Polyester–Polycarbonate Blends. VII. Ring-Containing Polyesters

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Synopsis

Thermal analysis was used to show that blends of poly(1,4-cyclohexanedimethylene succinate) (PCDS) with polycarbonate (PC) are completely miscible in the amorphous phase. Blends of PC with poly(ethylene orthophthalate) (PEOP) were found to have a miscibility gap in the midconcentration range and are thus not miscible in all proportions. Similarly, a commercial copolyester formed from ethylene glycol, 1,4-cyclohexanedimethanol, terephthalic acid, and isophthalic acid is partially miscible with PC. These observations are discussed in terms of the structural features of the three polyesters.
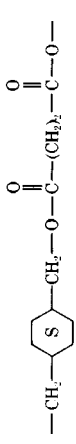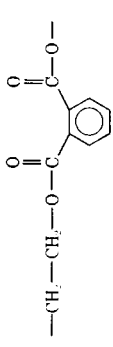
INTRODUCTION

Previous articles in this series[1-6] have shown that a considerable number of polyesters are miscible with polycarbonate (PC) owing to an exothermic interaction between the carbonyl of the ester linkage and the aromatic carbonate structure.[7] Linear, aliphatic polyesters are completely miscible with PC when the number of methylene units per ester linkage is less than about six[4,5]; however, branching can disrupt this favorable interaction.[6] Aromatic polyesters based on 1,4-cyclohexanedimethanol have also been found to be miscible with PC[3]; however, aromatic polyesters based on ethylene and butylene glycols are only partially miscible with PC.[1,2] The purpose of this article is to report additional observations on the state of miscibility of PC with selected polyesters containing ring structures in order to expand the general understanding of the relationship between molecular structure and the thermodynamic phase state in polycarbonate–polyester mixtures.

The three polyesters described in Table I were selected for this study because of the following reasons. The first entry in Table I, PCDS, is nonaromatic but contains a saturated ring from the 1,4-cyclohexanedimethanol monomer. Except for this cyclic character, this polymer is analogous to other aliphatic polyesters which have been found to be miscible with PC[4,5] and it was of interest to learn whether a polyester with this cyclic organization within the chain would behave similarly with regard to miscibility with PC. The second entry, PEOP, was selected because it is a structural isomer of poly(ethylene terephthalate) which was found to be completely miscible with PC in blends containing less than 30–40% PC but incompletely miscible in blends containing more PC than this. It was of interest to learn to what extent the location of the ester attachments on the aromatic ring affects the state of mixing the PC blends. The final entry, KODAR-PETG, is a new commercial polyester containing mixtures of both glycol

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TABLE I
Ring-Containing Polyesters

Chemical name	Designation used here	Source	Structure
Poly(1,4-cyclohexanedimethylene succinate)	PCDS	Aldrich Chemical Company	$-CH_2-\!\langle S\ ring\rangle\!-CH_2-O-C(=O)-(CH_2)_2-C(=O)-O-$
Poly(ethylene orthophthalate)	PEOP	Aldrich Chemical Company	$-CH_2-CH_2-O-C(=O)-\langle ortho\text{-}C_6H_4\rangle-C(=O)-O-$
—	KODAR-PETG	Eastman Chemical Products, Inc.	copolyester containing EG + CHDM + TA + IPA[a]

[a] $EG = HOCH_2CH_2OH$; $CHDM = HOCH_2-\langle S\ ring\rangle-CH_2OH$; $TA = HOOC-\langle C_6H_4\rangle-COOH$; $IPA = HOOC-\langle C_6H_4\rangle-COOH$ (meta)

and acid units. Qualitatively, this material is similar to KODAR-A150, which was found to be completely miscible with PC[3], except for the inclusion of ethylene glycol units. Therefore, it was of interest to learn how the inclusion of ethylene glycol into this polyester would affect miscibility with PC. The polycarbonate used in this study was from the same batch as that employed in earlier articles in this series.[1–6] No molecular weight information was available for any of these materials.

