Miscible Blends of a Vinylidene Chloride/Vinyl Chloride Copolymer with Aliphatic Polyesters

E. M. WOO, J. W. BARLOW, and D. R. PAUL, *Department of Chemical Engineering and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712*

Synopsis

A copolymer of vinylidene chloride and vinyl chloride containing 13.5% by weight of the latter has been solution blended with four aliphatic polyesters: poly(ε-caprolactone), poly(2,2-dimethyl-1,3-propylene adipate), poly(1,4-cyclohexanedimethylene succinate), and poly(2,2-dimethyl-1,3-propylene succinate). Each blend was examined visually and by differential scanning calorimetry. All blends with the copolymer form a single miscible amorphous phase at all compositions and all temperatures except for the latter mentioned polyester, which exhibits liquid–liquid phase separation at temperatures above a measured cloud point curve. Information about interactions between the components in each blend is estimated from melting point data and discussed.

INTRODUCTION

It has been known for more than a decade that poly(ε-caprolactone) is miscible with poly(vinyl chloride).[1] More recently, it has been shown that a range of aliphatic polyesters are miscible with PVC[2-4] and that poly(ε-caprolactone) is also miscible with certain chlorinated polypropylenes,[5] polystyrenes,[5] and polyethylenes.[6] Interestingly, poly(vinyl fluoride) and poly(vinylidene fluoride) are reported to be immiscible with several polylactones which are miscible with PVC[4,7]; however, PVF$_2$ is miscible with a range of polymers having carbonyls in their pendant groups[8]. The above suggest that further studies on blends involving other halogenated polymers would be fruitful both in terms of discovering new miscible blends and in understanding the basis and limits for miscibility in such systems. This report deals with miscible blends based on selected aliphatic polyesters and a copolymer of vinylidene chloride and vinyl chloride. The literature mentions miscibility of PCL with polymers based on vinylidene chloride,[5,9] but detailed reports have not yet appeared.

MATERIALS AND PROCEDURES

The vinylidene chloride/vinyl chloride copolymer was obtained from the Dow Chemical Co. through the courtesy of Mr. Don Sundquist. It is a commercial product (sold under the trademark SARAN) containing 13.5% by weight of vinyl chloride and has an average molecular weight of 101,000 based on GPC determination using polystyrene calibration. The polyesters used are described in Table I.

Blends of the copolymer, designated here as P(VCl$_2$/VCl), with the polyesters were made by solvent casting from tetrahydrofuran. Approximately 0.5 g of the

TABLE I
Description and Characteristics of Polymer Samples

Name	Structure	Abbreviation	Density (g/cm³)	Intrinsic viscosity (dL/g)	Molecular weight	Source
SARAN[a]	$-(CH_2CCl_2)_x(CH_2CHCl)_y-$ 13.5% by wt VCl	P(VCl₂/VCl)	1.70	—	101,000[b]	Dow Chemical Co.
Poly(ε-caprolactone) PCL-700	$-(CH_2)_5-C(=O)-O-$	PCL	1.095	0.67[c]	15,500 ($\bar{M}_n$)	Union Carbide Corp.
Poly(2,2-dimethyl-1,3-propylene adipate)	$-CH_2-C(CH_3)_2-CH_2-O-C(=O)-(CH_2)_4-C(=O)-O-$	PDPA	1.25	0.084[c]	—	SPP[d]
Poly(1,4-cyclohexane-dimethylene succinate)	$-CH_2-\langle C_6H_{10}S \rangle-CH_2-O-C(=O)-(CH_2)_2-C(=O)-O-$	PCDS	1.16	0.342[c]	—	SPP
Poly(2,2-dimethyl-1,3-propylene succinate)	$-CH_2-C(CH_3)_2-CH_2-O-C(=O)-(CH_2)_2-C(=O)-O-$	PDPS	1.17	0.080[c]	—	SPP

