

# Miscibility Behaviour of Bisphenol-A Polycarbonate and Poly(para-chlorostyrene)

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## SYNOPSIS

The miscibility behaviour of bisphenol-A polycarbonate (PC) and poly(para-chlorostyrene) (PpClS) has been investigated. Special attention has been paid to the influence of the molar mass of PpClS. Molar masses varying from 10 to > 1,000 kg/mol were used. The blends were studied by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and scanning and transmission electron microscopy (SEM and TEM). It was concluded that the blends of all three PpClS grades and PC phase separate. In the low concentration region, some intermixing was found, especially for the blend with the low molar mass PpClS. The most important effect of lowering the molar mass of PpClS was an acceleration of the phase separation. The combination of SEM with electron probe X-ray microanalysis (EPMA) gave qualitative information on the miscibility behaviour and was found to be a useful extension of routine microscopy techniques used in blend studies.

## INTRODUCTION

Until now, a variety of blends was known to be partially or completely miscible. These systems consist both of homopolymers and copolymers, such as PPO/PS<sup>1</sup> and PMMA/SAN.<sup>2</sup> In general, however, polymer mixtures tend to be immiscible. The miscibility behaviour at given temperature  $T$  and pressure  $P$  is controlled by the Gibbs free energy of mixing  $\Delta G_m = \Delta H_m - T\Delta S_m$ . Due to the connectivity of the polymer segments, the number of possible arrangements is reduced. Therefore, the combinatorial entropy for polymer blends is very small compared to mixtures of low molecular weight compounds. Since most polymer systems show positive values for the enthalpy of mixing, demixing is usually observed. In the case of specific interactions between the polymers, it is possible to obtain a negative value of  $\Delta H_m$ , which means that miscibility may be achieved.

In the literature, several studies dealing with miscibility of polyesters and chlorinated polymers are reported. For example poly(vinylchloride) (PVC) has been shown to be miscible with several types of polyesters including poly(caprolactone),<sup>3</sup> poly(butylene terephthalate),<sup>4</sup> poly(valerolactone),<sup>5,6</sup> and poly(1,4-butylene adipate).<sup>7</sup> The miscibility of the polyester/PVC blends is likely due to specific interactions between the carbonyl group of the polyester and the  $\alpha$ -hydrogens of PVC<sup>8</sup> (hydrogen-bonding type interaction).

Another type of chlorinated polymer used in blend studies is poly(chlorostyrene) (PClS). Blends of PPO and PClS or PPO and copolymers of PS and PClS have been investigated thoroughly.<sup>9-12</sup> It was found that PPO and poly(para-chlorostyrene) (PpClS) are immiscible.<sup>9</sup> Blends of PPO and copolymers of PS and PpClS<sup>9,10</sup> or copolymers of PpClS and poly(ortho-chlorostyrene) (PoClS)<sup>11,12</sup> are miscible for a certain range of copolymer composition. For these systems it is not clear whether miscibility is only due to the well-known repulsion effect in the copolymer, or whether specific interactions also play a role.

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Allard and Prud'Homme<sup>13</sup> investigated the blend of poly(caprolactone) and a copolymer of ortho- and para-chlorostyrene and concluded that the system was miscible over the whole range of compositions and temperatures studied.

From the above, one may conclude that there exists a favourable interaction between chlorinated polymers and polyesters. Because of the similarity between the structure of the ester unit and the carbonate unit, there is possibly also a favourable interaction between polycarbonate and chlorinated polymers. Furthermore, the solubility parameters of PpClS ( $\delta = 9.62 \text{ cal}^{0.5}/\text{cm}^{1.5}$ ) and bisphenol-A polycarbonate ( $\delta = 9.51 \text{ cal}^{0.5}/\text{cm}^{1.5}$ ) have almost the same value.<sup>14</sup> Although quantitative predictions are not to be expected using the solubility parameter approach, several miscible systems are reported in which the polymers, making part of the blend, show almost equal solubility parameters (e.g., PMMA/PVC,<sup>15</sup> PPO/PS<sup>16</sup>).

These considerations led to this study on the miscibility behaviour of polycarbonate and poly-(para-chlorostyrene).