All conclusions about miscibility are based on thermal analysis (DTA or DSC) of either solution or melt-processed blends. As mentioned in other articles in this series, PC and polyester blends are potentially reactive systems at high temperatures. However, based on the accumulated evidence, the present results are not affected by such possibilities.

PC BLENDS WITH PCDS

Blend Preparation

PC–PCDS blends were prepared by dissolving each polymer separately in methylene chloride, combining the two solutions in appropriate proportions, and evaporating the solvent in a vacuum oven at 60°C for 24 hr. The ternary solutions contained about 1 g polymer per 5 ml solvent and were single phase in every case.

As cast, some of the blends were hazy, owing to crystallinity, but became clear on heating past the melting point of each component. Further heating to 260°C failed to show any evidence of phase separation caused by lower critical solution temperature (LCST) behavior.

DSC Results

For thermal analysis, specimens were loaded into a Perkin–Elmer DSC 2, heated rapidly to 260°C to melt any PC crystallinity formed during casting, and then rapidly cooled to 180°C. Three heating and cooling cycles were made at 10°C/min. The upper and lower limits for these cycles were 180 and −20°C, respectively, for the first two cycles, and 260 and −20°C for the last cycle. Typical DSC traces are shown in Figure 1.

Pure PCDS exhibits a complex thermal behavior similar to that of other polyesters.[5] The DSC trace in Figure 1 shows a T_g at −1°C, followed by two exotherm peaks indicative of crystallization. A main melting peak occurs at 133°C, which is slightly lower than values reported in the literature for this polymer.[8,9] All of the blends of this polymer with PC exhibited a single glass transition that depends on composition, as shown in Figure 2.

The shape of the T_g curve in Figure 2 is similar to that for other miscible polyester–PC systems.[3–5] The magnitude of the PCDS melting endotherm decreased dramatically upon addition of PC, and, as seen in Figure 3, blends containing less than 50% PCDS did not develop crystallinity during the thermal cycle employed. The two crystallization exotherms exhibited similar responses as shown in Figure 4. The temperatures at which PCDS melted, however, was relatively unchanged by addition of PC. The single T_g for these blends and the kinetic suppression of PCDS crystallization caused by PC are positive evidence that this system forms a miscible amorphous phase.
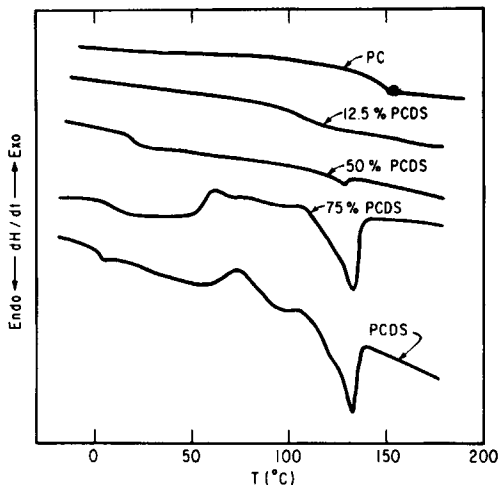
Fig. 1. Typical thermograms for PC–PCDS blends.

PCDS does not induce crystallization of PC as some miscible aliphatic poly-esters do, evidently because of the greater stiffness of the PCDS backbone which results in its higher T_g.

PC BLENDS WITH PEOP

Blend Preparation

Volatile matter was removed from the as-received PEOP by heating to constant weight in a vacuum oven at 80°C. Blends of this purified polymer with PC were solution cast from methylene chloride using the same procedures described above for PCDS. Blends in the midcomposition range showed a slight opacity. Heating to 260°C did not change the optical appearance of any of the blends.
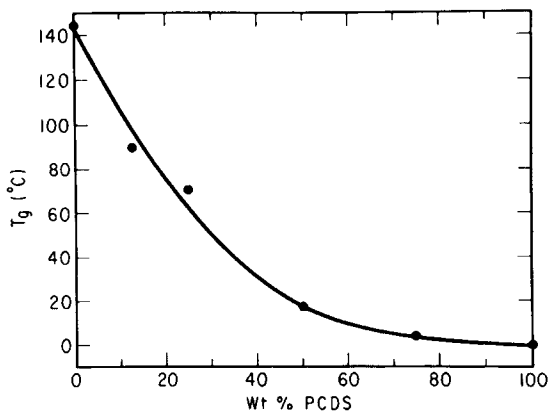