[a] Trademark of the Dow Chemical Co.
[b] Average value by GPC using polystyrene calibration.
[c] In benzene.
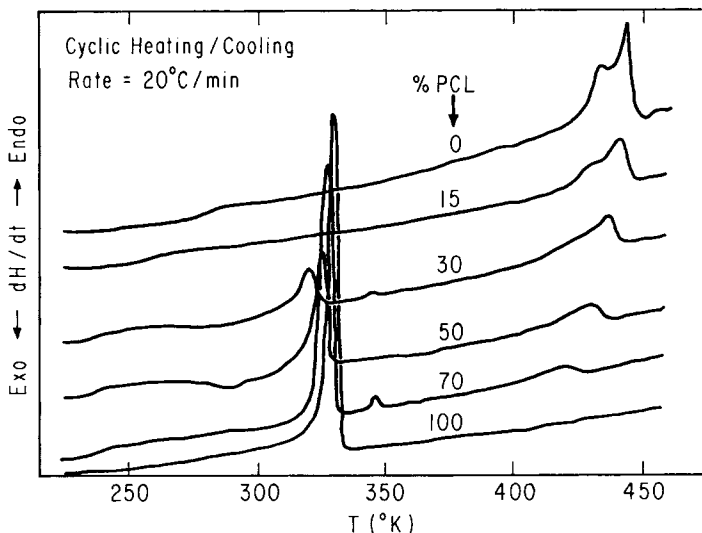[d] SPP = Scientific Polymer Products.

Fig. 1. DSC thermograms for blends with PCL using cyclic procedure.

two-component polymers in the desired ratio were mixed with 20 cm^3 of THF and stirred for 4 h.   The resulting solutions were poured into aluminum pans maintained at 50°C.   Most of the solvent was removed overnight; however, the samples were transferred to a vacuum oven set at 60°C, where they were kept for 5 days to complete solvent removal.

Each sample was examined by differential scanning calorimetry and optically for any evidence of lower critical solution temperature behavior.   The latter was done using techniques described earlier,[10] which consisted of heating at approximately 20°C/min to 240°C (where decomposition occurred rapidly) or until a cloud point was observed.   Glass transition and melting behavior were moni-
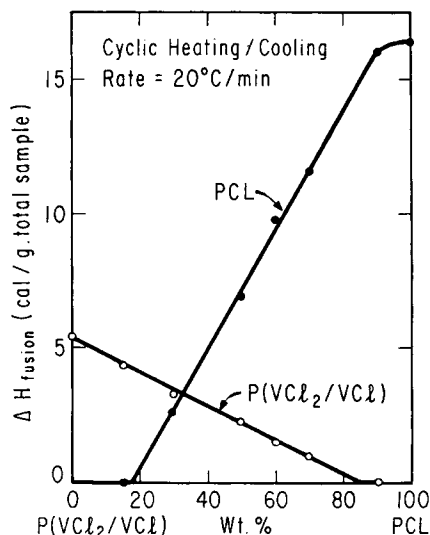

Fig. 2. Heats of fusion associated with PCL and P(VCl₂/VCl) melting peaks from thermograms like those in Figure 1.
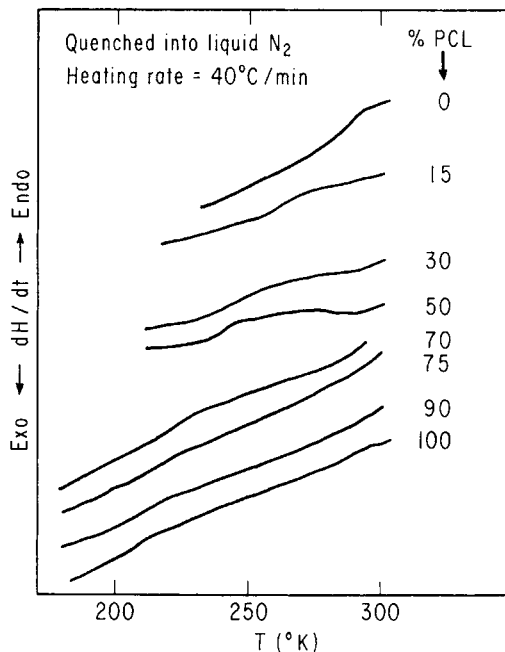
Fig. 3. Thermograms for quenced PCL blends for better examination of T_g region.

