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The Basis for Miscibility in Polyester–Polycarbonate Blends

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ABSTRACT: Miscible amorphous phase behavior often results when the polymer pairs are chosen to give specific interactions which lead to exothermic heats of mixing. A method for estimating miscibility, based on calorimetric measurements of heats of mixing of low molecular weight analogues of the polymer repeat units, is tested for polycarbonate blends with a series of different polyesters. Polymer blends whose analogues show negative heats of mixing usually exhibit at least partial miscibility whereas those whose analogues show positive heats of mixing are invariably immiscible. The heat of mixing data suggest that the specific interaction leading to miscibility in this series involves the physical interaction between the polyester carbonyl moieties and the polycarbonate molecule.

Physical blends of polymers which form a single amorphous phase and are therefore thermodynamically miscible usually have physical properties which vary uniquely with blend composition in a smooth and continuous fashion between the property values of the pure components. This property combination is comparable to what can be achieved by chemical means through copolymerization, but the cost of producing miscible blends may be much less since only a physical blending operation is involved. Consequently there has been a great deal of research interest in miscible polymer blend systems.

By rough count, over fifty miscible polymer binary blends are now known to exist. Given the possible tens of thousands of polymer blend combinations that could be (and perhaps have been) examined, it is fairly clear that polymer–polymer miscibility is a somewhat uncommon event. The thermodynamic analysis of Scott[1] which applied the Flory–Huggins theory[2] to mixtures of dissimilar polymers provides a conceptual framework for understanding the exceptional nature of polymer–polymer miscibility. According to Scott, the enthalpy and entropy of mixing of polymers 1 and 2 are given by

$$\Delta H_{\mathrm{mix}} = BV\phi_1\phi_2 \tag{1}$$

$$\Delta S_{\mathrm{mix}} = -\frac{RV}{V_{\mathrm{r}}}\left(\frac{\phi_1 \ln \phi_1}{x_1} + \frac{\phi_2 \ln \phi_2}{x_2}\right) \tag{2}$$

where V_{r} is a reference volume, V is the volume of the system, x_i is the degree of polymerization of species i in terms of the reference volume, ϕ_i is the volume fraction of i in the mixture, and B is the mixing energy density characteristic of the polymer–polymer segmental interactions in the blend. It is clear from these equations that the entropy of mixing is a function of the molecular sizes being mixed and that it decreases rapidly toward zero as the degrees of polymerization of the component polymers approach the values typically found in commercial materials. The enthalpy of mixing, on the other hand, is primarily dependent on the energy change associated with changes in nearest neighbor contacts during mixing[2] and is much less dependent on molecular lengths. The net result is that the free energy of mixing, $\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$, is primarily influenced by the sign and magnitude of ΔH_{mix} for high molecular weght mixtures. The general success of the regular solution theory[3] is an indication that most materials weakly interact to give positive heats of mixing. Consequently, one would expect that the free energy of mixing associated with blending randomly selected high molecular weight polymers would be positive, a situation indicative of immiscibility or multiple amorphous phase formation.

The above considerations immediately suggest that miscible polymer blends will most likely result when polymer pairs are carefully selected for their abilities to form strong interactions of a type which result in negative heats of mixing. Recently, a number of studies on several of the polymer blends known to be miscible support this viewpoint. For example, Olabisi[4] observed negative interaction parameters between miscible poly(vinyl chloride) and poly(ϵ-caprolactone) pairs by means of solvent probe techniques and spectroscopic measurements and proposed the possibility of charge-transfer interactions to account for this phenomena. Similarly, Kwei et al.[5] found that the interaction parameter for miscible polystyrene–poly(vinyl methyl ether) blends was likewise negative in the composition range, 35–65% polystyrene. Nishi and Wang[6] and Paul and Barlow et al.[7-10] have shown that the heat of mixing parameter in the classical theory of melting point depression was negative when that theory was applied to miscible blends of poly(vinylidene fluoride) and various amorphous oxygen containing polymers. The latter investigators suggest that a strong, probably dipole related, interaction between carbonyl groups and the PVF_2 segment is responsible for the observed miscibility.[10]

