

# Miscibility of Poly(caprolactone)/Chlorinated Polypropylene and Poly(caprolactone)/Poly(chlorostyrene) Blends

DANIELLE ALLARD and ROBERT E. PRUD'HOMME, *Groupe de Recherches sur les Macromolécules, Chemistry Department, Laval University, Québec, PQ, Canada G1K 7P4*

## Synopsis

Poly(caprolactone) (PCL) was blended with poly(chlorostyrene) (PSCI) and chlorinated polypropylene (PPCI). A single glass transition temperature  $T_g$  was found for these mixtures, indicating their miscibility. PCL crystallizes in these blends when the chlorinated polymer content is not too high. Otherwise,  $T_g$  becomes higher than the melting point of PCL and the high viscosity of the medium hinders the crystallization. The miscibility of PCL/PPCI blends cannot be due to hydrogen bonding between the  $\alpha$ -hydrogens of the chlorinated polymer and the carbonyl group of the polyester since PPCI does not have available a large number of  $\alpha$ -hydrogens. It is suggested that a dipole-dipole  $-\text{C}=\text{O}\cdots\text{Cl}-\text{C}-$  interaction is responsible for the observed miscibility phenomenon and that this interaction is probably also responsible for the miscibility between all other polyester-chlorinated polymer mixtures. Finally, it was observed that poly( $\alpha$ -methyl- $\alpha$ -*n*-propyl- $\beta$ -propiolactone), poly( $\alpha$ -methyl- $\alpha$ -ethyl- $\beta$ -propiolactone) and poly(valerolactone) are not miscible with PSCI or PPCI, despite the fact that they are miscible with poly(vinyl chloride).

## INTRODUCTION

The observation of a single glass transition temperature  $T_g$  in polymer-polymer blends is usually taken as a proof of the miscibility of the mixture, i.e., extensive mixing between the two polymers in the amorphous phase even if crystals can be formed simultaneously. Several polymer pairs have been recently shown to present miscibility.<sup>1,2</sup> Among them, poly(vinyl chloride) (PVC) is often present since it has been shown to be miscible with a large number of polymers,<sup>1,2</sup> and particularly with a large number of polyesters including poly(caprolactone) (PCL),<sup>3</sup> poly(butylene terephthalate),<sup>4</sup> poly(valerolactone),<sup>5,6</sup> poly(1,4-butylene adipate),<sup>7</sup> and several others.<sup>7-15</sup>

However, all polyesters are not miscible with PVC. Poly( $\beta$ -propiolactone)<sup>16</sup> and several others<sup>7-10,13-15</sup> are not. It has been suggested<sup>7-10</sup> that the  $\text{CH}_2/\text{COO}$  ratio of the polyester must be equal or larger than 4 in order to have enough chain mobility to allow miscibility.

For all miscible polyester/PVC blends, it is now believed that there is a specific interaction between the carbonyl group of the polyester and the  $\alpha$ -hydrogens of PVC<sup>3,17</sup> (hydrogen-bonding interaction). This specific interaction has, however, never been directly established, although Olabisi<sup>18</sup> has shown by inverse gas-liquid chromatography that the PCL/PVC interaction involves the presence of chlorine atoms and Fourier-transform infrared spectroscopy<sup>19</sup> indicates that the carbonyl group of PCL is part of the interaction.

If a specific interaction leads to miscibility between several polyesters and

PVC, it should also be expected to find miscibility between PCL and chlorinated polymers. Indeed, poly(epichlorohydrin)<sup>20</sup> and several chlorinated polyethylenes<sup>21</sup> have been shown to be miscible with PCL.

It is the purpose of the present paper to investigate the behavior of PCL/poly(chlorostyrene) (PSCI) and of PCL/chlorinated polypropylene (PPCl) blends to verify their miscibility. Since PSCI and PPCl have structures which are different from that of PVC, the behavior of these mixtures will give interesting information about the nature of the specific interaction between polyesters and chlorinated polymers. The miscibility behavior of several other polyesters with PSCI and PPCl will also be reported.