tored by DSC using both quenching and cyclic heating/cooling procedures. Quenched samples gave a more clear indication of the glass transition owing to the suppression of sample crystallinity, although the location of the T_g did depend in many cases on the thermal history of the sample for reasons enumerated
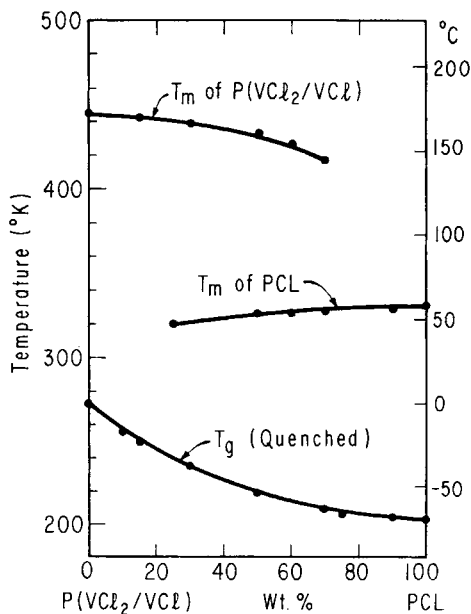

Fig. 4. Transition behavior for blends containing PCL. T_m from cyclic procedure.
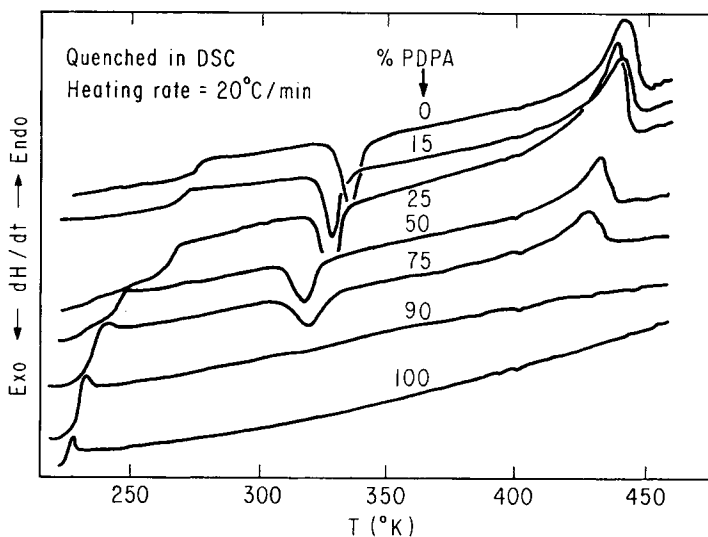
Fig. 5. Thermograms for PDPA containing blends using samples quenched in the DSC.

by Robeson et al.[11]   For blends containing PCL, samples were quenched directly into liquid nitrogen and then transferred to the DSC where heating proceeded at 40°C/min.   For all other blends, quenching was done in the DSC by employing the most rapid cooling rate (setting = 320°C/min) and was followed by heating at 20°C/min.   The cyclic program consisted of heating and cooling at 20°C/min between the limits of 215°K and 460°K.   Only results after the first cycle were recorded.

RESULTS

Poly(ε-Caprolactone)

The as-cast blend films were macroscopically homogeneous and were intermediate to the pure component polymers in terms of mechanical feel and optical character.   Cloudiness of blends rich in PCL became clearer on heating above the PCL melting point.   Above the T_m of P(VCl$_2$/VCl), the blends were quite transparent and showed no cloud point with heating to the highest possible temperature.   Figure 1 shows DSC thermograms for these blends obtained by the cyclic heating/cooling scheme described earlier.   The most prominent features are the melting peaks for PCL and P(VCl$_2$/VCl).   The heats of fusion associated with these peaks are plotted versus total blend composition in Figure 2.   Note that crystallinity of the minor component is totally suppressed at low concentrations for this thermal history.   The blends have a single composition dependent glass transition temperature, although the magnitude of this transition is not large owing to the reduced fraction of amorphous phase of the sample caused by crystallinity of the two components.