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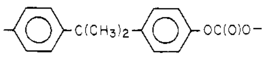
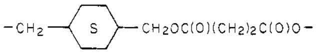
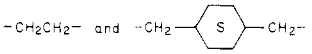
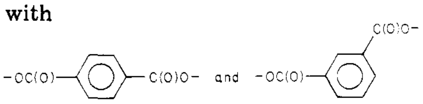
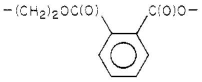
Table I
Characteristics of Polymers Used

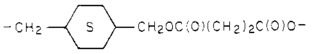
polymer	designation used here	structure of repeat unit	source
polycarbonate	PC $\bar{M}_w$ 29 000		General Electric Co. (Lexan)
poly(ethylene succinate)	PES	$-(CH_2)_2OC(O)(CH_2)_2C(O)O-$	Aldrich Chemical Co.
poly(ethylene adipate)	PEA	$-(CH_2)_2OC(O)(CH_2)_4C(O)O-$	Aldrich Chemical Co.
poly(1,4-butylene adipate)	PBA	$-(CH_2)_4OC(O)(CH_2)_4C(O)O-$	Aldrich Chemical Co.
poly(ϵ-caprolactone)	PCL-300 $\bar{M}_n$ 10 000 PCL-700 $\bar{M}_w$ 40 000	$-(CH_2)_5C(O)O-$	Union Carbide Corp.
poly(hexamethylene sebacate)	PHS	$-(CH_2)_6OC(O)(CH_2)_8C(O)O-$	Aldrich Chemical Co.
poly(pivalolactone)	PPL	$-C(CH_3)_2C(O)O-$	Polysciences, Inc.
poly(2,2-dimethyl-1,3-propylene succinate)	PDPS	$-CH_2C(CH_3)_2CH_2OC(O)(CH_2)_2C(O)O-$	Aldrich Chemical Co.
poly(1,4-cyclohexanedimethanol succinate)	PCDS		Aldrich Chemical Co.
KODAR-PETG	Kodar-PETG	copolymer of  with 	Eastman Kodak Corp.
poly(ethylene orthophthalate)	PEOP		Aldrich Chemical Co.

The practical problem of selecting systems which will exhibit exothermic mixing, however, is a difficult one owing to our general lack of ability to predict quantitatively the mixing thermodynamics of strongly interacting systems. The approach currently used by most investigators is to intuitively guess the potential for miscibility, mix the two polymers, and evaluate the results of the guess. Alternately, some laboratories have used the formation of single phase, dilute, ternary solutions of the two polymers in a mutual solvent as the criterion for assessing miscibility of the polymer pairs. Unfortunately, polymer-solvent interactions often predominate with misleading results.

To the extent that the heat of mixing is a function of nearest neighbor contacts and is independent of molecular weight, a better approach to the selection problem may be to measure directly the heats of mixing of low molecular weight compounds whose structures are analogous to those of the polymer repeat units. Polymers whose analogues show negative heats of mixing could be expected to be miscible. This approach is examined here for a series of polyester-polycarbonate blends.

Previous work has established that polycarbonate, PC, is partially miscible with poly(ethylene terephthalate), PET,[11] and with poly(butylene terephthalate), PBT,[12] and is completely miscible with poly(1,4-cyclohexanedimethylene terephthalate), PCDT, and with its copolyester containing isophthalic acid known as KODAR.[13] PC is also found to be completely miscible with poly(ϵ-caprolactone), PCL.[14] Recently,[15] this work has been extended with the result that four new completely miscible blends, four new partially miscible blends, and two completely immiscible blends of PC with various polyesters have been found. This polymer blend data base covers the whole spectrum of miscibility in response to chemical structural differences of the polyesters, and low molecular weight analogues of these polymers are readily available. The polyester-polycarbonate blend system is thus quite suitable for the investigation of the relationships between polymer blend miscibility, heats of mixing of analogue compounds, and polyester chemical structure presented below.

