Polyester–Polycarbonate Blends. V. Linear Aliphatic Polyesters

C. A. CRUZ, D. R. PAUL, and J. W. BARLOW, *Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712*

Synopsis

Polycarbonate blends with the linear aliphatic polyesters poly(ethylene succinate) (PES), poly-(ethylene adipate) (PEA), poly(1,4-butylene adipate) (PBA), and poly(hexamethylene sebacate) (PHS) were prepared by solution casting. Blends containing PES, PEA, and PBA exhibited a single T_g by DSC and thus form a single, miscible amorphous phase with polycarbonate. However, blends containing PHS exhibited only partial miscibility. Crystallinity of the polyesters was reduced by mixing with polycarbonate; however, plasticization by the polyesters induced crystallization of the polycarbonate. Miscibility in these systems is the result of an exothermic heat of mixing stemming from an interaction of the carbonyl dipole of the ester group with the aromatic carbonate. The effect of polyester structure on miscibility with polycarbonate is interpreted by and correlated with heats of mixing obtained by direct calorimetry of low molecular weight liquid analogs of the polymers.

INTRODUCTION

Earlier papers in this series[1-4] have shown that several polyesters are miscible with the polycarbonate of bisphenol A (PC). It is especially interesting that poly-ε-caprolactone is miscible with PC[4] since it is one of many possible aliphatic polyesters. It is the purpose of this paper to explore the extent that other similar polyesters of varying aliphatic structure may also be miscible with PC.

For the majority of the cases, it is our opinion that miscibility in polymer–polymer blends is the result of an exothermic heat of mixing caused by some specific interaction between polar groups within the two polymers.[5] We have recently employed direct calorimetry to measure the heat of mixing of low molecular weight liquid analogs of polycarbonate and various polyesters.[6,7] These results have added considerable insight into the nature of the interaction operative in this series and readily explain the miscibility observations for linear aliphatic polyesters with PC presented here.

The PC used in these studies is a commercial grade of Lexan obtained from the General Electric Co. Table I lists all of the polyesters employed in this paper which were obtained as uncharacterized specialty polymers from Aldrich Chemical Co.

BLEND PREPARATION

Blends of PES, PEA, and PBA with PC were prepared by solution casting using methylene chloride as the solvent. Approximately 1 g of each polymer was dissolved separately in 5 ml solvent. For the polyesters, this step was facilitated by warming the mixture to near the boiling point of methylene chloride, 39.5°C; however, the clear solutions thus formed were stable on prolonged

0021-8995/79/0024-2101$01.00

TABLE I
Polyester Structures

Name	Abbreviation	Structure
Poly(ethylene succinate)	PES	$-(CH_2)_2-O-\overset{\overset{\displaystyle O}{\|\|}}{C}-(CH_2)_2-\overset{\overset{\displaystyle O}{\|\|}}{C}-O-$
Poly(ethylene adipate)	PEA	$-(CH_2)_2-O-\overset{\overset{\displaystyle O}{\|\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|\|}}{C}-O-$
Poly(1,4-butylene adipate)	PBA	$-(CH_2)_4-O-\overset{\overset{\displaystyle O}{\|\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|\|}}{C}-O-$
Poly(hexamethylene sebacate)	PHS	$-(CH_2)_6-O-\overset{\overset{\displaystyle O}{\|\|}}{C}-(CH_2)_8-\overset{\overset{\displaystyle O}{\|\|}}{C}-O-$

standing at room temperature. Solutions of the polyesters were mixed with the PC solution, in appropriate amounts, to form ternary solutions of the desired PC–polyester proportions. In each case the clear ternary solutions were poured into aluminum pans, and the solvent was evaporated in a vacuum oven at 60°C for 24 hr. Under these conditions, the PC crystallized, primarily because of the presence of solvent,[4,8] thus necessitating premelting of this component as described later.

Thin film samples of blends prepared in this way were placed between glass slides and heated on a hot plate for visual observation. At 260°C, above the T_m of PC, blends of all three polyesters with PC were transparent, which suggests miscibility. Heating to higher temperatures, in search of lower critical solution temperature (LCST) behavior, was precluded by thermal decomposition of the polyesters,[9,10] which causes some bubble formation beginning at about 220°C.