## EXPERIMENTAL

The principal samples used in this study are listed in Table I along with their weight average molecular weight  $\bar{M}_w$ , determined by gel permeation chromatography in tetrahydrofuran at 298 K, their glass transition temperature  $T_g$ , their melting point  $T_m$ , and their intrinsic viscosity  $[\eta]$ , determined in tetrahydrofuran at 298 K. All polymers used have high molecular weights. Unless stated otherwise, the PSCI polymer is a mixture of ortho and para isomers. A limited number of experiments were conducted with the ortho isomer of PSCI. As indicated in Table IV, the two types of PSCI have the same miscibility behavior. It is believed that the chlorine atoms are located mainly in  $\alpha$ -position on the PPCl chains<sup>22,23</sup> and consequently that only a small number of  $\alpha$ -hydrogens are remaining for a possible specific interaction with PCL.

Blends were prepared by slowly casting films from tetrahydrofuran solutions. Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC-1B apparatus calibrated with mercury, gallium, and indium. Reported melting points  $T_m$  were recorded at the end of the melting curve and a heating rate of 20 K/min was used in all cases. In the DSC apparatus, the samples were first cooled to 173 K and maintained at that temperature for 30 min. They were then brought to 410 K (PSCI) or 480 K (PPCl) (first fusion) and kept at that temperature for 5 min before being quenched to 173 K. The samples were then reheated a certain number of times (subsequent fusions) under the same thermal regime.

Polarized microscopy experiments were made using a Zeiss polarizing microscope and when necessary a Mettler FP52 hot stage.

TABLE I  
Characterization of Principal Polymers Used in This Study

Polymer	Acronym	$\bar{M}_w$	$T_g$ (K)	$T_m$ (K)	$[\eta]$ (dL/g)
Poly(chlorostyrene) <sup>a</sup>	PSCI	99 000	398	—	0.43
Chlorinated polypropylene <sup>b</sup>	PPCl	57 000	461	—	0.41
Poly(caprolactone)	PCL	20 000	212	351	0.26
Elvaloy 741 <sup>c</sup>	—	375 000	247	356	0.92

<sup>a</sup> Mixture of ortho and para isomers.

<sup>b</sup> Contains 66% by weight of Cl according to a C, H analysis.

<sup>c</sup> Dupont trademark for an ethylene/vinyl acetate/carbon monoxide terpolymer.

## RESULTS AND DISCUSSION

## PCL/PSCL Blends

Some of the DSC curves obtained for PCL/PSCL blends are shown in Figure 1. They are characterized by a single  $T_g$  which changes with composition. According to the  $T_g$  criterion, these blends are then miscible, i.e., there is extensive mixing between the segments of the two polymers. This conclusion is confirmed by a decrease in melting point observed when PSCL is added to PCL. This decrease is of the order of 15 K. All results obtained are summarized in Table II and in the phase diagram presented in Figure 2. Despite the experimental scatter of the results, the  $T_g$ -composition curve, which is concave, can be expressed by the Gordon-Taylor equation<sup>24</sup>

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (1)$$

where  $T_g$  is the glass transition temperature of the blend,  $T_{g1}$  and  $T_{g2}$  those of components 1 and 2,  $w_1$  and  $w_2$  are the corresponding weight fractions, and  $k$  is defined by

$$k = \frac{\alpha_{l2} - \alpha_{g2}}{\alpha_{l1} - \alpha_{g1}} \quad (2)$$

where the  $\alpha$ 's are the volume expansion coefficients, in the glassy ( $g$ ) and in the liquid ( $l$ ) states, of components 1 and 2. In this work,  $k$  is taken as an adjusting parameter. In Figure 2,  $k = 0.39$ .