Quenching the samples diminishes the crystallinity and makes the T_g more prominent as shown by the thermograms in Figure 3 which only display the temperature range spanning the glass transition region.   The lower part of Figure
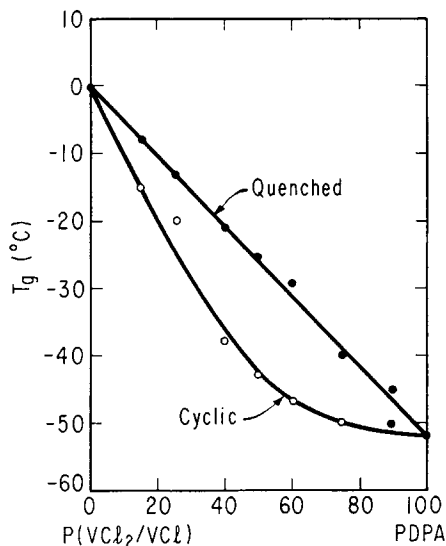
Fig. 6. Glass transition behavior of PDPA blends for both quenched and cyclic treated samples.

4 shows the single composition dependent glass transition obtained from thermograms for quenched specimens while the upper part displays the melting points of PCL and P(VCl$_2$/VCl) obtained during cyclic heating runs. The T_g behavior indicates these blends to have a totally miscible amorphous phase. The melting points of the crystalline phases are somewhat depressed, as would be expected.[8] An analysis of these data will be presented in a later section.

Poly(2,2-Dimethyl-1,3-Propylene Adipate)

As-cast blend films rich in P(VCl$_2$/VCl) were quite ductile and had limited cloudiness. Films rich in PDPA were somewhat more cloudy which cannot likely be attributed to crystallinity of this component since it is not readily crystallizable even in the pure state. This cloudiness disappeared upon heating to ~155°C. The samples remained clear on cooling to room temperature but turned cloudy again after several minutes. This phenomenon may be the result of formation of large P(VCl$_2$/VCl) spherulites in this composition region. Above the T_m of P(VCl$_2$/VCl), all blends with PDPA were completely transparent and remained so with heating to the highest possible temperature.

Figure 5 shows thermograms for samples quenched in the DSC and subsequently heated at 20°C/min. Each blend shows a single composition dependent glass transition followed by P(VCl$_2$/VCl) crystallization and subsequent melting when the composition of this component is greater than 10% by weight. As shown in Figure 6, the single T_g is a linear function of total blend composition for quenched samples. However, for samples which have undergone a cyclic heating/cooling procedure, there is still a single T_g; but it is shifted to considerably lower temperatures, and the relation to total blend composition has pronounced curvature. The main factor responsible for these differences is, as pointed out by Robeson et al.,[11] that the composition of the amorphous phase
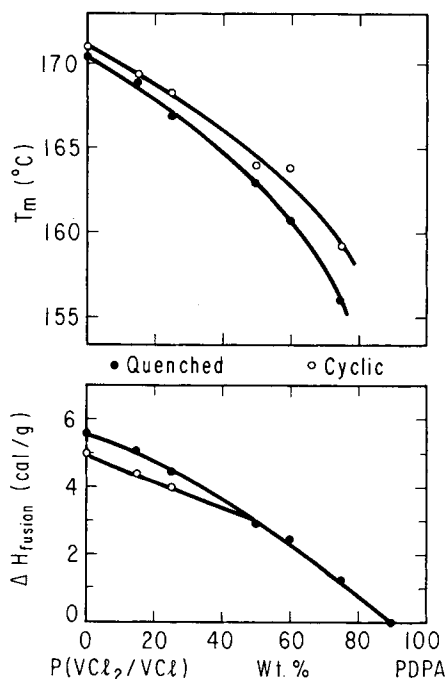
Fig. 7. Melting behavior of P(VCl2/VCl) in PDPA-containing blends.

is not the same for the two thermal histories. The quenched samples are essentially free of crystallinity when the T_g is traversed; thus, total blend composition and that of the amorphous phase are essentially the same. However, P(VCl2/VCl) crystallizes on cooling at 20°C/min so that the amorphous phase for the blends designated as "cyclic" is more rich in PDPA than indicated by total blend composition and, thus, has a lower T_g. Estimates of crystallinity and subsequent adjustment of the amorphous phase composition brings the T_g's for the two series of samples in closer but not total agreement. The remaining discrepancy is probably the result of an actual change in the amorphous phase and hence its T_g resulting from crystallinity—this effect has been documented for several polymers.[11,12]

Figure 7 shows the magnitude and location of the P(VCl2/VCl) melting peak as a function of blend composition following both the quenched and cyclic thermal histories. The differences between the two are rather slight considering that crystallization occurred on heating in one case (quenched) and on cooling in the other (cyclic).