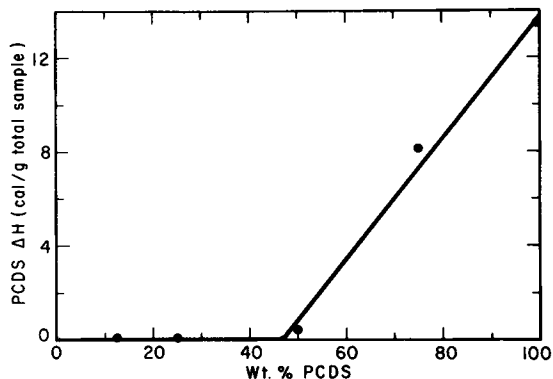Fig. 2. Glass transition behavior of PC–PCDS blends.

Fig. 3. Crystallinity (proportional to ΔH) of PCDS in PC–PCDS blends.

DSC Results

The thermal cycles in the DSC were performed exactly as those for PCDS except that a lower limit of −10°C was used instead of −20°C. Some typical thermograms are shown in Figure 5.

Pure PEOP exhibited a T_g of 17°C, which coincides with the reported value.[8] No other thermal event was noted. A T_m of 108°C has been reported[10]; however, even after annealing for 12 hr at 40°C there was no evidence of crystallinity in the DSC traces. All of the midrange compositions of PEOP–PC blends exhibited two distinct glass transitions. As seen in Figure 5, the T_g for PC is depressed and broadened by addition of PEOP. On the other hand, the PEOP transition remains relatively sharp and is increased only slightly by PC addition. The T_g locations are plotted against overall blend composition in Figure 6. Blends rich in either PEOP or PC seem to have only one T_g, although this observation is more certain for the former than for the latter.

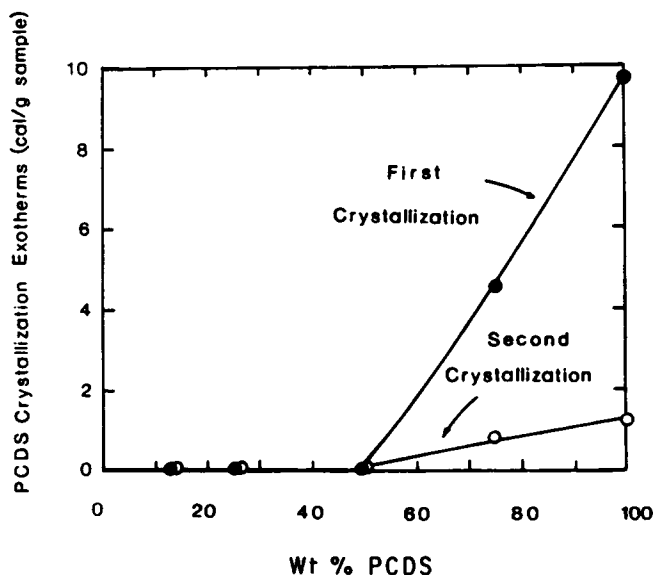The shape of the T_g responses shown in Figure 6 supports the following ten-

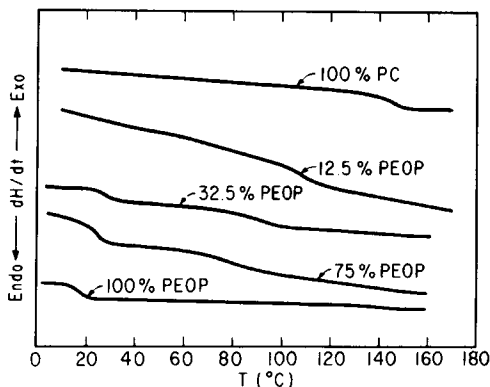Fig. 4. Effect of blend composition on PCDS crystallization exotherms.