## EXPERIMENTAL

### Materials

The polymers used in this study were bisphenol-A polycarbonate (PC) (CD-2000, Bayer AG, FRG) and poly(para-chlorostyrene). From the latter polymer, three grades with different molar masses were used. The two grades with the highest molar masses were obtained from Aldrich Chemical Corporation and were used as received. The low molar mass PpClS-3 was synthesized in our laboratory (see below). Table I shows the values for the number and mass average molar masses, molar mass distribution, and glass transition temperatures of the polymers used.

$M_w$  and  $M_n$  were determined by gel permeation chromatography with tetrahydrofuran as eluent at

25°C. The values reported are relative to polystyrene standards. The absolute value (as reported by the supplier) of  $M_w$  of PC is 20 kg/mol. The molar mass of PpClS-1 was too high to be determined by GPC.

### PpClS-3 Synthesis

The low molar mass PpClS-3 was synthesized by free radical solution polymerisation of para-chlorostyrene (pClS) (Aldrich). The solvent used was toluene and the initiator AIBN (2,2-azo-bis-isobutyronitrile). Monomer and solvent were distilled before use. *p*-Chlorostyrene was dissolved in 150 ml toluene 21.74 g (0.158 mol) and heated at 70°C; subsequently 0.73 g (0.004 mol) AIBN was added. The reaction was carried out in a nitrogen atmosphere and the reaction mixture was stirred continuously. After 8 h, the mixture was cooled to room temperature and poured into 500 ml isopropanol. The precipitated polymer was filtered and dried under vacuum at 70°C for 3 d.

### Blend Preparation

Blends were prepared by solution casting. The solvent used was dichloromethane for all cases. After evaporation of the solvent, the obtained films were dried under vacuum at 90°C for several days until a constant  $T_g$  was obtained.

The DSC experiments were performed on a Perkin-Elmer DSC-7. For all measurements, the scan rate was 20°C/min. The location of the  $T_g$  was determined at half height of the  $c_p$  transition.

The samples used for dynamic mechanical thermal analysis (DMTA) experiments were made by coprecipitation. Dichloromethane was used as solvent and methanol as nonsolvent (ratio 1 : 5). The coprecipitate was moulded in a press at 180°C. The DMTA measurements were performed on a Polymer Laboratories DMTA in bending mode (clamping dual cantilever). The scan rate used was 2°C/min. The frequency of the cyclic deformation was 1 Hz.

The sample for the TEM analysis containing 50% PpClS was prepared as follows: A small droplet of a dilute solution (2 g polymer in 100 ml dichloromethane) was put on a copper grid. After evaporation of the solvent and subsequent drying at 90°C, a thin film was obtained, which was used as such.

**Table I** Data on the Various Polymers Used in This Study

	$M_w$ (kg/mol)	$M_n$ (kg/mol)	$M_w/M_n$	$T_g$ (°C)
PC	35.7	16.7	2.1	145
PpClS-1	> 1,000	—	—	126
PpClS-2	232	45.4	5.1	126
PpClS-3	10	6.1	1.6	116

## RESULTS AND DISCUSSION

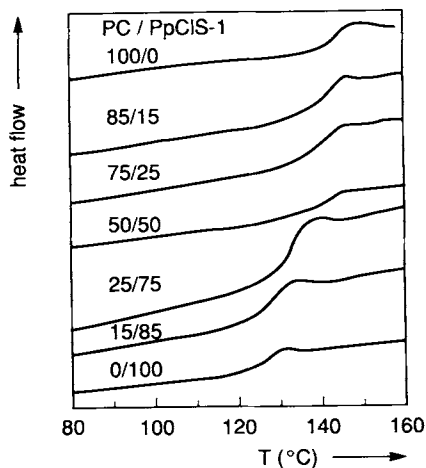
To find the relationship between the glass transition temperature and the blend composition, blends were

made by solution casting of the high molecular weight PpClS-1 and PC. Figure 1 shows the DSC curves for the various blends with different compositions. These curves show the presence of only one  $T_g$  for all compositions, which varies continuously with concentration. Figure 2 shows a plot of the glass transition temperatures vs. blend composition. The broken line represents the average glass transition temperature, given by:

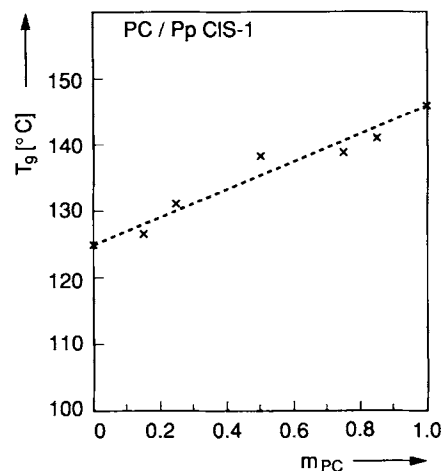
$$T_g = m_{PC} \times T_g(PC) + (1 - m_{PC}) \times T_g(PpClS). \quad (1)$$

The experimental points follow this relationship quite well, suggesting that the polymers PC and PpClS-1 are completely miscible for all compositions. However, a miscible blend normally gives homogeneous and transparent films. The blend films used for these DSC experiments were optically inhomogeneous, especially for the PpClS-1-rich compositions. Some parts of the films were almost transparent and other parts were almost completely white.

Figure 3 shows two scanning electron microscopy (SEM) pictures of the surface of one of these films (PC/PpClS-1 25/75). From the left picture, it is possible to distinguish two phases. One of these phases contains a lot of bubbles that have been trapped during evaporation of the solvent. The right shows the same spot using electron probe X-ray microanalysis (EPMA) with an energy dispersive detector, which shows a "chlorine-map." With this technique, the X-rays emitted by the chlorine atoms in PpClS-1 are detected. Chlorine-rich domains ap-



**Figure 1** DSC curves for various compositions (as indicated) of the PC/PpClS-1 blend (second scans).



**Figure 2** The glass transition temperature as a function of composition (mass fraction) for the PC/PpClS-1 blend.

pear as white speckles in the micrographs. From this picture, it is obvious that two different phases exist: one PpClS-1-rich phase and a PC-rich phase. At this time, it is not possible to make a statement on the absolute compositions of both phases; the picture shows only qualitative differences. Blend films with other compositions gave similar results.

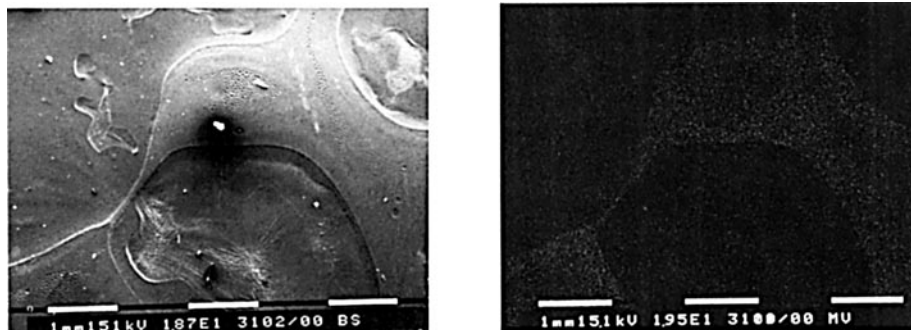
The occurrence of only one  $T_g$  in the differential scanning calorimetry (DSC) measurements suggests that the difference in the glass transition temperature of both phases is rather small. Demixing of the system occurs, but completion of the process is hampered due to the extremely high molecular weight of PpClS-1.

To find out whether the phase separation can be enhanced by increasing the temperature (LCST type of phase behaviour), the blends were annealed for 15 min at temperatures varying from 180–300°C. After annealing, the samples were quenched to room temperature.

DSC analysis did not show any progress in the phase separation process. For all compositions, only one single  $T_g$  was found, independent of the annealing temperature and equal to the initial value. Only after 15 min at 300°C, a shift of the  $T_g$  to lower values was observed, probably due to the degradation of the polymers.

Lowering the molar mass of the polymers normally leads to an increase of the miscibility and an increase of the rate of demixing. To study the effect of lowering the molar mass of PpClS, blends of PpClS-2 and PC have been prepared.

Figure 4 shows the DSC curves for the various blends. These results are summarized in Figure 5, where the  $T_g$ s as a function of the blend composition



**Figure 3** SEM picture of the surface of a cast film of the PC/PpClS-1 75/25 blend (left) and its chlorine map as obtained by EPMA analysis (right).

are depicted. The broken line corresponds to eq. (1). Between 20 and 80% PC, the blends show two glass transition temperatures, clearly indicating a two-phase region. The values are not the same as those of the pure components, meaning that some intermixing has taken place. Outside this region, only one  $T_g$  is found. Most probably the sensitivity of the DSC is not sufficient to observe the small  $c_p$  transition of the second phase. Also, for these compositions the films did not have a homogeneous appearance.