Blends of PHS with PC were formed in a similar manner, except that dioxane was used as the solvent. Dioxane was removed by heating the film specimens at 110°C to constant weight. The ternary solutions were clear; however, the solvent-free blends were opaque at 270°C even though both pure polymers are clear at this temperature. Thus, in the melt state this system is not a one-phase mixture. PHS was observed to be thermally more stable than the three previous polyesters.

RESULTS AND DISCUSSION

Thermal analysis of these blend systems was done with a Perkin–Elmer DSC-2 equipped with a full-range subambient accessory. Here, the T_g was taken as the onset of the step change in the baseline while T_m was taken at the maximum of the melting endotherm as commonly done in DTA.

As mentioned earlier, solvent casting induces crystallization of PC which normally does not occur on cooling this polymer from the melt. This history effect can be erased by melting the specimen, but in these systems some care must be exercised to prevent degradation of the polyester or to ensure that no interchange reactions occur between the polyester and PC.[3,4] As a compromise, the following strategy was used. The original solution-cast specimens were introduced into the DSC chamber and heated at 10°C/min to 180°C. At this point, heating proceeded at 320°C/min up to 260°C to melt the PC. The specimens were then cooled at 320°C/min to 180°C. Next, cyclic heating and cooling was

performed at 10°C/min between 180°C and a lower limit set depending on the glass transition of the polyester. Two cycles were run in this manner, and then a final heat was made from the lower limit to 260°C to examine the possible appearance of a PC melting point. Good reproducibility was obtained by this scheme. In the thermograms shown subsequently, the polarity convention of DTA is employed.

Poly(ethylene Succinate) Blends

As seen in Figure 1, PES exhibits a rather complex thermal behavior. A T_g is observed at −17°C, compared to the value of −1°C reported in the literature.[11] Following cooling from the melt at 10°C/min, two crystallization exotherms appear on heating—a large one at 44°C and a smaller one at 86°C. A melting endotherm is observed at 101°C. Several polymers are reported[12-15] to show dual crystallization peaks.

Representative thermograms for two PC–PES blends are shown in Figure 1. All blends exhibited a single T_g with the composition dependence shown in Figure 2. This behavior is evidence for a single, miscible amorphous phase in this system.

Figure 3 shows the heat of fusion of PES observed as a function of blend composition. During cyclic heating and cooling, crystallinity of PES is completely suppressed for blends containing 22% by weight or less of this component. Similar responses for miscible blends have been observed previously.[5,8] Figure 4 shows the effect of blend composition on the magnitude of the two crystallization isotherms mentioned previously.
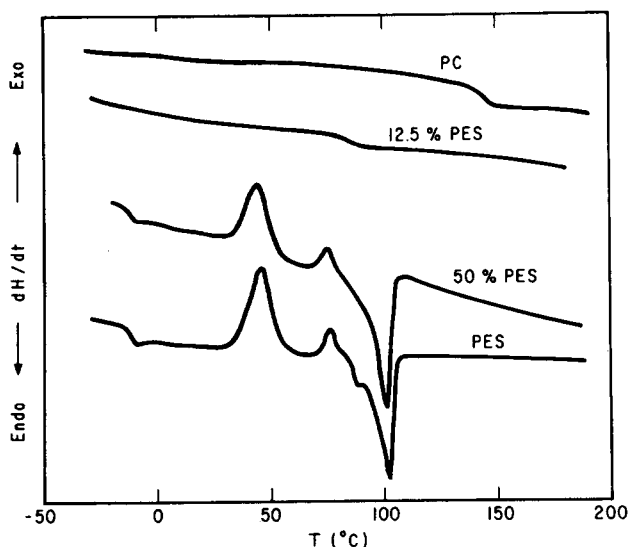
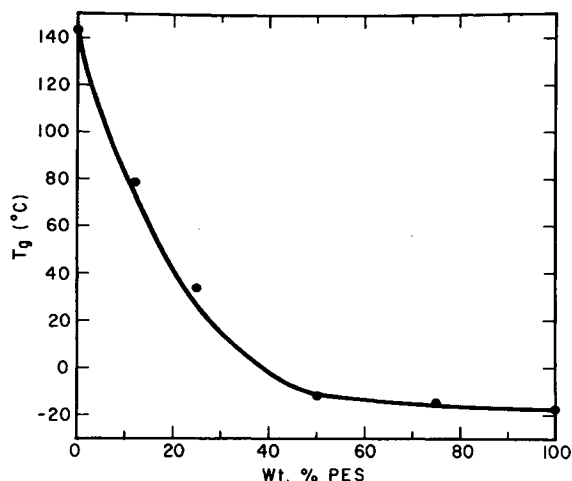

