Polyester–Polycarbonate Blends. VI. Branched Aliphatic Polyesters

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Synopsis

Polycarbonate blends with poly(pivalolactone) were found to be completely immiscible based on the glass transitional behavior observed by thermal analysis. Crystallinity of the poly(pivalolactone) was unaffected by blending with polycarbonate. The heat of mixing of low molecular weight analogs of this system, ethyl pivalate and diphenyl carbonate, were found to be endothermic, in contrast to exothermic mixing observed for similar linear esters. Methyl branching adjacent to the ester carbonyl is believed to shield the specific interaction of this unit with the aromatic carbonate structure which leads to exothermic mixing and miscibility of similar unbranched esters with polycarbonate. Blends of poly(2,2-dimethyl-1,3-propylene succinate) were found to be partially miscible with polycarbonate because the shielding is not so great since the methyl groups are further removed from the ester group.

INTRODUCTION

In the last paper[1] of this series,[1-5] it was established that linear aliphatic polyesters are miscible with the polycarbonate of bisphenol A, PC, provided the ratio of methylene to ester groups does not exceed about six. Calorimetric measurement of the heat of mixing of low molecular weight analogs has shown that this is the result of an exothermic heat of mixing caused by an interaction between the carbonyl group in the ester with the aromatic carbonate structure.[6,7] The purpose of this paper is to explore the effect of branching in the hydrocarbon portion of the polyester on miscibility with PC. Two polyesters were chosen for this study:
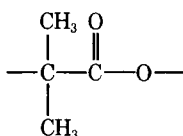
poly(pivalolactone), PPL
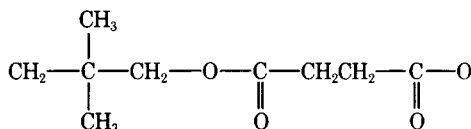
poly(2,2-dimethyl-1,3-propylene succinate), PDPS

The polycarbonate employed here was the same as that used in earlier studies.[1-7]

PC BLENDS WITH PPL

Blend Preparation

The PPL was obtained from Polysciences, Inc. A dry blend of PPL and PC pellets of the desired proportions was dried in a vacuum oven for 3 hr at 125°C. Following this, a blend was prepared by melt mixing in a Brabender Plasticorder at 260°C for 8 min. The discharge from the mixing bowl was not processed further, and specimens were obtained directly from the solidified mass for thermal analysis.

The pure PPL became clear after melting in the Brabender; however, all blends with PC were completely opaque in the melt state. This is a strong indication that the two polymers are not miscible. If there is a lower critical solution temperature, LCST, for this system, it lies below the T_m of PPL and could not be detected.

Thermal Analysis Results

Differential thermal analyses of these materials were performed with an R. L. Stone DTA using both a conventional furnace and a subambient assembly. The subambient unit employed cyclic heating and cooling at 10°C/min between the limits of −40°C and 260°C in a nitrogen atmosphere. The furnace does not allow programmed cooling so samples were only heated at 10°C/min in an atmosphere of air. Equivalent results were obtained by both methods.

Typical thermograms obtained with the furnace are shown in Figure 1. During cyclic heating and cooling, PPL exhibited a melting point of 242°C which coincides with the value found by Marchessault.[8] Oosterhof [9] has reported that PPL exhibits a T_g at −10°C; however, we were not able to detect this either by DTA facility or by DSC. Apparently, this is a consequence of the high degree of crystallinity developed by PPL, which reaches up to 70%,[9] and the rapid crys-
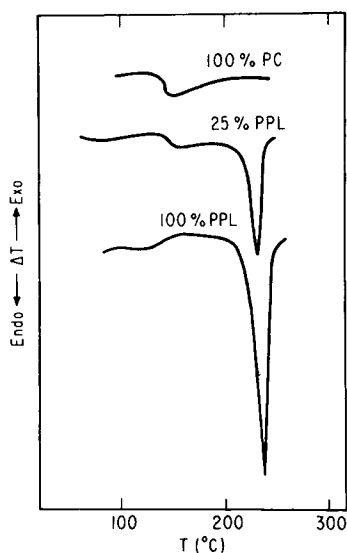

Fig. 1. Typical thermograms for PC, PPL, and a blend obtained with DTA furnace.

tallization of this polymer which precluded observations in a specimen with a significant amorphous fraction. Blends of PPL and PC exhibited only the T_g of the PC which appeared at the same location as for pure PC (see Fig. 2). No other T_g type transitions were observed in these blends with either the furnace or subambient assemblies. The PPL melting point was essentially the same from blends as from pure PPL as seen in Figure 2. Figure 3 shows that the area of the PPL melting endotherm is essentially proportional to the fraction of PPL in the blend.

Based on these observations, it is obvious that PPL and PC are completely immiscible.