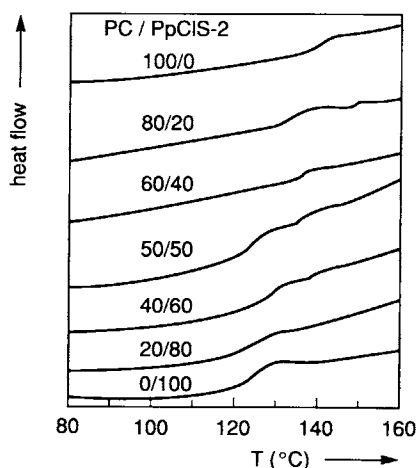
The existence of two phases has also been shown by enthalpy relaxation effects. After a few weeks at room temperature, the blend films showed two relaxation peaks, clearly indicating a two-phase system (Fig. 6).<sup>17,18</sup>

To find out if demixing into the pure components is possible by an increase in temperature, the blends were annealed in the same way as before. The results

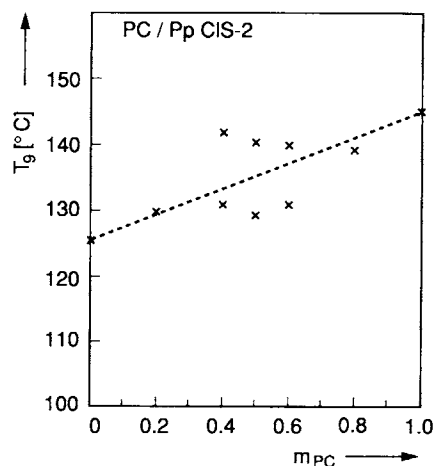
of these experiments did not show any change in the glass transition temperatures for both regions. There is no shift of the  $T_g$ s towards the pure components. Only after 15 min at 300°C was a decrease of the  $T_g$  of the PpClS-rich phase found, probably also due to degradation of the polymers. Although the molar mass of PpClS is reduced by more than a factor of 10, the phase separation is still not complete.

The blends of PpClS-2 and PC were also studied using DMTA. The resolution of this technique to distinguish different glass transition temperatures is in general somewhat higher than for DSC. For this reason, DMTA is very useful in studying blends consisting of polymers with a small difference in  $T_g$ . Samples with different compositions were made by coprecipitation and subsequent compression moulding. The results are depicted in Figure 7.

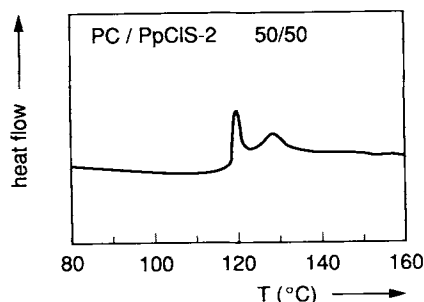
The blends containing 50, 75, and 90% PC show



**Figure 4** DSC curves for various compositions (as indicated) of the PC/PpClS-2 blend (second scans).



**Figure 5** The glass transition temperature as a function of composition (mass fraction) for the PC/PpClS-2 blend.



**Figure 6** DSC curve of an annealed (a few weeks at room temperature) PC/PpClS-2 50/50 blend (first scan).

a peak in the  $\tan \delta$  curves, accompanied by a shoulder at the low-temperature side. The maximum of the peak is shifted somewhat to the right compared to pure PC. This small and unexpected effect is not yet really understood. It may be that the low molar mass PC is "extracted" from the PC phase (into the PpClS), leading to an increase of the  $T_g$  of the PC phase. The shoulder is positioned at higher temperatures than the pure PpClS-2 transition. The samples with 10 and 25% PC show one broad peak. The occurrence of only one peak for these two compositions is probably due to the broad transition of pure PpClS-2 as a result of its broad molar mass distribution (see Table I), which might hide the PC transition. The DSC results mentioned above also revealed that at the extremes of the composition range it is difficult to distinguish the different phases.