Fig. 1. Thermograms for the PC–PES system.

Fig. 2. Glass transition temperature behavior of PC–PES blends.

Poly(ethylene Adipate) Blends

Figure 5 illustrates the thermal behavior of PEA. A T_g is observed at $-47°C$, which agrees rather well with a reported value of $-50°C$.[11] A large crystallization exotherm is seen at $-3°C$ which is followed by a smaller one at $29°C$. The T_m is observed at $47.5°C$, which falls within the range of values reported by others.[11-13]

All blends showed a single T_g which varies with blend composition as shown in Figure 6. Based on this result, it is concluded that the PC–PEA system forms a single miscible, amorphous phase.

Addition of PC severely reduces the crystallinity of PEA that develops during the present cyclic heating and cooling scheme as shown in Figure 7. The observed heats of fusion were converted to crystallinity values in Figure 7 using the value of 29.4 cal/g for the heat of fusion of 100% crystalline PEA estimated
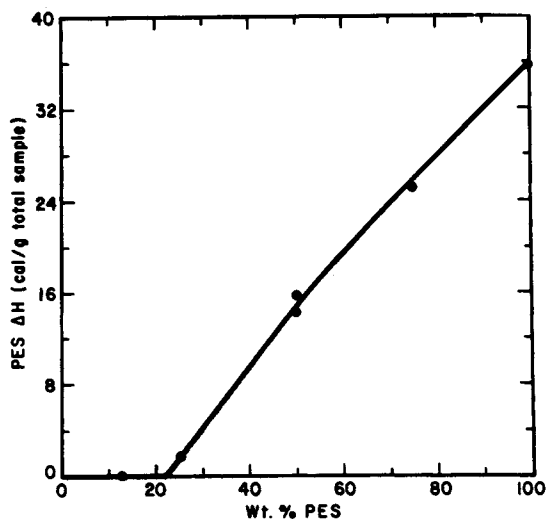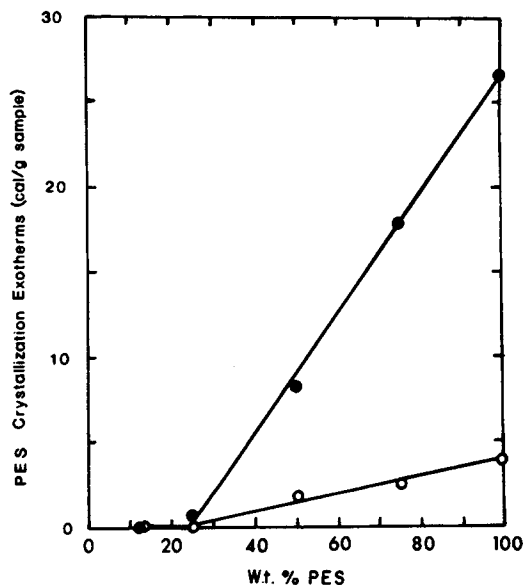

Fig. 3. PES heat of fusion observed in PC–PES blends.

Fig. 4. Crystallization exotherms for PES: (●) low-temperature exotherm; (○) high-temperature exotherm.

by Hobbs and Billmeyer.[16] Blends containing less than 50% PEA did not develop any crystallinity. Figure 8 shows the magnitude of the two crystallization peaks mentioned earlier. These peaks occurred at slightly higher temperatures for the blend than they did for pure PEA.

