 9** Structural long spacing $L$ as a function of the SMA concentration for SMA/PCL blends isothermally crystallized at 40°C for 14 days. □, SMA14; △, SMA25

*10*). All correlation functions exhibit a linear decrease of the self-correlating triangle typical of the presence of a well defined core of lamellar crystals. A distinct minimum is observed for the correlation functions of blends containing up to 30 wt% SMA14; a further increase of the SMA content results in a flattening and/or disappearance of the maximum probably due to a lack of correlation of lamellae in stack-like structures.

The occurrence of interlamellar segregation and the absence of interspherulitic segregation in SMA/PCL blends can be fully understood if one considers the low chain mobility of SMA in SMA/PCL blends. SMA molecules diffuse away from the crystal growth nucleus slowly as compared to CPE and Phenoxy in blends with PCL[8–10]. The low chain flexibility and high $T_g$ and/or high thermodynamic interaction parameter $\chi$ of SMA with PCL could be responsible for the hindered diffusion process. However, no experimental data are actually available with respect to the latter parameter.

### *Melting behaviour of PCL in the semicrystalline SMA/PCL blends*

A double melting behaviour is observed for isothermally crystallized SMA/PCL blends containing at least 50 wt% PCL in SMA14/PCL blends (*Figure 11*) and 60 wt% PCL in SMA25/PCL blends (*Figure 12*). A similar behaviour was previously reported for miscible semicrystalline CPE/PCL[8,9] and Phenoxy/PCL[10] blends, as well as in the literature for other miscible blends of crystallizable and amorphous polymers. The position of

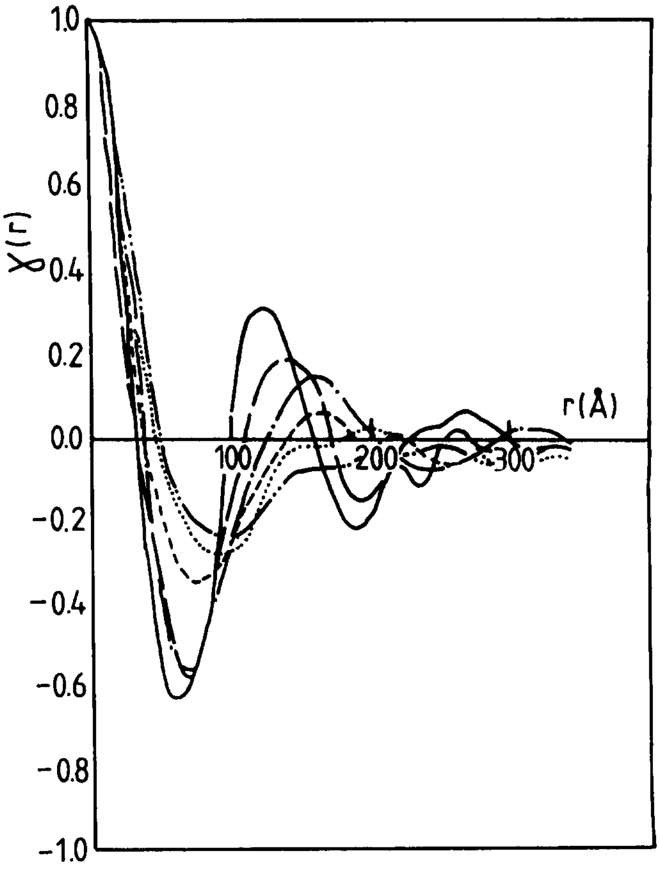

**Figure 10** One-dimensional correlation functions for SMA14/PCL blends isothermally crystallized at 40°C for 14 days. Blends: ——, 0/100; — —, 10/90; —·—, 20/80; ---, 30/70; ·····, 40/60; —··—, 50/50

the maximum of the second melting endotherm ($T_{m2}$) decreases with increasing SMA14 and SMA25 content (*Figure 13*), a phenomenon that can be explained by the decrease of the thickness of the crystalline lamellae of PCL and/or the thermodynamic melting-point depression caused by a negative $\chi$ parameter. The decrease of $T_{m2}$ in SMA25/PCL is more pronounced than in SMA14/PCL blends, which is also attributed to both morphological (thinner crystalline lamellae as a result of the higher $T_g$ of SMA25) and/or thermodynamic (a more negative $\chi$ parameter in SMA25/PCL blends) effects.