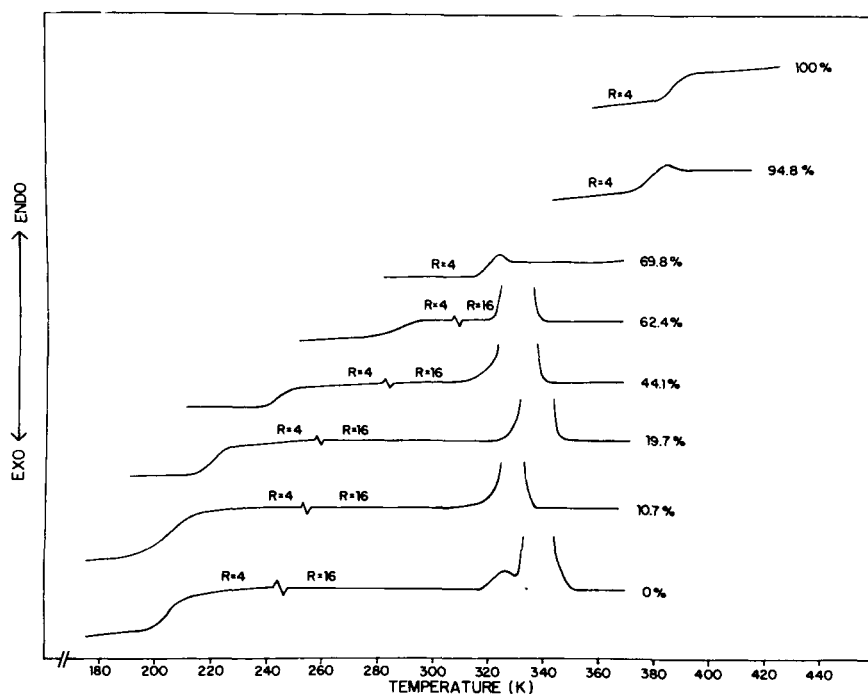


Fig. 1. DSC curves of poly(caprolactone)/poly(chlorostyrene) blends. Curves were often recorded at two different ranges ( $R = 4$  and  $R = 16$ ).

TABLE II  
Glass Transition Temperature, Melting Point, and Enthalpy of Fusion of PCL/PSt Blends

PSt wt %	$T_g$ (K)	$T_m^a$ (K)	$\Delta H_m$ (J/g)
0	212	351	109
10.7	209	337	89
19.7	212	346	108
31	230	338	n.d. <sup>b</sup>
44.1	249	340	79
52	252	335	n.d. <sup>b</sup>
62.4	295	340	82
69.8	318	343	61
79	n.d. <sup>b</sup>	334	15
91	351	—	—
94.8	388	—	—
100	398	—	—

<sup>a</sup> Same result obtained upon the first or the subsequent fusions.

<sup>b</sup> n.d.: not determined.

It is also observed in Figure 1 that the width of the transition zone is the same (of the order of 10–15 K) for all blends as it is for the pure components. This result suggests extensive mixing between the polymer segments since several examples are known where a broadening of the transition zone is observed despite the presence of a single  $T_g$ , and this broadening has been generally interpreted as being due to incomplete miscibility at the molecular level.<sup>12,25</sup>

In addition, Figure 3 shows that the  $\Delta C_p$  jump at  $T_g$  changes in a nonlinear

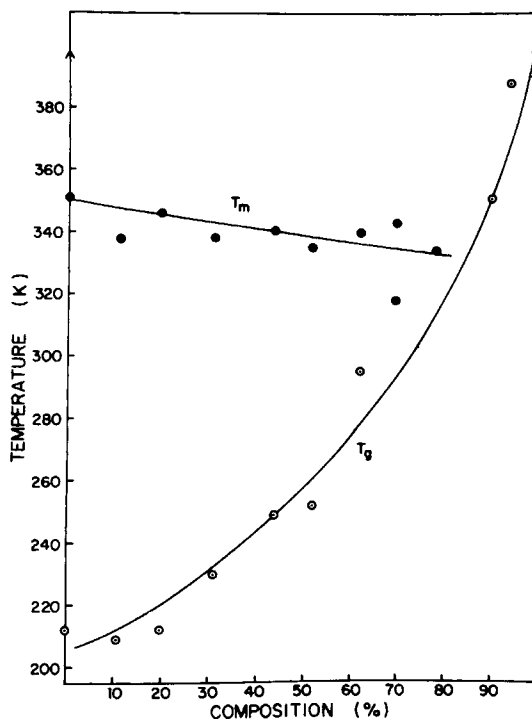


Fig. 2. Phase diagram of poly(caprolactone)/poly(chlorostyrene) blends.