Figure 9 shows the magnitude in the baseline shift at the T_g for PC–PEA blends after normalization by the amount of amorphous material in the sample. The sizable difference in this quantity for the two pure polymers is attributable to the differences in chain stiffness of PC compared to PEA.[4]
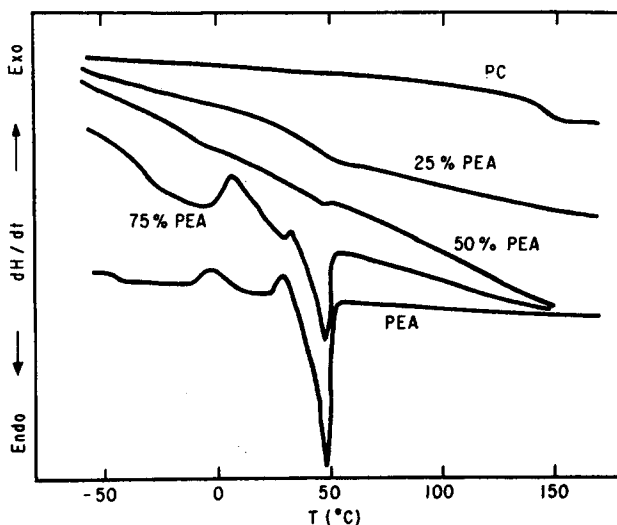
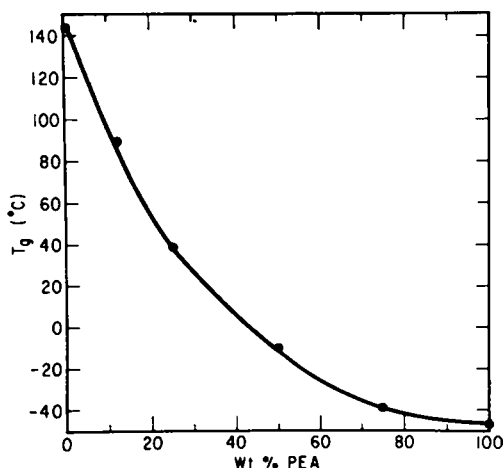

Fig. 5. Thermograms for the PC–PEA system.

Fig. 6. Glass transition temperature behavior of PC–PEA blends.

Poly(1,4-butylene Adipate) Blends

Selected thermograms for this system are shown in Figure 10. PBA showed a T_g of $-57°C$, which is within the range of $-70°$ to $50°C$ reported in the literature. The observed T_m of $57°C$ agrees quite well with reported values.[17,18] This polymer crystallizes rapidly on cooling and thus shows no crystallization exotherms on heating.

All blends showed a single T_g which varies with blend composition as shown in Figure 11. The heat of fusion of PBA observed on heating is shown in Figure 12. PBA crystallinity is totally suppressed in blends containing 25% or less of this component.

From the above, it is evident that the system PC–PBA also forms a single, miscible phase.

Poly(hexamethylene Sebacate) Blends

Thermograms for the PC–PHS system are shown in Figure 13. Pure PHS shows a very weak T_g at $-59°C$, whereas a totally amorphous specimen of this polymer is reported to have a value of $-79°C$.[19] The observed T_m of $67°C$
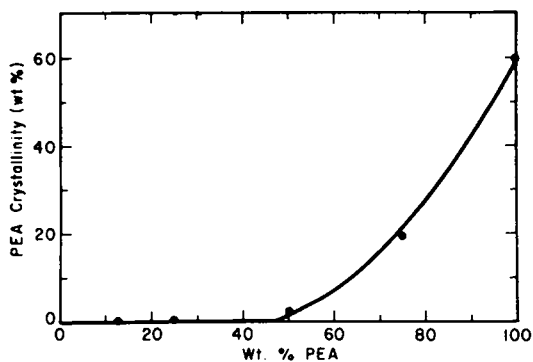