Table II
Miscibility Behavior Observed for Blends of Various Aliphatic Polyesters with Polycarbonate

	structure	miscibility	CH_2/C(O)O
PES	$-(CH_2)_2OC(O)(CH_2)_2C(O)O-$	miscible	2
PEA	$-(CH_2)_2OC(O)(CH_2)_4C(O)O-$	miscible	3
PBA	$-(CH_2)_4OC(O)(CH_2)_4C(O)O-$	miscible	4
PCL	$-(CH_2)_5C(O)O-$	miscible	5
PCDS		miscible	(5)
PHS	$-(CH_2)_6OC(O)(CH_2)_8C(O)O-$	partially miscible	7

Experimental Section

Polymer Blends. A summary list of the polyesters recently examined for miscibility with PC is given in Table I. As indicated here, many of these polyesters were purchased in small quantities from chemical specialty houses and are largely uncharacterized.

Depending on the quantity of polyester available and on its thermal stability, polymer blends with PC were either cast from solution or melt blended. PC blends with KODAR-PETG, PCL, and PPL were melt blended in a Brabender Plasticorder operated at 240-260 °C for approximately 5 min with a rotor speed of 80 rpm. The melt blend was then compression molded into sheets with a small hydraulic press. PC blends with PEA, PBA, PDPS, PCDS, PES, and PEOP were solvent cast into thin sheets by dissolving the two polymers independently in methylene chloride, mixing the two solutions to form a single-phase ternary, and removing the solvent over a 24-h period by placing it in a vacuum oven kept at 60 °C. PC blends with PHS were similarly cast from dioxane.

Blends that showed a single composition-dependent glass-transition temperature, T_g, throughout the entire composition range, as measured by an R. L. Stone differential thermal analyzer or by a Perkin-Elmer Model DSC-2 differential scanning calorimeter, were judged to be miscible. Some blends showed single-phase behavior over only a portion of the composition range, and some showed multiple-phase behavior, but the multiple phases contained both materials as determined by their T_g's. These systems were judged to be partially miscible. Blends judged to be immiscible showed the T_g's of the pure components. The phase behavior of these and of some of the previously studied blends

Table III
Miscibility Behavior of Branched Aliphatic Polyesters with Polycarbonate

PDPS	$-CH_2C(CH_2)_2CH_2OC(O)(CH_2)_2C(O)O-$	partially miscible
PPL	$-C(CH_3)_2C(O)O-$	immiscible

is summarized in Tables II–IV. Further details of the phase behavior of blends formed from the polyesters in Table I are presently being prepared for presentation at a later time.

Adiabatic Calorimeter. One cell of a two-cell adiabatic calorimeter designed to determine the heats of mixing of the low molecular weight analogues is shown in Figure 1. The cell, a miniature dewar vessel, consists of an upper, 17 cm^3, sample chamber and a lower, 6 cm^3, sample chamber separated by a tapered orifice which can be blocked by a small glass plunger valve. Mercury, placed above the plunger valve, serves to separate the two liquids prior to mixing and, when the valve is opened, to displace the fluid in the lower chamber forcing it into contact with the fluid in the upper chamber. A 2 in. long by 0.1 in. diameter, glass coated, thermistor probe (Fenwall Electronics No. GB32P28) is used to measure the temperature within the upper chamber.

In operation, two identical cells are placed in a bath thermostated to ±0.1 °C, and the signals from the two matched and calibrated thermistors are compared through a Wheatstone bridge circuit to eliminate signal variations due to swings in the bath temperature. The two fluids of interest are placed in the active cell so that the fluid with the lower density is in the lower chamber. One of the two fluids of interest is placed in both chambers of the inactive cell along with comparable amounts of mercury so that the thermal masses of the two cells are similar. As judged by direct measurement of cell temperatures and their temperature difference, ΔT, 3 h are normally required for complete thermal stabilization prior to test.