Poly(1,4-Cyclohexanedimethylene Succinate)

Blends containing PCDS were completely transparent in the melt state and remained so to the highest temperature to which these samples could be heated. Any haze or cloudiness at lower temperatures may be attributed to component crystallinity.

Figure 8 summarizes the pertinent features of thermograms obtained using the cyclic procedure. Unfortunately, P(VCl2/VCl) and PCDS have T_g's located
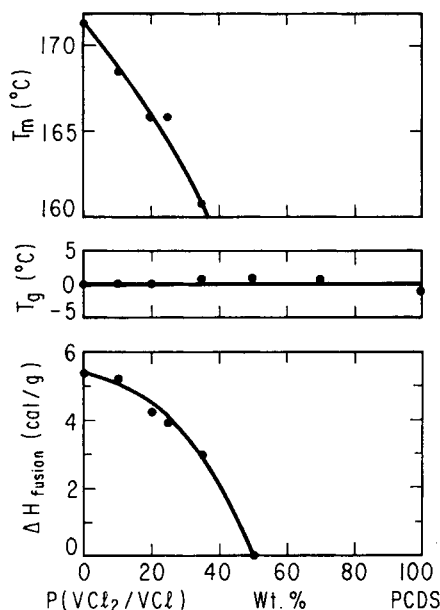
Fig. 8. Thermal behavior of blends containing PCDS using cyclic procedure.

only about 1°C apart so that the usual criterion using this transition provides no definitive statement about miscibility. However, based on the clarity of the melt, the severe suppression of crystallinity caused by PCDS, and the large depression of the P(VCl₂/VCl) melting point, we feel very confident in concluding that this pair forms a completely miscible amorphous phase. The more significant suppression of P(VCl₂/VCl) crystallization (no crystallinity of this component is noted for blends containing less than 50% using the cyclic history) caused by PCDS is owing to the fact that it has a higher T_g than does PDPA or PCL.[13]
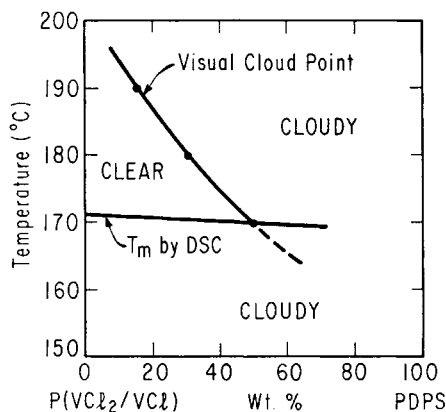

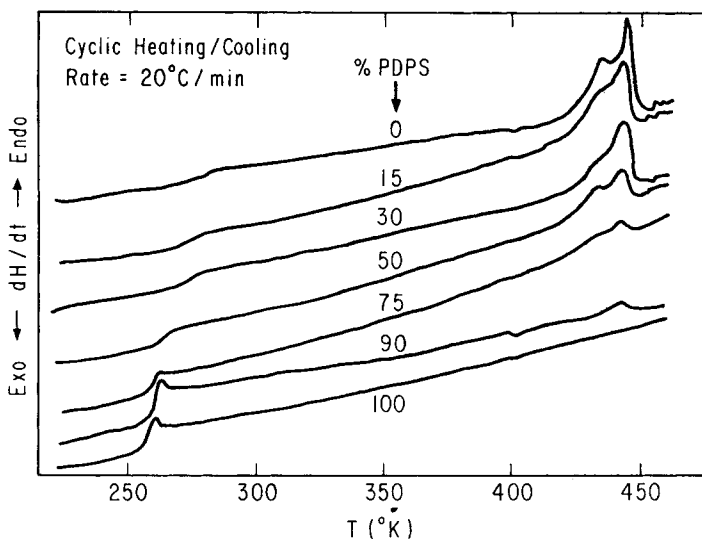Fig. 9. Phase behavior of blends containing PDPS.

Fig. 10. Thermograms for quenched PDPS containing blends.