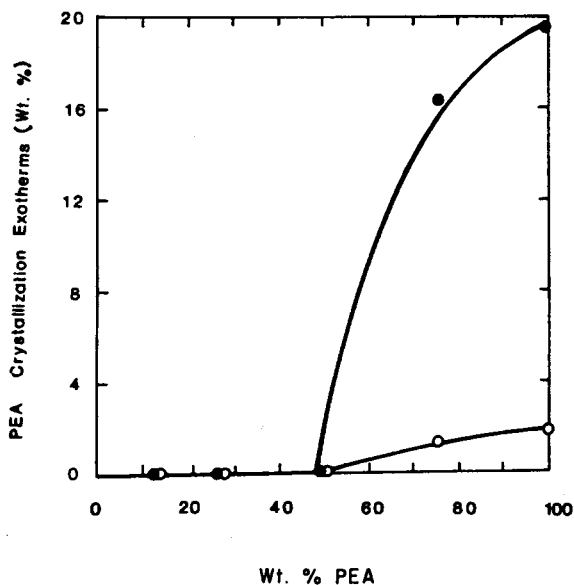Fig. 7. PEA crystallinity observed for PC–PEA blends.

Fig. 8. Crystallization exotherms for PEA: (●) low-temperature exotherm; (O) high-temperature exotherm.

compares well with a reported value.[18]   No crystallization exotherms were noted on heating.

The T_g values observed for this system are very small in magnitude. Specimens containing 25 and 50 wt % PC exhibit signs of a glass transition around $-59°C$; however, both blends are hazy at higher temperatures, as mentioned previously. Therefore, the possibility of partial miscibility or a lower critical solution temperature exists. The melting point of PHS is depressed from the 67°C value for the pure polymer to 62°C for both of these blends.

In samples containing 25% and 12.5% PHS there appears to be a glass transition at around $-50°C$, followed by melting of the PHS crystalline phase in the interval
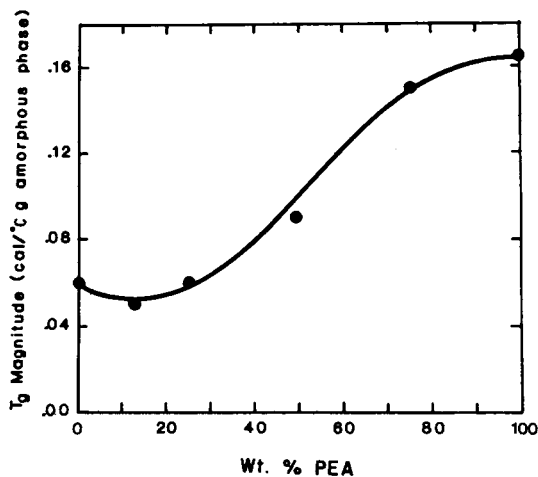

Fig. 9. Magnitude of baseline shift at T_g for PC–PEA blends per unit mass of amorphous phase.
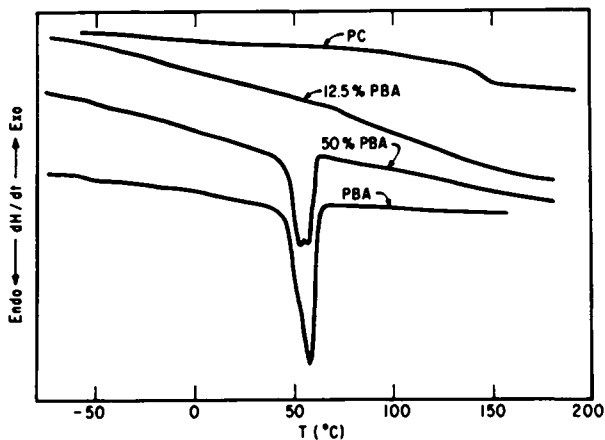
Fig. 10. Thermograms for the PC–PBA system.

62–67°C. A second T_g is also apparent at about 50°C in the specimen containing 25% PHS and at 85°C in the sample with 12.5% PHS (See Fig. 13).

It is interesting to note that the degree of crystallinity of PHS is affected by blending with PC. A plot of the heat of fusion of PHS versus blend composition is shown in Figure 14. ⸱In immiscible systems, such a plot generally yields a straight line connecting the point for the pure crystallizable polymer with the origin. This behavior is not observed here. Instead, PHS crystallizes to a lesser extent than it does in the pure state as shown in Figure 14.