Rapid mixing is accomplished by simply opening the valve. Typically, ΔT reaches a maximum absolute value approximately 10 s after mixing and then slowly decays to zero over a period of 40 to 50 min for this calorimeter design. As a first approximation, the heat of mixing is related to the temperature change at zero time, ΔT_0, through

$$\Delta H_{mix} = (n_1 C_{p_1} + n_2 C_{p_2} + n_{Hg} C_{p_{Hg}}) \cdot \Delta T_0 \tag{3}$$

where ΔT_0 is determined by extrapolating the ΔT vs. time recording to zero time, n_1 and n_2 are the moles of the fluids being mixed, C_{p_1} and C_{p_2} are their respective heat capacities at the temperature of the experiment, $C_{p_{Hg}}$ is the molar heat capacity of mercury, and n_{Hg} is the mean number of moles of mercury involved in the energy exchange in the upper chamber computed by

$$n_{Hg} = (n_{Hg_0} + n_{Hg_f})/2 \tag{4}$$

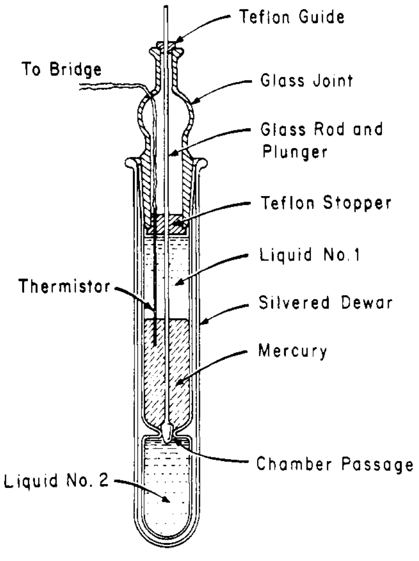


Figure 1. Schematic of calorimeter cell.

where n_{Hg_0} is the initial mercury charge in the system and n_{Hg_f} is that remaining in the upper chamber after mixing.

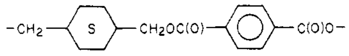
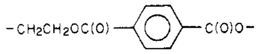
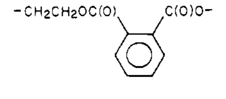
Since vapor spaces are present in the calorimeter, the heat of mixing calculated by eq 3 must be corrected for vaporization effects. These corrections based on the assumption that vapor–liquid equilibrium had been established[16] were found to be less than 10% for all fluids mixed at the usual temperature of 85 °C and to be still less for fluids mixed at 25 °C.

For calibration purposes, dichloromethane–acetone[17] and n-heptane–benzene[18] pairs were tested at 25 °C and pyridine–water[18] pairs were tested at 80 °C. Heats of mixing measured as described above were found to agree with those reported for these three systems to within 10%. Measurement reproducibility, based on the observed ΔT signals, was found to be within 5% relative error.

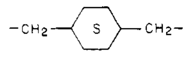
Model Compounds. Diphenyl carbonate, DPC, was chosen as a reasonable analogue of the polycarbonate repeat unit. The 80 °C melting point of this material required that mixing experiments be done at 85 °C—a temperature high enough to melt the DPC but low enough to avoid excessive volatilization of the esters. Propylene carbonate, PPCB, and dimethyl carbonate, DMC, were also tested with different esters to determine the effect on ΔH_{mix} of aliphatic groups attached to the carbonate structure.

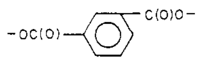
Polyesters were modeled with low molecular weight esters by requiring that the overall hydrocarbon content and basic carbonyl structure of the ester be as close as possible to the structural repeat unit of the polyester within the constraint that all esters be readily available from commercial sources. A summary of some of the

Table IV
Miscibility Behavior Observed for Blends of Various Aromatic Polyesters with Polycarbonate[a]

PCDT		miscible
KODAR A150	CHDM + TA + IPA	miscible
PET		partially miscible
KODAR-PETG	EG + CHDM + TA + IPA	partially miscible
PEOP		partially miscible

[a] EG = $-CH_2CH_2-$

CHDM = 

IPA = 

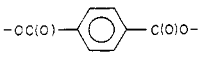
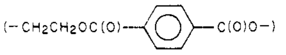
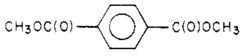
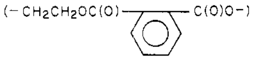
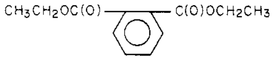
TA = 