Poly(2,2-Dimethyl-1,3-Propylene Succinate)

Cast films based on PDPS were similar in appearance and behavior to the previously described cases when they were rich in P(VCl₂/VCl). However, some significant differences were noted for blends rich in PDPS. The latter were cloudy as cast and did not clear up on heating as would be expected if this optical appearance resulted from crystallinity—note that PDPS like PDPA does not readily crystallize. In fact, these blends became even more cloudy after heating above the T_m of P(VCl₂/VCl), which is contrary to what was observed for the PDPA blends. On the other hand, blends poor in PDPS became quite clear above T_m but upon further heating became cloudy again. Figure 9 summarizes these observations. We conclude there is a cloud point curve stemming from LCST behavior which lies just above the T_m for P(VCl₂/VCl) at low PDPS concentrations but dips below this T_m curve at high PDPS contents. Thus, there is only a small window of clear blends on the left side of the phase diagram. Blends rich in P(VCl₂/VCl) are somewhat cloudy at low temperatures owing to crystallinity but are quite cloudy at high temperatures owing to LCST behavior. Upon cooling below the cloud point curve, these blends became clear again. Blends rich in PDPS are never completely clear owing to the intersection of the T_m and cloud point curves. There are, however, differences in the extent and nature of cloudiness stemming from crystallinity and amorphous phase separation.

Thermograms for quenched and for cyclic heated/cooled samples are shown in Figures 10 and 11. The glass transitions obtained using the two procedures are plotted vs. composition in Figure 12. There seems to be a single composition-dependent glass transition except for some of the quenched specimens which may have a possible second T_g just higher than the first. An example of this can be seen in the thermogram for the 75% PDPS blend shown in Figure 10. We are not at all certain that the shape of this thermogram is the result of two glass
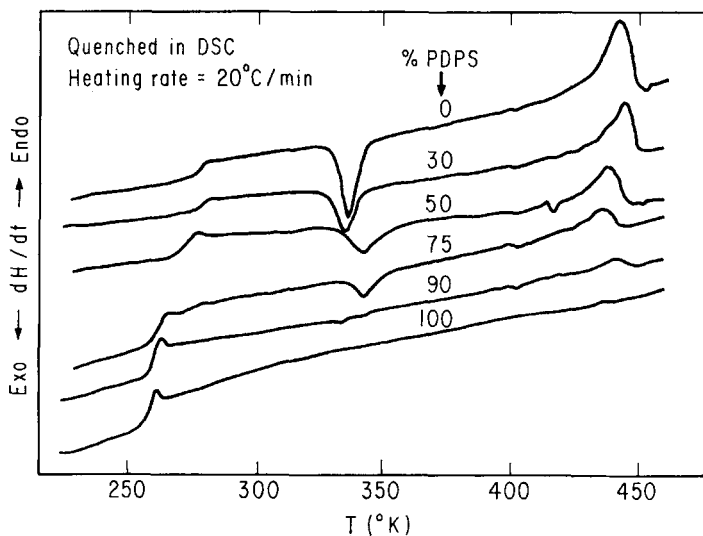
Fig. 11. Thermograms from cyclic procedure for PDPS containing blends.

transitions but simply wish to point out the possibility of this interpretation. Very likely the liquid–liquid cloud point curve mentioned earlier lies well above the T_g curve shown in Figure 12.   If this is the case, the equilibrium state in the region of T_g is a single amorphous phase; however, rapidly cooling a phase separated mixture may not allow enough time for a single phase to reform, and the observation of two glass transitions would then be reasonable.   All blends cooled slowly in the DSC showed a single glass transition.

Figure 13 shows the melting temperature for the P(VCl$_2$/VCl) and its heat of fusion.   Interestingly, blending with PDPS causes no suppression of crystallization and very little depression of the P(VCl$_2$/VCl) melting point.