Fig. 5. Typical thermograms for PC–PEOP blends.

tative conclusions for the PEOP–PC system. At compositions less than about 25% or greater than those of about 87.5% PEOP, the two components appear to be completely miscible. However, there is a miscibility gap between these limits, but we cannot say whether it stems from UCST or LCST behavior. The flatness of the two branches of the T_g relation in this gap suggests that the composition of the two phases does not vary as overall blend composition is changed. The upper transition is considerably lower than the T_g of pure PC, and the break point suggests that the corresponding phase contains about 75% PC. That the lower transition is so slightly above the T_g of PEOP might at first glance suggest that the corresponding phase contains very little PC. However, it must be recalled that the T_g diagrams for all miscible polyester–PC systems are similar in shape and are very flat in their approach to the polyester side of the diagram.[4,5] Figure 2 is typical. Based on this consideration, the PEOP-rich phase may contain as much as 25% PC. It must be emphasized that there is an inherent problem associated with constructing phase diagrams from T_g behavior, viz., the diagram is not isothermal. The results obtained here are affected to some degree by the thermal history imposed by the cyclic heating and cooling pattern employed. Equilibrium phase boundaries and compositions must be established by other means; however, the present results provide a useful starting point for such detailed studies.

No PC crystallinity was observed in blends with PEOP after that which is induced during solvent casting had been melted.
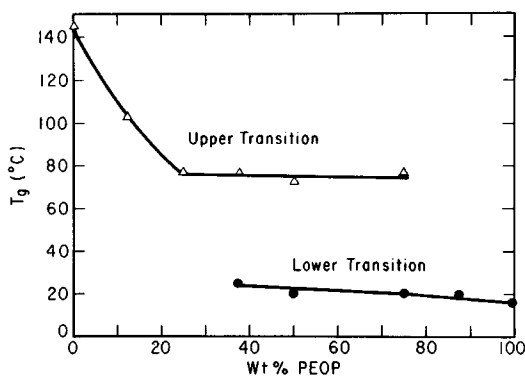

Fig. 6. Glass transition behavior of PC–PEOP blends.

PC BLENDS WITH KODAR-PETG

Blend Preparation

KODAR-PETG is a commercial product from Eastman Chemical Products, Inc., marketed for molding, profile extrusion, and film and sheet applications. It is a copolyester consisting of undisclosed proportions of terephthalic and isophthalic acids and two glycol monomers, ethylene glycol and 1,4-cyclohex-anedimethanol. This copolymer apparently does not crystallize at all. Blends with polycarbonate were made by both melt and solution methods.

Melt blends were made by introducing the desired mixture of pellets of KODAR-PETG and PC into the bowl of a Brabender Plasticorder preheated to 250°C using precautions to exclude oxygen. Mixing continued at 80 rpm for about 8 min, by which time the torque had stabilized. The molten mass was taken from the bowl, and specimens for thermal analysis were excised without further processing. All blend melts were clear. Specimens were heated to 270°C with no change in appearance.

Blends were also cast from methylene chloride solutions and dried of solvent at 50°C in a vacuum oven to constant weight. The solutions were single phase; however, the cast film was slightly translucent.

DTA Results

Thermal analysis for this system was performed with an R. L. Stone DTA outfitted with a furnace platform which contains no provision for programmed cooling. In each run, heating occurred at 10°C/min to 250°C, whereupon the furnace was cooled to 30°C by forced air circulation. All heats after the first were reproducible and all results here are from second heats. Figure 7 shows typical thermograms.