Figure 8 shows the results of analysis of the blends using SEM on the surface of coprecipitated and subsequent moulded samples, which were cryofractured. For a good comparison, the SEM pictures of the pure components are also included. At low concentrations, small spheres of PC or PpClS-2 in a matrix can be observed. The blends containing 50 and 25% PpClS-2 are also inhomogeneous and form a continuous structure. From this it is clear that all the blends contain two distinct phases. This holds true even for the blends containing 10 and 25% PC, which showed only one single peak in the  $\tan \delta$  curves (see Fig. 7).

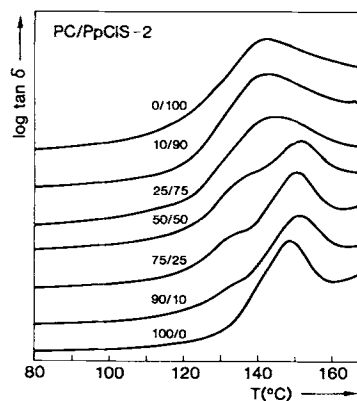
Figure 9 shows a transmission electron microscopy (TEM) picture of the blend with 50% PpClS. From the left picture, it is obvious that two phases exist. The bright phase contains some dark spots and the dark phase contains some bright spots. As a result of the fast evaporation of the solvent, aggregation of the separated phases is probably not complete. The right picture is made using the EPMA technique with chlorine mapping. The white speck-

les are indicative of chlorine-rich domains. Both phases contain PpClS. The contrast for this solvent cast sample, however, is not very strong, which indicates that the difference in chlorine content in the two phases is rather small.

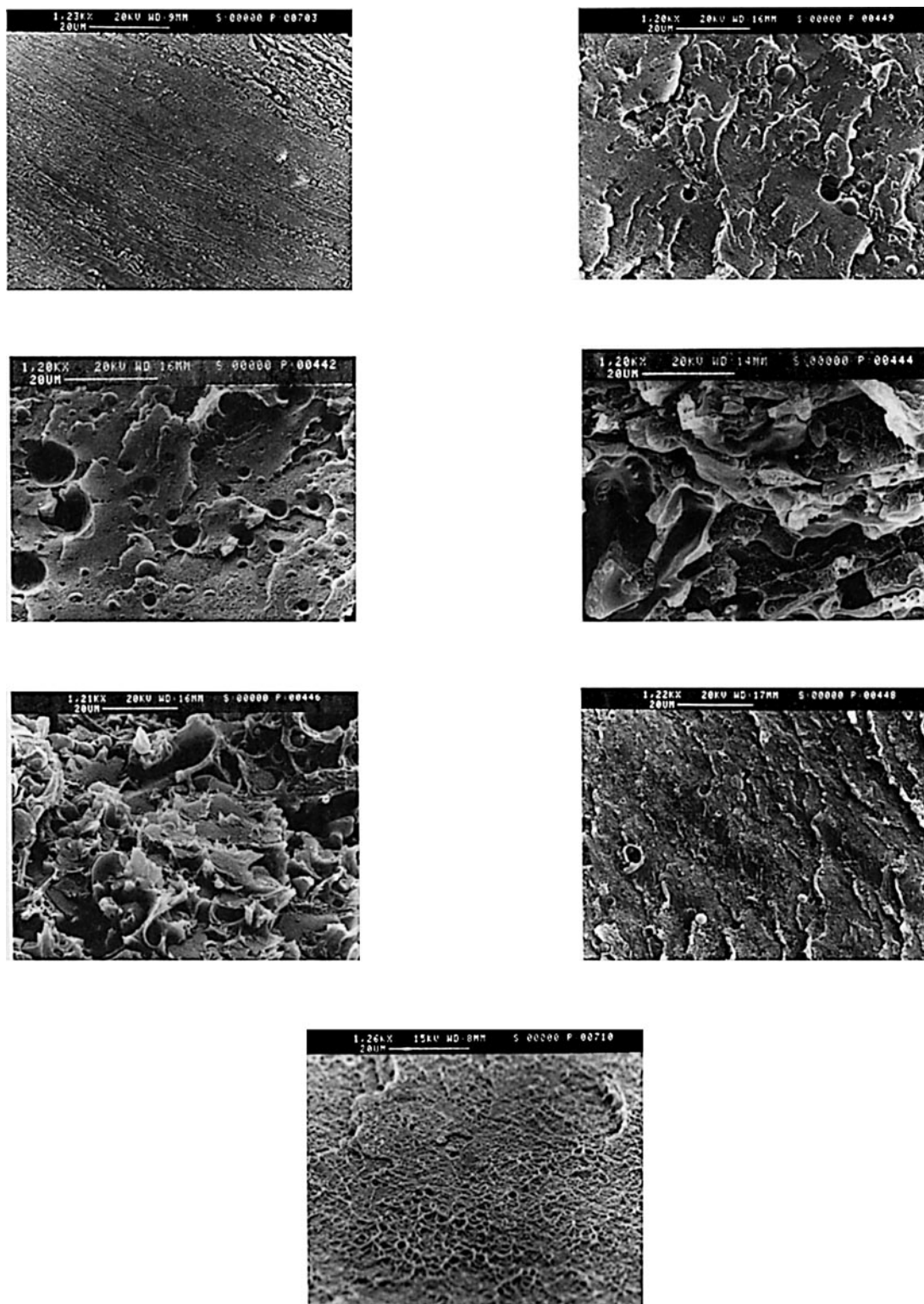
Until now, we saw that lowering the molar mass of PpClS by a factor of 10 is obviously not enough to reach complete miscibility. Therefore, a grade with low molar mass was synthesized (PpClS-3) and blends with PC were prepared as before. The results of the DSC measurements are depicted in Figure 10. With the exception of the sample containing 10% PC, every composition shows two glass transition temperatures. In the case of the former, the expected second phase is probably again too small to be detected by DSC.