The above evidence suggests that blends of PC and PHS do not form a single amorphous phase for all blend proportions; however, the two polymers appear to be partially miscible instead. The weakness of the glass transitions in this system precluded a better definition of the nature of this partial miscibility in this exploratory study.
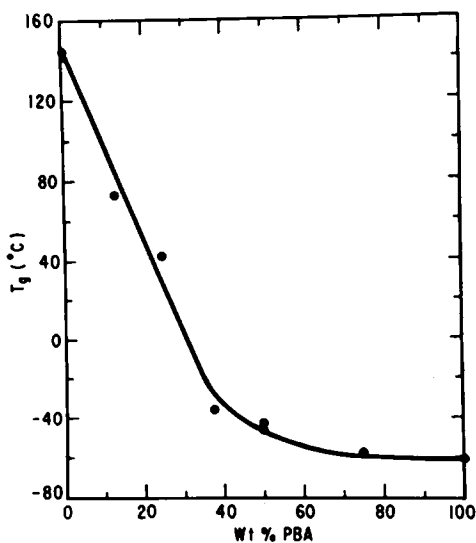

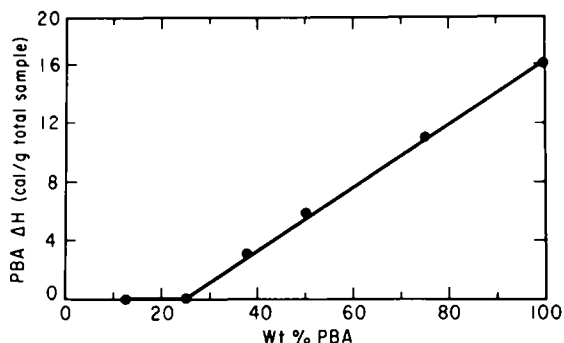Fig. 11. Glass transition behavior of PC–PBA blends.

Fig. 12. PBA heat of fusion observed in PC–PBA blends.

Induced Crystallization of Polycarbonate

Melt-processed polycarbonate generally does not crystallize on cooling; however, it is well known that solvents or plasticizers will induce its crystallization. This was also observed in the blends of poly-ϵ-caprolactone with PC described earlier.[4] Block copolymers of PC with PEA have also been noted to form PC crystallinity.[20] The blends described in this paper also exhibited a small but broad endotherm at about 220°C on the final DSC heat which went up to 260°C. This endotherm may be attributed to melting of PC crystallinity developed earlier. Recall that any solvent-induced PC crystallinity was removed in the first DSC heat. Not all polymers which are miscible with PC will cause the polycarbonate to crystallize. Evidently, plasticization analogous to that caused by solvents is required to develop PC crystallinity. Low T_g polyesters with flexible chains can serve this purpose by reducing the glass transition temperature of the blend and thus creating a sufficiently mobile environment from which the PC segments can crystallize. The glass transition temperature of the pure polyester has been found to provide a good measure of its ability to
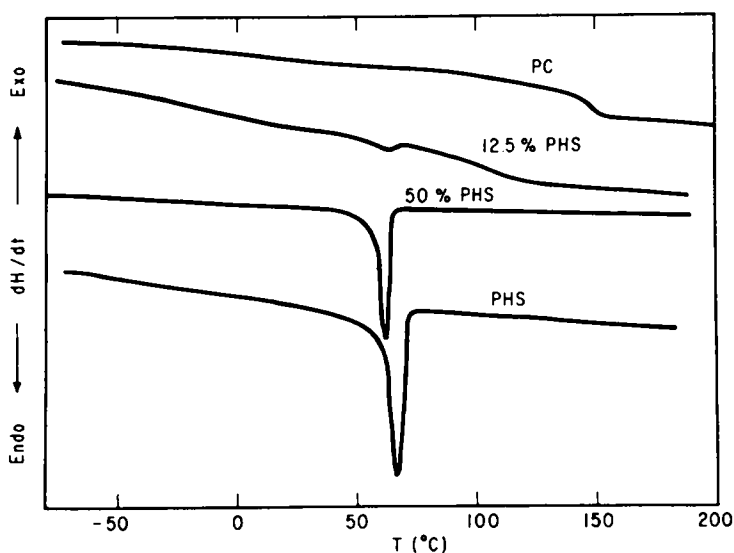