Pure KODAR-PETG exhibits a T_g at 77.5°C, which is within the range of other polyesters of related structure. Blends rich in PC show two glass transitions; however, for blends containing 75% or more KODAR-PETG, only one T_g was detected. Figure 8 shows the temperature location of glass transitions observed for the various blend compositions. To better illustrate the magnitude of these transitions, Figure 9 shows plots of the baseline shift at each transition (in arbitrary units normalized for sample mass). The magnitude of the upper tran-
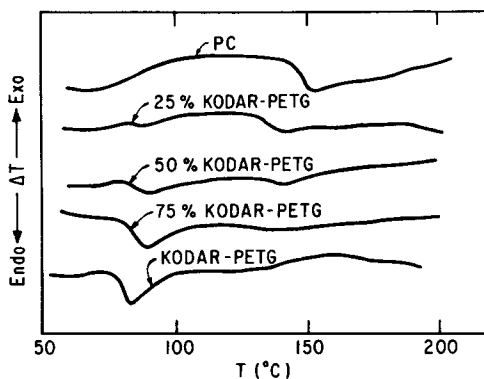

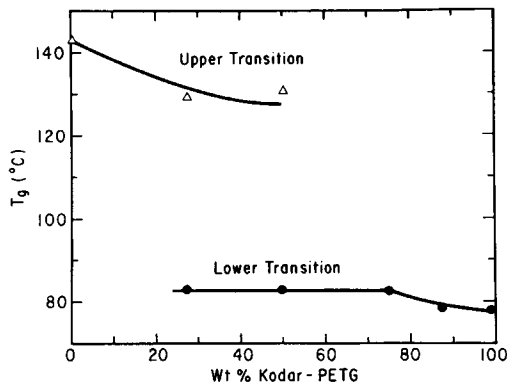Fig. 7. Typical thermograms for PC/KODAR–PETG blends.

Fig. 8. Glass transition behavior of PC/KODAR–PETG blends.

sition, associated with a PC-rich phase, decreases steadily as KODAR-PETG is added, and goes to zero at about 75%. The magnitude of the lower transition, associated with a KODAR-PETG-rich phase, decreases steadily with PC addition, and by its shape would appear to go to zero at a finite KODAR-PETG concentration, although this was not actually observed since no sample containing less than 25% of this component was tested. The sum of the magnitudes of the upper and lower transitions falls slightly below the weighted mean line drawn between those for the two pure components.

Based on the above results we conclude that this system forms two amorphous phases containing mixtures of both components over most of the composition range. However, it seems likely that blends very rich in KODAR-PETG consist of a single miscible phase. There is a possibility that a similar situation may also exist for blends very rich in PC.

No PC crystallinity was observed in the melt-processed blends.

DISCUSSION AND CONCLUSIONS

The evidence reported here demonstrates conclusively that PCDS is miscible with PC in all proportions in the amorphous phase with no evidence of any liquid–liquid phase boundaries. The endothermic contributions to the heat of mixing from dispersion interactions involving the hydrocarbon units between the ester linkages should be similar to those in linear aliphatic polyesters. If we
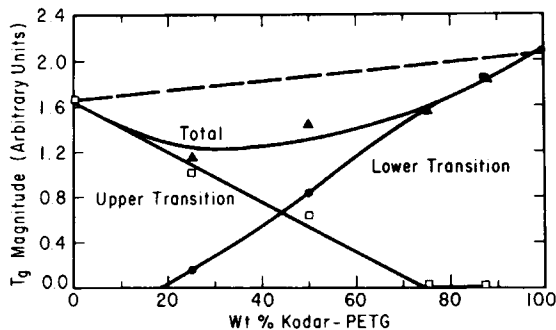

Fig. 9. Magnitudes of the baseline shifts at the glass transitions observed in PC/KODAR–PETG blends.

count the aliphatic carbons in the saturated ring with the same weighting as in a linear structure, we find the total aliphatic carbon-to-ester linkage ratio for PCDS to be 5. Based on past experience with miscibility of linear polyesters with PC, the balance of interactions with PC should be such that a net exothermic heat of mixing is obtained.[5,7] The observed miscibility confirms this expectation, and apparently we may regard the saturated ring as effectively similar to six linear methylene units.