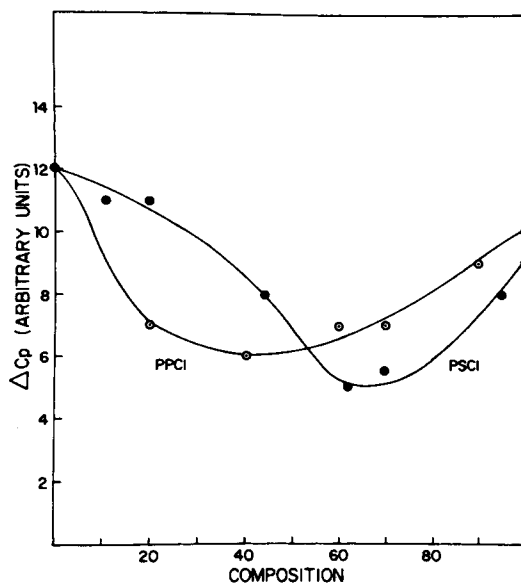


Fig. 3.  $\Delta C_p$ -composition diagram of poly(caprolactone)/poly(chlorostyrene) (●) and poly(caprolactone)/chlorinated polypropylene (○) blends.

way as a function of composition. The  $\Delta C_p$ 's of the blends are, in fact, smaller than those expected on the basis of an additivity rule.

The depression in  $T_m$  with PSCI content indicates a negative thermodynamic interaction parameter  $\chi$  between PCL and PSCI. The exact value of  $\chi$  was not, however, calculated since decreases of  $T_m$  of a few degrees may be the result of changes in lamellar thickness with composition<sup>26</sup> or changes in environment<sup>27</sup> and since recent measurements indicate that  $\chi$  varies with blend composition,<sup>28,29</sup> thus invalidating the use of the polymer-diluent theory which assumes a unique value of  $\chi$ .

Table II and Figure 4 also indicate that PCL crystallizes in PCL/PSCI blends for compositions up to 80% in PSCI; but at high PSCI contents, the crystallization is hindered. The composition where this hindrance occurs corresponds to mixtures where  $T_g$  becomes larger than  $T_m$  (Fig. 2). The crystallization is then impeded by kinetics factors, i.e., the viscosity of the mixture is too high to allow crystallization.

### PCL/PPCI Blends

Figures 5 and 6 and Table III give the results obtained pertaining to the PCL/PPCI blends. These results are very similar to those obtained for PCL/PSCI blends:

- (1) A unique value of  $T_g$  is found at each composition, indicating the miscibility of these two polymers.
- (2) The  $T_g$ -composition curve can be expressed by eq. (1), using  $k = 0.30$  (Fig. 6).
- (3) The width of the transition zone of the blends is in general slightly broadened as compared to that of their pure components (Fig. 5), indicating that the miscibility may not extend to the molecular level.<sup>25</sup>

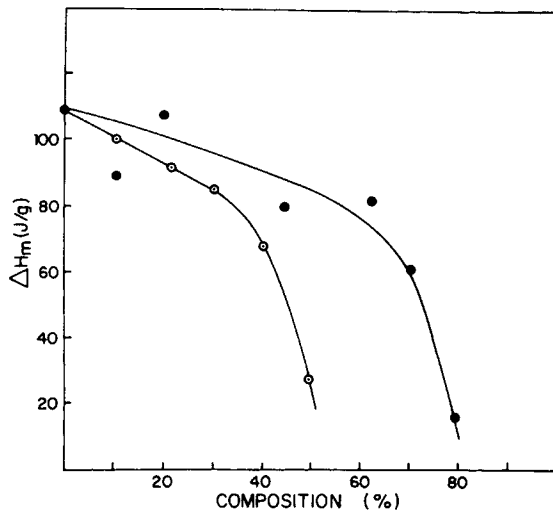


Fig. 4. Enthalpy of fusion vs. composition of poly(caprolactone)/poly(chlorostyrene) (●) and poly(caprolactone)/chlorinated polypropylene (○) blends.