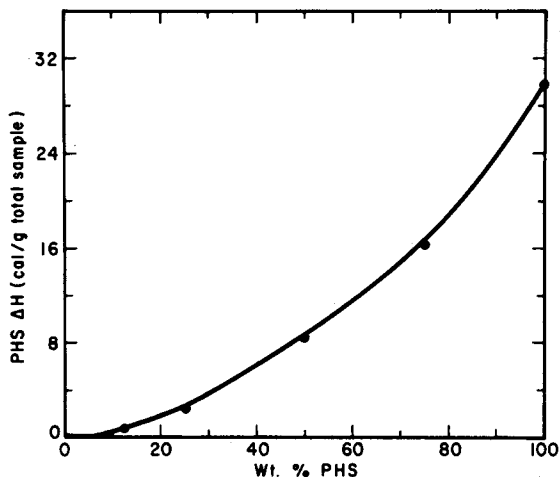Fig. 13. Thermograms for the PC–PHS system.

Fig. 14. PHS heat of fusion observed in PC–PHS blends.

create this necessary condition for PC crystallization. Figure 15 shows the percent PC crystallinity observed in 50/50 blends versus the T_g of the polyester in the blend. Interestingly, no PC crystallinity develops unless the diluent T_g is about −15°C or lower. Beyond this, the PC crystallinity increases as the diluent T_g is reduced further. For most blends, the maximum PC crystallinity occurred in 50/50 blends. In this diagram, the low T_g misicible polyesters are PES, PEA, PBA, and PCL,[4] while the partially miscible point corresponds to PHS. The other points corresponds to systems that have been described previously[1–4] or will be presented in future papers in this series.[6]

SUMMARY AND CONCLUSIONS

In this paper it has been shown that blends of bisphenol-A polycarbonate with aliphatic polyesters of the structure

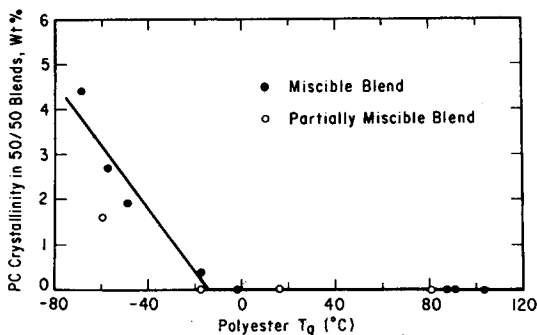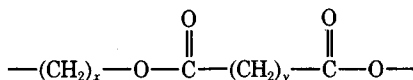$$-(CH_2)_x-O-\overset{O}{\underset{\parallel}{C}}-(CH_2)_y-\overset{O}{\underset{\parallel}{C}}-O-$$


Fig. 15. Effect of the polyester T_g on the degree of polycarbonate crystallinity developed in 50/50 PC–polyester blends: (●) miscible blend; (○) partially miscible blend.

exhibit single glass transitions by DSC and thus are miscible in the amorphous phase when $x = 2, y = 2; x = 2, y = 4;$ and $x = 4, y = 4$. However, when $x = 6$, $y = 8$, these mixtures are only partially miscible. In an earlier paper it was shown that the polyester

$$—(CH_2)_5—\overset{\overset{\displaystyle O}{\|}}{C}—O—$$
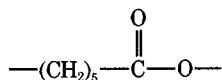
was also miscible with polycarbonate.[4] Apparently, these systems are miscible as the result of a specific interaction which produces an exothermic heat of mixing which causes a negative free energy of mixing in spite of a negligible contribution from configurational entropy of mixing predicted for polymer–polymer blends. In other blend systems it has been possible to explore the magnitude of the interaction through the classical melting point depression phenomenon; however, this approach is complicated in present systems and was not explored. Rather, we examined directly the heat of mixing of low molecular weight analogs of these polymers using a calorimetric technique described earlier.[6,7] Diphenyl carbonate was selected as the analog of PC while various mono- and diester compounds were used to model the polyesters. It was found that the heat of mixing in these cases was exothermic so long as the number of methylene groups per ester linkages was less than seven; however, at this higher hydrocarbon content the mixing became endothermic.[6,7] This corresponds well to the present observations on polymer–polymer miscibility.