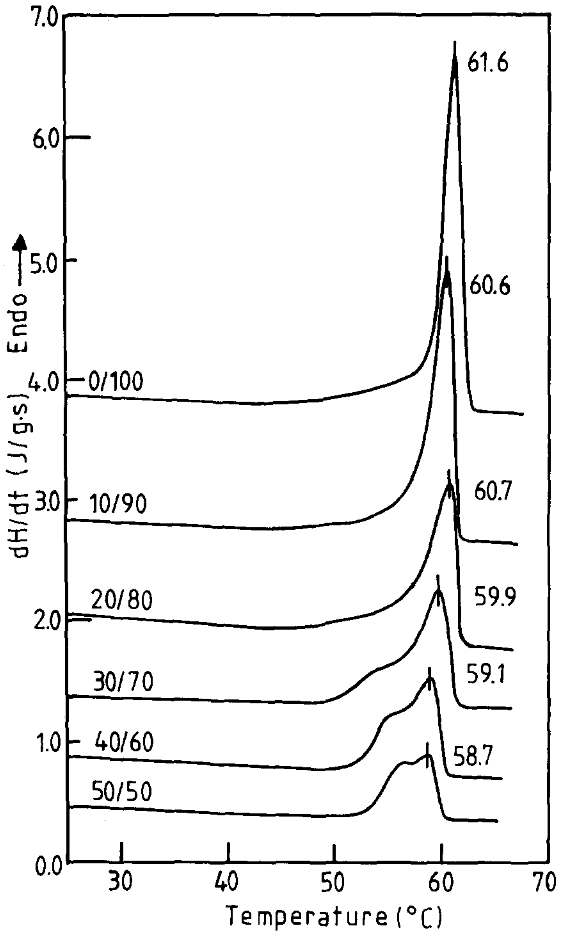

**Figure 11** D.s.c. melting traces of SMA14/PCL blends isothermally crystallized at 35°C for 14 days

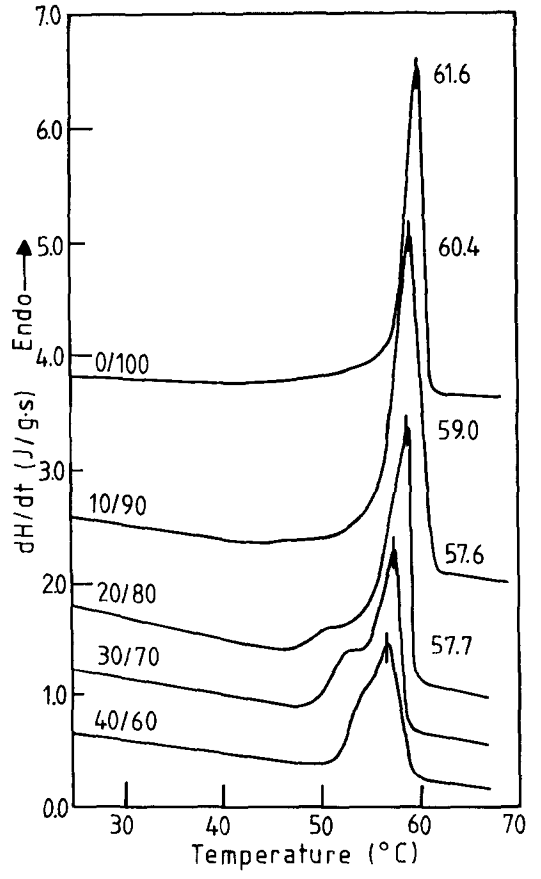

**Figure 12** D.s.c. melting traces of SMA25/PCL blends isothermally crystallized at 35°C for 14 days

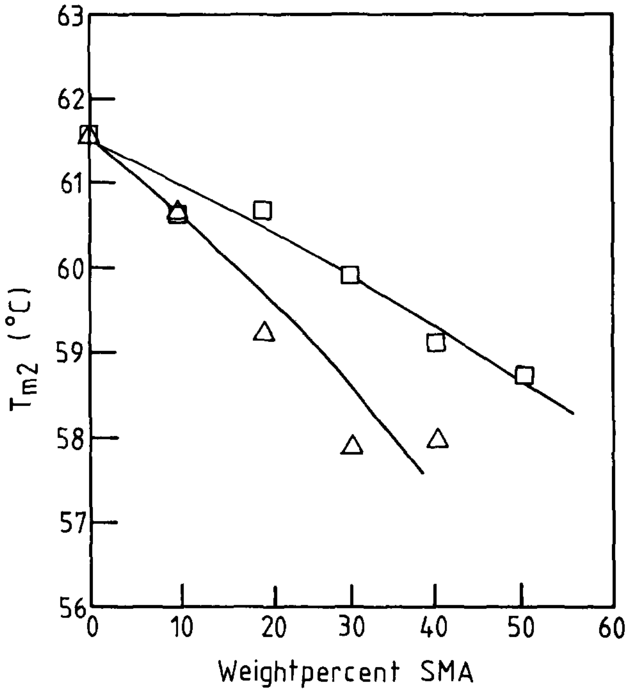

**Figure 13** Influence of the SMA content on the position of the second melting endotherm of PCL in SMA/PCL blends, isothermally crystallized at 35°C for 14 days. □, SMA14; △, SMA25