(4) The  $\Delta C_p$  of the blends are smaller than those expected from the additivity rule (Fig. 3).

(5) The  $T_m$  of PCL decreases with an increase in PPCI content, indicating a negative value of  $\chi$  and miscibility.

(6) The crystallization of PCL is hindered in blends containing more than 50% PPCI (Fig. 4). On the basis of the phase diagram presented in Figure 6, it is believed that the crystallization of PCL is hindered for kinetics reasons.

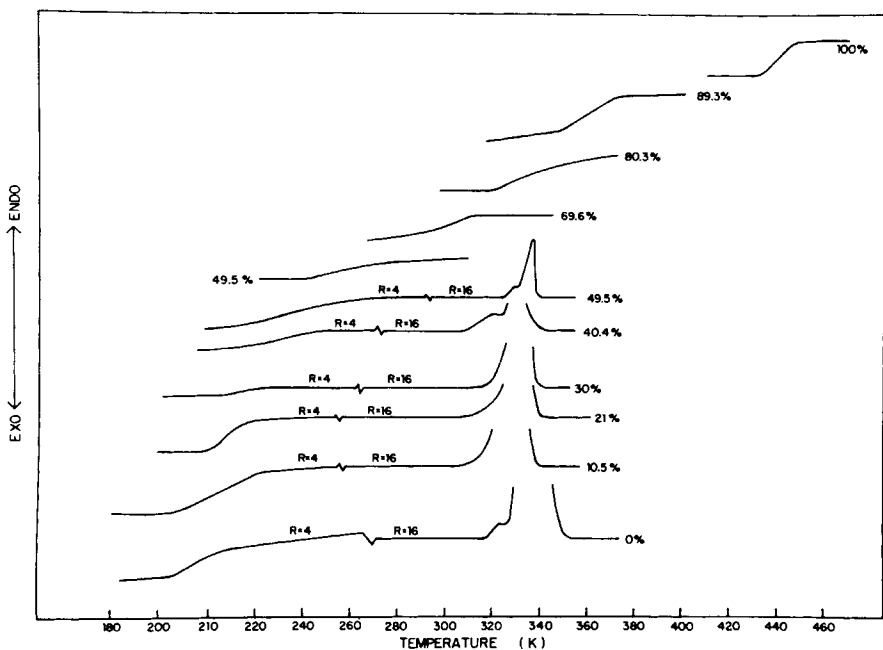


Fig. 5. DSC curves of poly(caprolactone)/chlorinated polypropylene blends. Curves were often recorded at two different ranges ( $R = 4$  and  $R = 16$ ).

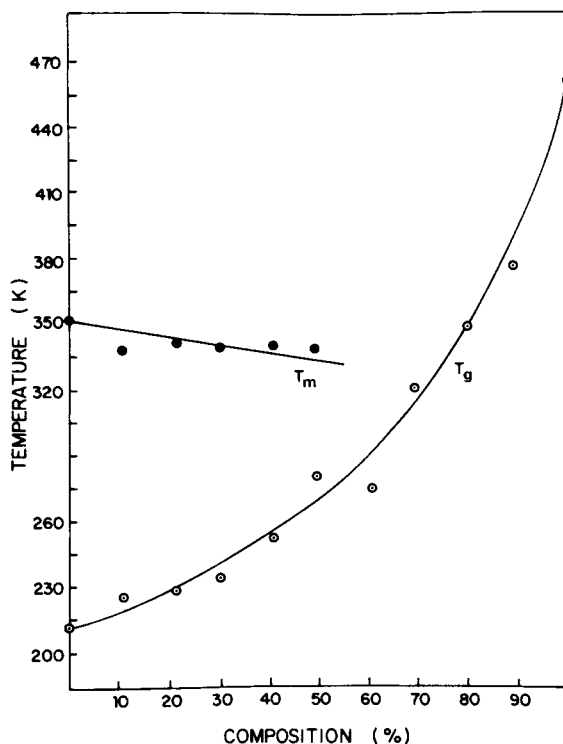


Fig. 6. Phase diagram of poly(caprolactone)/chlorinated polypropylene blends.