Based on the above observations, we conclude this system is miscible but has a cloud point curve caused by LCST behavior, which is fortuitously only slightly above the P(VCl$_2$/VCl) melting point for a narrow range of compositions.   The molecular weight of this polyester is rather low as may be seen from the intrinsic viscosity information in Table I.   Blends using a high molecular weight PDPS
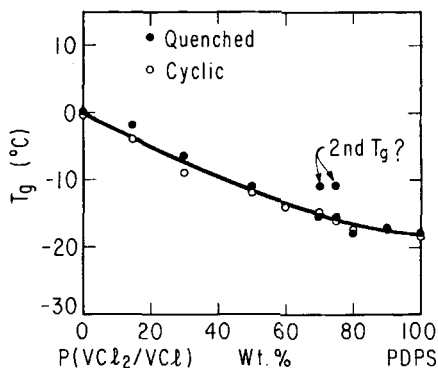

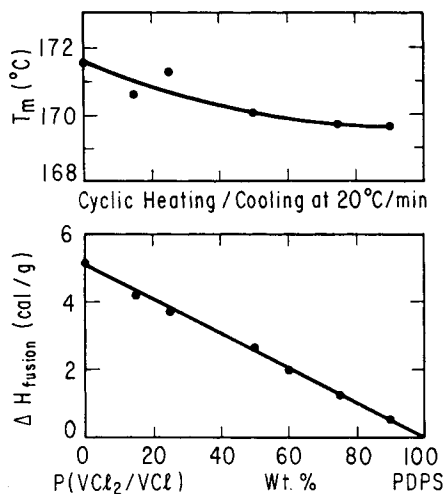Fig. 12. Glass transition behavior for blends with PDPS.

Fig. 13. Melting behavior of P(VCl₂/VCl) in PDPS containing blends.

would probably have a cloud point curve at much lower temperatures owing to the reduced combinatorial entropy, and there might be no region of clear blends.

SUMMARY AND DISCUSSION

The results described here show conclusively that a copolymer consisting of 86.5% vinylidene chloride and 13.5% vinyl chloride is miscible with the polyesters PCL, PDPA, PCDS, and PDPS, although LCST behavior is noted for the latter. No doubt, this copolymer is probably miscible with a number of other polyesters. The exact limits on polyester structures for which miscibility exists will be the object of future work. However, some intuition about the effect of polyester structure on the interaction responsible for miscibility in these systems can be gained by examining the melting point data described earlier.

Ideally, melting point data used for thermodynamic analyses of interactions ought to be corrected for any effects of crystal size that might exist[14]; however, this has not been done here owing to the preliminary nature of this study. Rather, melting point data from cyclic thermal histories are used with the belief that any errors so incurred will not alter the structural trends discerned from the analysis. When both components have rather large molecular weights, the depression of the melting point of component 2 by blending with species 1 reduces to

$$\Delta T_m = -T_{m2}(V_{2u}/\Delta H_{2u})B\phi_1^2 \tag{1}$$

using the Flory–Huggins treatment,[8] where B = an interaction parameter, ϕ_1 = volume fraction of 1, $(\Delta H_{2u}/V_{2u})$ = heat of fusion per unit volume of 2, and T_{m2} is the melting point of pure 2. For this analysis, we will use the value of $(\Delta H_{2u}/V_{2u})$ for poly(vinylidene chloride), which is reported[15] to be 26.2 cal/cm³. The melting points for P(VCl₂/VCl) in blends with the various polyesters are plotted in Figure 14 in the form indicated by eq. (1). The interaction parameters
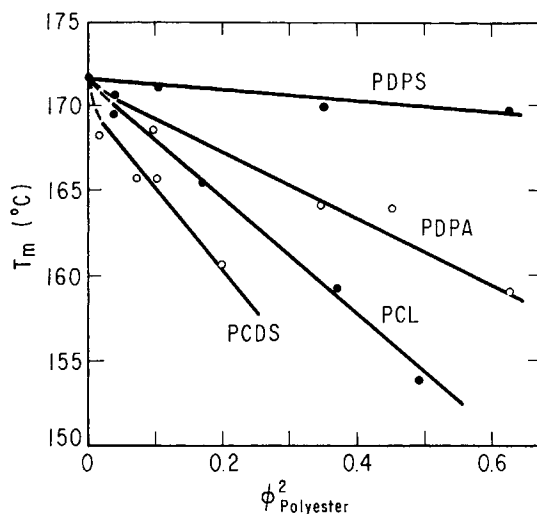
Fig. 14. Analysis of P(VCl₂/VCl) melting point depression caused by various polyesters.