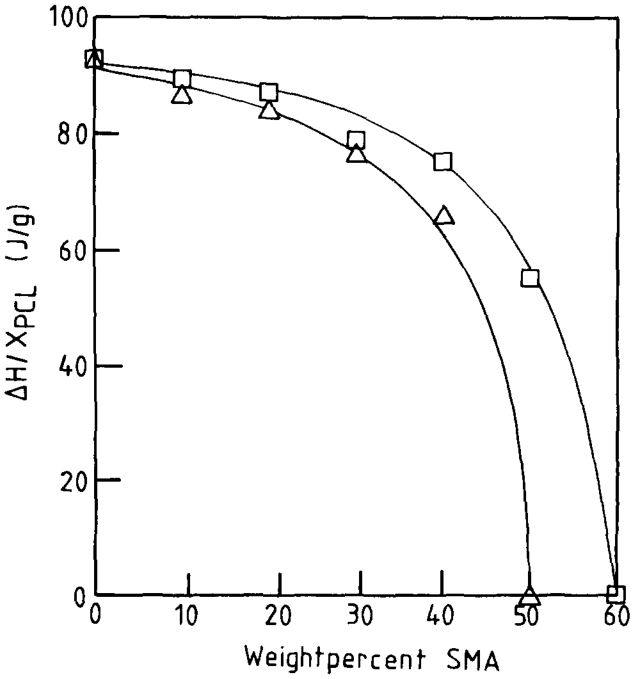

**Figure 14** Influence of the SMA content on the melt enthalpy of PCL in SMA/PCL blends isothermally crystallized at 35°C for 14 days. □, SMA14; △, SMA25

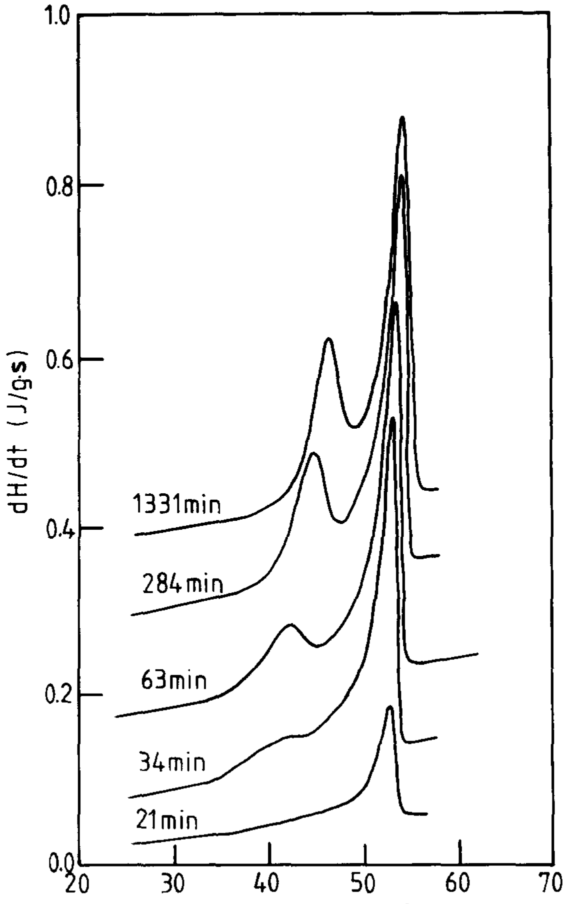

**Figure 15** Double melting behaviour of SMA14/PCL 40/60 blends isothermally crystallized at 25°C for different times

The melting enthalpy of PCL, which is a measure of the degree of crystallinity, is much more affected by addition of SMA25 than by addition of SMA14 (*Figure 14*), a phenomenon that can be understood in terms of the higher $T_g$ of SMA25. The blend $T_g$ exceeds the isothermal crystallization temperature at lower SMA contents for SMA25. As a consequence, the crystallization process of PCL is kinetically prevented at lower concentration of the amorphous diluent SMA in the SMA25/PCL blends.

The double melting behaviour of semicrystalline SMA/PCL blends has been studied by time-controlled crystallization experiments, as previously reported for CPE/PCL[8,9] and Phenoxy/PCL[10] blends. The isothermal crystallization process was interrupted after different crystallization times and the melting trace was immediately recorded (*Figure 15*). The second melting endotherm corresponding to the highest melting peak ($T_{m2}$) reaches a constant surface and position on the temperature scale after isothermal crystallization of about 30 min. The melting peak at lower temperatures only appears after prolonged crystallization times and is ascribed to a secondary crystallization process occurring in the amorphous phase segregated during the primary crystallization. These crystals melt at lower temperatures, since they were formed in the presence of an increased SMA concentration.

## CONCLUSIONS

On the basis of different experimental approaches, SMA containing 14 and 25 wt% MA has been shown to be completely miscible with PCL. SMA is segregated interlamellarly during the crystallization process of PCL in the blends over the whole composition and temperature range, since the long-range diffusion and segregation of SMA is prevented. Amorphous blends were obtained above 40 wt% (SMA25) and 50 wt% (SMA14) amorphous diluent. The double melting behaviour of semicrystalline blends has been proved to be due to a secondary crystallization process.

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