PC BLENDS WITH PDPS

Blend Preparation

The PDPS was obtained from Aldrich Chemical Co. The as-received polymer contained a small amount of material which was insoluble in methylene chloride. By thermal analysis it was determined that the insoluble residue consisted almost totally of succinic acid, which probably remained from the synthesis as an impurity. Thus, as-received PDPS was first dissolved in methylene chloride, and the solution was decanted off to leave behind the insoluble material. The solvent was eliminated by evaporation and the resulting powder was placed in an aluminum pan and heated for 2 min on a hot plate at 220°C to eliminate any solvent or succinic acid remaining. After cooling to room temperature, this specimen remained as a very viscous liquid for at least three days, when the onset of crystallization occurred. No traces of impurities were detected by DTA in the pure polymer after this treatment.
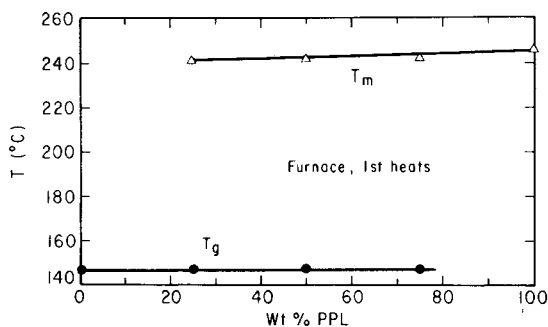

Fig. 2. T_m and T_g behavior for PC–PPL system using DTA subambient assembly.
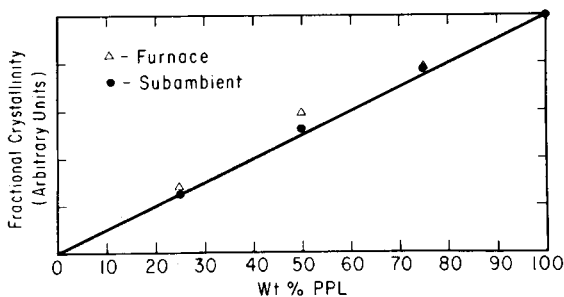

Fig. 3. Area of PPL meeting endotherm for PC–PPL blends: (△) furnace; (●) subambient.

Blends were prepared by mixing methylene chloride solutions of PDPS and PC in the desired ratios. Clean one-phase solutions containing 1 g polymer in 5 ml solvent were obtained in this manner. Small amounts of these solutions were poured into aluminum pans and placed in a vacuum oven, which was preheated to 80°C. Evaporation of the solvent was carried out for 10 hr under these conditions. There was no visible evidence of LCST behavior for this system.

The blends prepared in this manner were opaque; however, as noted previously,[1] such solvent casting induces crystallization of the polycarbonate. After heating to 260°C, all blends remained somewhat hazy.

Thermal Analysis Results

All thermal analysis was done with a Perkin–Elmer DSC-2 equipped with a Full Range Subambient Accessory. Because of the solvent-induced crystallization of the PC, it was necessary to premelt the samples as described earlier.[1] After premelting at 260°C, three heating and cooling cycles were made at 10°C/min. The upper and lower temperature limits for these cycles were 180°C and −30°C, respectively, for the first two cycles and 260°C and −30°C for the last one. Typical DSC traces are shown in Figure 4.

After annealing at room temperature, pure PDPS showed a melting point of 84°C in the first DSC run. However, during cyclic heating and cooling the PDPS did not crystallize. In these cases the only thermal event was the T_g observed at −18°C, which coincides with the value reported by others.[10]

The thermograms for all of the blends examined exhibited two glass transitions, and their temperature locations are plotted versus blend composition in Figure 5. The lower transition in Figure 5 corresponds to an essentially pure PDPS phase since its location is only slightly different from that of the pure polymer. The only significant effect produced by blending appears to be some broadening of this transition as PC is added. On the other hand, an upper transition also appears in all blends. In contrast with the lower one, which is relatively sharp for PDPS-rich samples, the upper transition is a very broad and weak thermal effect, which is very likely due to a PC-rich phase containing a significant amount of PDPS.

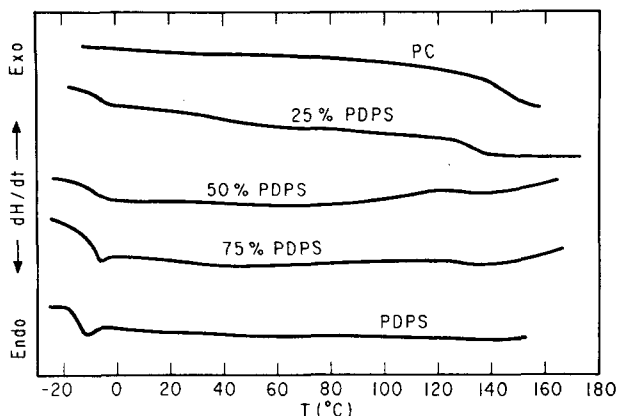No traces of crystallinity of any of the two polymers were observed during cyclic