Figure 11 shows the glass transition temperatures vs. blend composition. The broken line corresponds to eq. (1). Again, the glass transitions of the demixed phases lie between those of the pure components. Because both components have relatively low molar masses, hampering of the phase separation is not expected here. There probably exists some miscibility between PC and PpClS-3 in the low-concentration region. Because of the rather low viscosity of the blends, phase separation into the pure components should be possible at elevated temperatures. Therefore, the samples were annealed at different temperatures, 15 min in each case. The results are given in Table II.

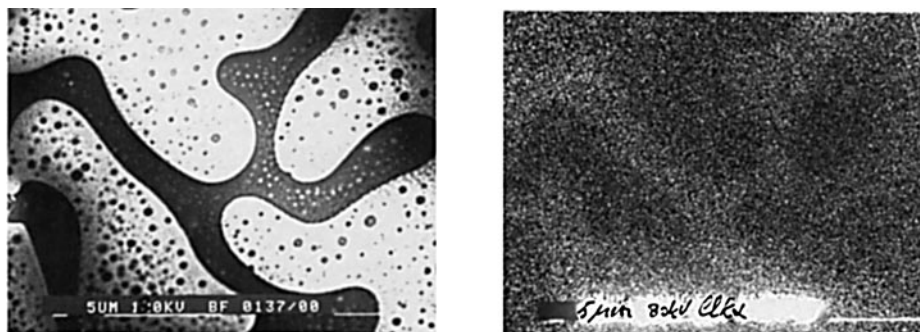
In this case, annealing results in a shift of the glass transition temperatures toward the pure components. The PpClS-3-rich blends demix completely into the pure components after annealing at 300°C. The other compositions demix into a pure PC phase and a PpClS-3-rich phase. The effect of thermal



**Figure 7** DMTA curves for the various (as indicated) coprecipitated and subsequent moulded PC/PpClS-2 blends.



**Figure 8** SEM analysis of the surface of cryofractured samples for various PC/PpClS-2 blends. (a), 100/0; (b), 90/10; (c), 75/25; (d), 50/50; (e), 25/75; (f), 10/90; (g), 0/100.



**Figure 9** TEM picture of a solvent-cast PC/PpClS-2 50/50 blend (left). The right picture is the corresponding chlorine map as obtained with EPMA.

degradation on the shift of the  $T_g$ s is probably much smaller than the effect of the phase separation.

Blends containing PpClS-3 were also studied by DMTA. Because of the brittleness of the low molecular weight PpClS-3, only samples containing up to 60% PpClS-3 could be measured. The results are given in Figure 12. For all three compositions, two distinct transitions in  $\tan \delta$  are observed.