deduced from the slopes of the lines drawn are listed in Table II. The molecular weights of PCL and PCDS are high enough to neglect the entropy effects on the melting point which eq. (1) does not include; however, the molecular weights of PDPA and PDPS may not be. The absence of absolute molecular weights on the latter precluded an exact allowance for this effect, but, as shown previously,[16] its inclusion would result in a slight reduction in the values of B listed for these two cases. It is interesting to note that the interaction parameter for blends with PDPS is quite small, which is consistent with the fact that this system phase separates near the T_m. The other polyesters exhibit more exothermic interactions as judged by the B values and do not show any evidence of LCST behavior in the accessible temperature range. One might conclude from the data in Table II that there is something of a trend for the interaction parameter to become more exothermic as the ratio of aliphatic carbons per ester linkage increases, as was found for PVC[2]; however, the fact that these structures include linear sequences of methylenes, branching and saturated rings makes such an interpretation very uncertain. It is quite interesting to see that apparently PCDS has a stronger interaction with P(VCl₂/VCl) than does PCL, even though both have the same number of aliphatic carbons in the repeat unit.

The information in Table II is based on the depression of the P(VCl₂/VCl) melting point. The blends containing PCL are unique in that this component is also readily crystallizable and exhibits a melting point depression that may

TABLE II

Interaction Parameter for Blends Based on the Depression of the P(VCl₂/VCl) Melting Point

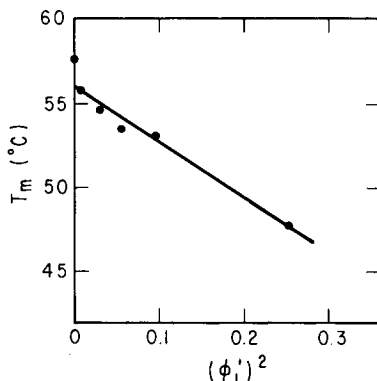| Polyester	CH_x/COO	B (cal/cm³)
PDPS	3.5	−0.2
PDPA	4.5	−1.1
PCL	5	−2.0
PCDS	5	−3.1

Fig. 15. Analysis of PCL melting point depression.

be similarly analyzed. However, in this case, there is some P(VCl₂/VCl) crystallinity present at the temperature at which PCL melts, and this alters the composition of the amorphous phase which is in equilibrium with the last traces of PCL crystals. By using the data in Figure 2 and the estimate of $(\Delta H_u/V_u)$ for P(VCl₂/VCl) mentioned above, this crystalline fraction can be computed thereby allowing the calculation of the actual amorphous phase composition. A melting point depression plot for PCL is shown in Figure 15, where ϕ_1' is the corrected volume fraction of P(VCl₂/VCl) in the amorphous phase for these blends. Using $(\Delta H_{2u}/V_{2u}) = 35.0$ cal/cm^3 for PCL,[17] a value of B of -3.77 cal/ cm^3 is obtained. This is a substantially larger value than obtained from analysis of the P(VCl₂/VCl) melting data; however, it should be recalled that the latter applies to a temperature of the order of 170°C while the PCL derived value would describe the system at about 55°C. If we assume both values are correct and that these differences stem from a temperature dependence of B, then a linear extrapolation of these two points indicates that B goes to zero at about 300°C. That is, based on this extrapolation, PCL–P(VCl₂/VCl) blends are predicted to have an LCST at about that temperature. Owing to decomposition problems, it is not possible to heat these blends to that temperature to check this prediction.

It has been suggested that carbonyl groups experience a specific interaction, or hydrogen bonding, with PVC through the α-hydrogen which is presumed to be polarized by the presence of the chlorine.[18] An alternate view is that therᵉ is an exothermic heat of mixing induced as a result of a chlorine–carbonyl interaction that does not directly involve the α-hydrogen.[5,19] Miscibility of carbonyl containing polymers with chlorinated polymers not having any α-hydrogen certainly speaks strongly for the second explanation of the exothermic interaction.[5,20] The copolymer employed here contains 13.5% by weight of vinyl chloride, which does have α-hydrogens; however, it is unlikely that the miscibility observed here is solely the result of this minor fraction of vinyl chloride. Rather, we expect there is also a favorable interaction involving the vinylidene chloride units, and those have no α-hydrogens.

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