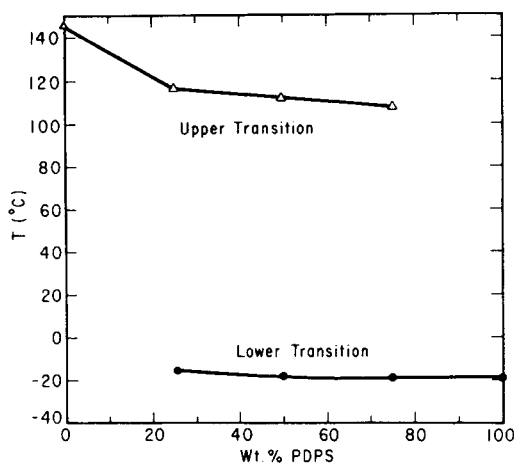Fig. 4. Typical DSC thermograms for PC–PDPS blends.

Fig. 5. Glass transitional behavior of PC–PDPS blends.

heating and cooling. Thus, blends of these polymers yield two-phase amorphous systems, in which one phase consists of practically pure PDPS, whereas the other is composed of a mixture of PC and PDPS.

SUMMARY AND CONCLUSIONS

The results presented here conclusively demonstrate that poly(pivalolactone) is completely immiscible with polycarbonate. This is an interesting contrast to earlier findings,[1,6,7] which showed that a wide range of linear aliphatic polyesters are miscible with polycarbonate. Several low molecular weight analogs of the latter polyesters were shown[6,7] to exhibit exothermic heats of mixing with diphenyl carbonate which was used as a structural analog of polycarbonate (see sample results in Table I). However, when the ratio of methylene to ester groups exceed about six, linear aliphatic polyesters are no longer completely miscible with polycarbonate, and the corresponding low molecular weight analogs exhibit endothermic heats of mixing with diphenyl carbonate. The hydrocarbon content of PPL is far below this limit, and apparently its immiscibility with PC is related to the branched structure of this polyester. This was explored by measuring the heat of mixing of a low molecular weight branched aliphatic ester analog, ethyl pivalate,

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}-O-CH_2CH_3$$
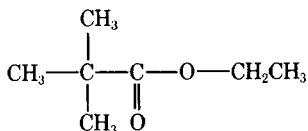
with diphenyl carbonate. As shown in Table I, this compound mixes endothermically with diphenyl carbonate, whereas unbranched low molecular weight esters of similar hydrocarbon content mix exothermically. Apparently, the methyl branches adjacent to the carbonyl, in effect, shield or block the specific interaction of the ester carbonyl with the aromatic carbonate unit and consequently an endothermic heat of mixing results.[6,7] The same phenomenon would

TABLE I
Heats of Mixing of Low Molecular Weight Ester Compounds with Diphenyl Carbonate at 85°C

Compound		ΔH_{mix},[a] cal/cm^3
$CH_3-(CH_2)_x-\underset{\underset{O}{\parallel}}{C}-O-(CH_2)_y-CH_3$		
$x = 1$	$y = 1$	−0.25
0	3	−0.39
1	2	−0.40
1	3	−0.06
2	2	−0.08
2	3	+0.20
$CH_3-\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-\underset{\underset{O}{\parallel}}{C}-O-CH_2CH_3$		+0.22

[a] Measured at 50% by volume of each component.

then be expected to cause a positive heat of mixing between PPL and PC and therefore lead to immiscibility for this blend system. Alternately, but less likely, the methyl substitution may result in some electronic alterations of the ester group that would weaken its interaction with the aromatic carbonate.

Poly(2,2-dimethyl-1,3-propylene succinate) contains 3.5 aliphatic carbon atoms per ester group in its structure, which is well below the limit of 6 for complete miscibility of linear, aliphatic polyesters with polycarbonate. Thus, based on the balance between endothermic and exothermic interactions one would expect PDPS to be completely miscible with PC; however, the results reported here show this pair to exhibit only incomplete miscibility. Evidently, this is also the result of some form of shielding of the exothermic interaction of the ester group with the PC molecule by the methyl branches. We believe that the further removal of the methyl branches in PDPS from the ester group as compared to PPL results in less effective shielding and explains the partial miscibility observed.

The two systems reported here contain chemical groups that can interact exothermically and a potentially favorable balance between negative and positive contributions to the net heat of mixing. However, because of reduced accessibility between these groups caused by adjacent methyl branches, their blends do not show the complete miscibility that would otherwise be predicted. Thus, accessibility appears to be an additional, important requirement in the relationship between polymer structure and blend miscibility.

Finally, it is important to comment that interchange reactions between the polyester and polycarbonate components are unlikely to have influenced the results presented here.[4,5] The PDPS system was solution blended and did not have a thermal history that would provide an opportunity for such reactions. The PPL system was melt-blended at temperatures where such reactions might occur, but the fact that the PPL–PC pair was observed to be immiscible makes this a moot point.

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