The evidence described above shows that PEOP is not miscible with PC in all proportions, since there is a miscibility gap in the midconcentration range. In previous work[2] we found that PC blends with poly(ethylene terephthalate) (PET) are completely miscible in the amorphous phase when there is more than about 60–70% PET present. However, PC-rich blends contained two mixed amorphous phases. Thus, it was of considerable interest to compare the miscibility of PEOP with PC to that of PET since the two are isomers. One might expect the location of the ester attachments to the aromatic ring to affect the heat of mixing with PC and, thus, miscibility. Support for this expectation is seen in Table II, where we show the calorimetrically measured heats of mixing of low-molecular-weight ester analogs with an analog of PC, diphenyl carbonate.[7] Disubstitution on the ortho positions, diethyl orthophthalate (DEOP), results in a much larger exothermic mixing than that on the para positions, dimethyl terephthalate (DMT). Based on the results for the three structures in Table II, one may conclude that symmetry of substitution on the aromatic ring has a significant effect on the interaction with the aromatic carbonate structure. To the extent that DEOP is an analog for PEOP and that DMT is an analog for PET, one would expect PEOP to be considerably more miscible with PC than is PET. However, the results described above do not support a substantial difference in the extent of miscibility of PEOP with PC compared to PET. One might conclude that conformational characteristics of PEOP preclude its realizing the preferred interaction capability that its unrestrained low-molecular-weight analog demonstrates calorimetrically. Obviously, more work along these lines would be a fruitful area for understanding the role of interaction "accessibility" in polymer blend miscibility.

The copolyester KODAR-PETG shows only partial miscibility with PC, and

TABLE II
Heats of Mixing of Low-Molecular-Weight Aromatic Ester Compounds with Diphenyl Carbonate

Compound	ΔH_{mix},[a] cal/cm^3
$CH_3-O-\overset{\overset{O}{\|}}{C}-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{C}-O-CH_3$	−0.010
$\bigcirc-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$	−0.067
$\bigcirc\begin{smallmatrix}\overset{O}{\|}\\C-O-CH_2CH_3\\C-O-CH_2CH_3\\\underset{O}{\|}\end{smallmatrix}$	−0.378

[a] Measured at 50% of volume with diphenyl carbonate.

it would be of interest to relate this observation to its structure. However, this cannot be done completely at this time since its exact composition has not been revealed. Nevertheless, some comments about related systems are in order. First, it is interesting to note that the aromatic polyester based on 1,4-cyclo-hexanedimethanol, poly(1,4-cyclohexanedimethylene terephthalate) (PCDT), is completely miscible in the amorphous phase with polycarbonate.[3] Second, a copolyester related to PCDT in which a small percent of terephthalic acid is replaced with isophthalic acid, known commercially as KODAR A150, is also completely miscible in the amorphous phase with PC.[3] Thus, polyesters based on CHDM + TA + IPA have the proper structural features to be miscible with PC. Evidently, the introduction of EG into this structure or the concomitant structural randomness greatly reduces the propensity for miscibility with PC. Results to date suggest that the propensity for miscibility with PC decreases as the extent of hydrocarbon character is increased in the glycol unit of both ali-phatic polyesters[5,7] and aromatic polyesters (PBT vs. PET).[1,2] From this point of view, it is somewhat puzzling to understand why PCDT and KODAR A150 are completely miscible with PC. A more thorough investigation of the system PC–KODAR A150 is in progress.

This series of articles has shown a significant number of examples of complete or partial miscibility of polyesters with polycarbonate. An exothermic inter-action between the carbonyl oxygen of the ester linkage with the aromatic car-bonate structure has been shown to be responsible for this.[7] Clearly, the degree to which this favorable interaction can produce a net exothermic interaction and, thus, miscibility is related to the remaining structure of the polyester chain. These articles have also developed some insight into the relationship between polyester structures and miscibility with PC; however, the picture is still in-complete.

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