The morphology of PCL/PPCl blends was also studied on the polarizing microscope (Fig. 7). Large spherulites are observed for pure PCL. With the addition of PPCI, the spherulite radii fall rapidly from 153 to 114, 79, 39, and 8  $\mu\text{m}$  for compositions of, respectively, 0, 21.1, 30, 40.4, and 49.5% in PPCI. The chlorinated polymer then acts as a better nucleating agent than PCL, as seen previously.<sup>5,21,25,30</sup>

TABLE III  
Glass Transition Temperature, Melting Point, and Enthalpy of Fusion of PCL/PPCl Blends

PPCl wt %	$T_g$ (K)	$T_m^a$ (K)	$\Delta H_m$ (J/g)
0	212	351	109.
10.5	225	338	100
21	228	341	92
30	234	340	85
40.4	252	340	67
49.5	281	339	27
61.	275	—	—
69.6	322	—	—
80.3	349	—	—
89.3	377	—	—
100.	461	—	—

<sup>a</sup> First fusion and subsequent fusions.

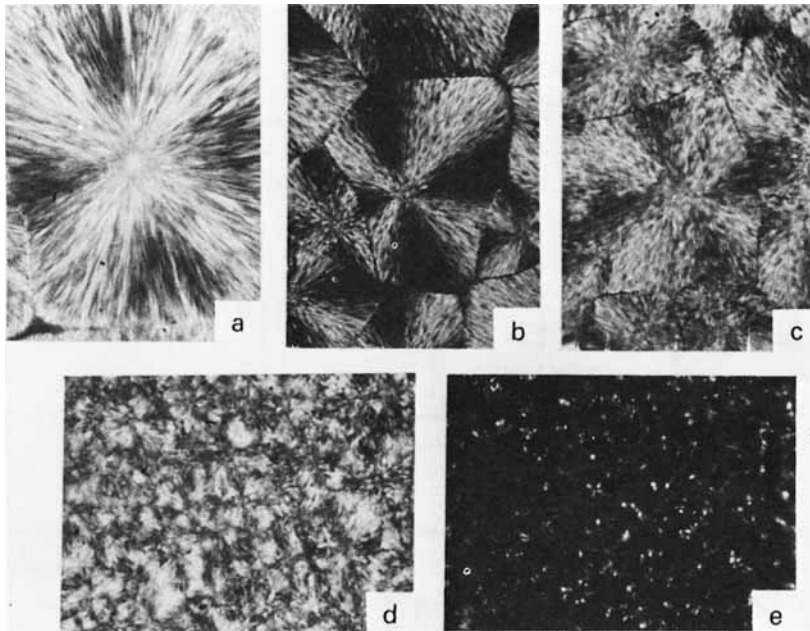


Fig. 7. Optical photomicrographs of poly(caprolactone)/chlorinated polypropylene blends containing (a) 0%, (b) 21.1%, (c) 30%, (d) 40.4%, and (e) 49.5% PPCl; magnification: 40X.

### Other Blends

Finally, a large number of polyesters have been blended with PSCI and PPCl (Table IV). Most of them give rise to two  $T_g$ 's which are unperturbed as compared to those of the pure components. These blends are then immiscible. The immiscibility of PEA and PES was already predicted since the  $\text{CH}_2/\text{COO}$  ratio of these polymers is low<sup>7</sup> and, consequently, since these polymers are not even

TABLE IV  
Miscible and Immiscible Blends Investigated in This Study<sup>a</sup>

Miscible blends	Immiscible blends
PCI/PPCI	PMPPL/ <i>o,p</i> -PSCI
PCI/ <i>o</i> -PSCI	PMPPL/PPCI
PCL/ <i>o,p</i> -PSCI	PMEPL/ <i>o,p</i> -PSCI
Elvaloy 741/PPCI	PVL/PPCI
Elvaloy 741/ <i>o,p</i> -PSCI	PVL/ <i>o,p</i> -PSCI
	PEA/PPCI
	PEA/ <i>o,p</i> -PSCI
	PES/PPCI
	PES/ <i>o,p</i> -PSCI
	PHMS/PPCI
	PHMS/ <i>o,p</i> -PSCI
	E-12.8% CO/ <i>o,p</i> -PSCI
	E-18% CO/ <i>o,p</i> -PSCI