A further reduction of the molar mass of PpClS obviously did not lead to a miscible system. The most important effect is the acceleration of the kinetics of the phase separation due to enhanced mobility in the molten state. Upon copolymerization of pClS with styrene or oClS, miscibility may be induced and this is the subject of further research.

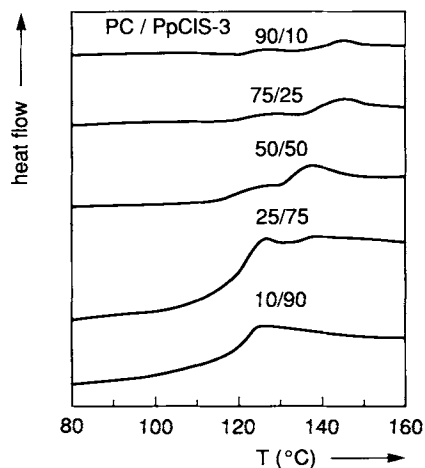
## CONCLUSIONS

The blend of PC and PpClS is not completely miscible over the whole range of compositions. The

blends containing the high molecular weight PpClS-1 showed only one single  $T_g$  in DSC for all compositions. However, the films were not optically transparent and also SEM analysis revealed a two-phase structure: a chlorine-rich and a chlorine-poor phase. DSC measurements on annealed samples gave no evidence for further phase separation. The high molecular weight of the PpClS likely hampers the demixing process kinetically.

The blends containing the low molar mass PpClS showed two distinct glass transition temperatures by DSC and DMTA. The shifts of the  $T_g$ s indicated that the two phases do not consist of the pure components, but that a PpClS-rich and a PpClS-poor phase exist. Annealing at elevated temperatures did not induce further phase separation into the pure components for the PpClS-2 having an  $M_w$  of about 230 kg/mol. However, for the low molecular weight PpClS-3 ( $M_w$  10 kg/mol) further demixing could be accomplished for almost all compositions. This means that lowering the molar mass did not increase miscibility of the PpClS/PC blend, but that the most important effect of the molar mass lies in the kinetics (enhancement) of the phase separation.

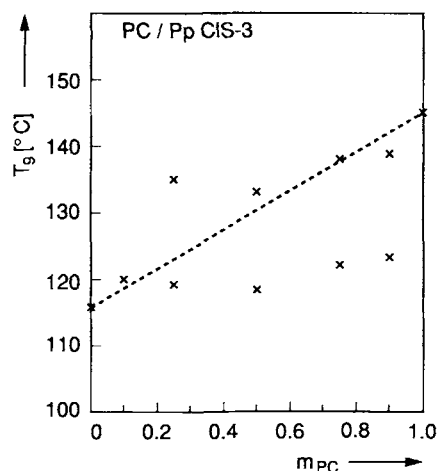
Furthermore, we showed in this article that SEM



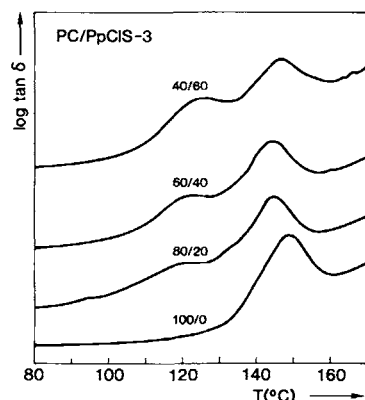
**Figure 10** DSC curves for various compositions (as indicated) of the PC/PpClS-3 blend (second scans).

**Table II** Effect of Annealing at Different Temperatures (for 15 min) on the  $T_g$ s of Various Blend Compositions

PC/PpClS-3	Temperature			
	180°C	220°C	260°C	300°C
90/10	136/145	128/145	127/145	126/145
75/25	129/139	127/143	123/144	121/144
50/50	127/144	125/144	120/143	116/144
25/75	122/144	121/144	119/145	116/145
10/90	124/144	122/143	117/144	116/144



**Figure 11** The glass transition temperature as a function of composition (mass fraction) for the PC/PpCIS-3 blend.



**Figure 12** DMTA curves for the various (as indicated) coprecipitated and subsequent moulded PC/PpCIS-3 blends.

and TEM studies can be complemented by using EPMA analysis, which selectively gives qualitative information on the presence of a typical atom in one of the blend components.

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