Additional calorimetry work on model compounds showed that the aromatic nature of the polycarbonate is essential to develop an exothermic heat of mixing. Mixtures of esters with propylene carbonate or dimethyl carbonate always yielded endothermic heats of mixing. Ketones gave comparable heats of mixing with diphenyl carbonate, as did the analogous esters. Thus, we conclude that miscibility in the polyester–polycarbonate blends stems from the interaction of the carbonyl dipole of the ester group with the highly polarizable aromatic carbonate structure. As the hydrocarbon content of the polyester is increased, the net heat of mixing becomes positive when the proportion of endothermic interactions outweigh the exothermic interaction mentioned above. We expect that all unbranched aliphatic polyesters that do not violate this balance will be miscible with polycarbonate.

All of the polyesters employed here crystallized from the miscible blends with PC. However, because of the kinetic restrictions imposed by the cyclic heating and cooling thermal analysis scheme used here,[5,8] complete elimination of polyester crystallinity was observed for some blends rich in PC. Polyesters with low glass transitions sufficiently plasticized the PC to cause it to crystallize.

The methods of blend preparation employed here should have greatly minimized the possibility of any interchange reactions between the polyesters and the polycarbonate.[3,4]

References

1. D. C. Wahrmund, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **22**, 2155 (1978).

2. T. R. Nassar, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **23**, 85 (1979).

3. R. N. Mohn, D. R. Paul, J. W. Barlow, and C. A. Cruz, *J. Appl. Polym. Sci.*, **23**, 575 (1979).

4. C. A. Cruz, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **23**, 589 (1979).

5. D. R. Paul, J. W. Barlow, R. E. Bernstein, and D. C. Wahrmund, *Polym. Eng. Sci.*, **18**, 1225 (1978).

6. C. A. Cruz, Ph.D. Dissertation, The University of Texas at Austin, 1978.

7. C. A. Cruz, J. W. Barlow, and D. R. Paul, *Macromolecules*, **12**, 726 (1979).

8. D. R. Paul and J. W. Barlow, *ACS Organ. Coat. Plast. Chem. Prepr.*, **40** (1), 745 (1979).

9. R. E. Bernstein, C. A. Cruz, D. R. Paul, and J. W. Barlow, *Macromolecules*, **10**, 681 (1977).

10. E. Nolley, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **23**, 623 (1979).

11. O. G. Lewis, *Physical Constants of Linear Homopolymers*, Springer-Verlag, New York, 1968.

12. B. Ya. Teitel'baum and L. I. Tuzova, *Polym. Sci. USSR*, **15**, 1032 (1973).

13. B. Ya. Teitel'baum, *J. Thermal Anal.*, **8**, 511 (1975).

14. V. I. Kovalenko, N. P. Anoshina, N. A. Palikhov, A. A. Mukhutdinov, and B. Ya. Teitel'baum, *Polym. Sci. USSR*, **18**, 1596 (1976).

15. C. S. Fuller and C. J. Frosch, *J. Phys. Chem.*, **43**, 323 (1939).

16. S. Y. Hobbs and F. W. Billmeyer, Jr., *J. Polym. Sci. A-2*, **8**, 1387 (1970).

17. M. Sh. Yagfarov, *Polym. Sci. USSR*, **17**, 2476 (1975).

18. H. Mark, N. Bikales, and N. G. Gaylord, Eds., *Encyclopedia of Polymer Science and Technology*, Vol. II, Wiley, New York, 1969, p. 20.

19. J. J. O'Malley and W. J. Stauffer, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 865 (1974).

20. S. H. Merrill, *J. Polym. Sci.*, **55**, 343 (1961).