<sup>a</sup> *o* = ortho isomer; *o,p* = mixture of the ortho and para isomers; PMPPL = poly( $\alpha$ -methyl- $\alpha$ -*n*-propyl- $\beta$ -propiolactone); PMEPL = poly( $\alpha$ -methyl- $\alpha$ -ethyl- $\beta$ -propiolactone); PEA = poly(ethylene adipate); PES = poly(ethylene succinate); PHMS = poly(hexamethylene sebacate); PVL = poly(valerolactone); E-12.8% CO = copolymer of ethylene and carbon monoxide containing 12.8% CO; and E-18% CO = copolymer of ethylene and carbon monoxide containing 18% CO.



miscible with PVC. However, it is surprising to find that PMPPL, PMEPL, and PVL are immiscible with PSCL and PPCL despite the fact that they are completely miscible with PVC.

## CONCLUSIONS

It has then been shown that PCL is miscible with PSCL and PPCL in the solid state. This conclusion is reached from the presence of a single  $T_g$  for both systems intermediate between those of their pure components. PCL, however, crystallizes in both cases when the concentration of the chlorinated polymer in the blend is not too large.

The miscibility between PCL and PPCL cannot be due to a specific interaction between the  $\alpha$ -hydrogens of the chlorinated polymer and the carbonyl group of the polyester since the chlorine atoms in PPCL are mainly present in  $\alpha$ -position. Another type of interaction must exist, and it can be a dipole-dipole interaction between the C—Cl and the C=O groups since several esters have been shown to give a negative heat of mixing when blended with  $\text{CCl}_4$ , indicating the presence of this type of interaction.<sup>31</sup> Some of our preliminary measurements support this hypothesis since PCL is also miscible with poly(vinylidene chloride) where obviously the  $\alpha$ -hydrogens cannot play any role.<sup>32</sup>

It has also been demonstrated that Gordon-Taylor  $k$  parameters of 0.39 and 0.30 are found for PCL/PSCL and PCL/PPCL blends, respectively. These values are lower than that reported for PCL/PVC mixtures: 0.79.<sup>33</sup>

Finally, our results indicate that the  $\text{CH}_2/\text{COO}$  ratio  $x$  of the polyester is an important factor in determining the miscibility of polyester/PPCL and of polyester/PSCL blends just as it was shown before to be important in polyester/PVC blends.<sup>7</sup> Low  $\text{CH}_2/\text{COO}$  ratios ( $x \leq 4$ ) give rise to immiscible blends because the polyester chains are then too rigid and because they cannot adopt the conformations required to have specific interaction with the chlorinated polymer. Higher  $\text{CH}_2/\text{COO}$  ratios ( $x \geq 7$ ) also lead to immiscible blends due to a too low concentration in carbonyl groups. Only the intermediate ratio ( $x = 5$ ) give miscible blends with PPCL and PSCL.

However, the blends made from the Elvaloy sample do not follow the preceding rule. As indicated in Table I, Elvaloy is an ethylene/vinyl acetate/carbon monoxide terpolymer (the exact composition of the product is not known). It is believed that its carbon monoxide content is less than 15% per weight, leading to a  $\text{CH}_2/\text{CO}$  ratio of about 14. Such a high ratio normally leads to immiscibility as stated in the previous paragraph. But the vinyl acetate monomer adds to the polymer COO groups, decreases the  $\text{CH}_2/\text{COO}$  ratio and favors miscibility. The vinyl acetate contribution is large enough such that miscibility is experimentally found (Table IV) between Elvaloy and PPCL and PSCL. Without vinyl acetate, ethylene/carbon monoxide copolymers containing 12.8% or 18% carbon monoxide are immiscible with PSCL, as indicated in Table IV.

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