Table V
Comparison between Polymer Pair Miscibility and Heat of Mixing of Low Molecular Weight Analogues

polymer 2 structural unit	analogue 2 structural unit	heat of mixing of analogue	polymer 2 miscibility with polymer 1
Polymer 1 is Polycarbonate; Analogue 1 is Diphenyl Carbonate			
poly(pivalolactone) (-$CH_2C(CH_3)_2C(O)O$-)	$C(CH_3)_3C(O)OCH_2CH_3$	+	immiscible
poly(ethyl methacrylate) (-$CH_2C(CH_3)$-) $C(O)OCH_2CH_3$	$C(CH_3)_3C(O)OCH_2CH_3$	+	immiscible
poly(ϵ-caprolactone) (-$OC(O)(CH_2)_5$-)	$CH_3C(O)O(CH_2)_3CH_3$	−	miscible
poly(ethylene succinate) (-$(CH_2)_2OC(O)(CH_2)_2C(O)O$-)	$CH_3OC(O)(CH_2)_2C(O)OCH_3$	−	miscible
poly(butylene adipate) (-$(CH_2)_4OC(O)(CH_2)_4C(O)O$-)	$CH_3CH_2OC(O)(CH_2)_4C(O)OCH_2CH_3$	−	miscible
poly(ethylene adipate) (-$(CH_2)_2OC(O)(CH_2)_4C(O)O$-)	$CH_3CH_2OC(O)(CH_2)_4C(O)OCH_2CH_3$	−	miscible
poly(ethylene terephthalate) 		*a*	partially miscible
poly(ethylene orthophthalate) 		−	partially miscible
Polymer 1 is Polystyrene; Analogue 1 is Ethylbenzene			
poly(ϵ-caprolactone) (-$OC(O)(CH_2)_5$-)	$CH_3C(O)O(CH_2)_3CH_3$	*a*	immiscible

[a] Slightly minus.

polymers and their analogues used in this study may be seen in Table V.

Results and Discussion

As shown in Table V, there is a remarkably good agreement between sign of the heat of mixing observed for the polymer analogue and the phase behavior observed for the polymer blend. Those polymers whose analogues show positive or endothermic heats of mixing are invariably immiscible while those whose analogues show exothermic or negative heats of mixing indicative of strong specific interactions generally show at least some miscible behavior.

An exception to these conclusions is represented by the polystyrene–poly(ϵ-caprolactone) system which is immiscible despite the observation that the analogues show slightly negative heats of mixing. As noted by Kern,[19] who found that poly(p-chlorostyrene)–poly(p-methylstyrene) blends were immiscible despite the fact that the chlorobenzene and toluene model compounds show negative heats of mixing, the critical factor appears to be the orientation of benzene rings in the polystyrene molecule. The benzene rings in polystyrene are oriented perpendicularly to the main backbone, and this arrangement in the polymer may shield the aromatic π electron cloud and prevent interaction with the ester group moiety in PCL, whereas such interactions are possible between analogue pairs whose spatial arrangements are less constrained. Challa et al. have similarly demonstrated the importance of the spatial organization of interacting moieties in determining polymer blend miscibility for blends of stereoisomers of poly(methyl methacrylate) with poly(vinyl chloride)[20] and with poly(vinylidene fluoride),[21] where they found that the syndiotactic arrangement gives the strongest interaction.

It is clear from these considerations that the presence of strong interactions between low molecular weight analogues is a necessary but not sufficient condition for polymer blend miscibility. The interacting moieties which can give negative heats of mixing when low molecular weight molecules are mixed may be constrained by steric considerations from interacting properly when attached to polymer backbones. Due to the lack of entropy of mixing effects in polymer blends, on the other hand, polymers whose low molecular weight analogues give positive heats of mixing will probably be immiscible. Measurement of heats of mixing of model compounds is thus a useful but not totally sufficient way to screen potential polymer pairs for miscibility.

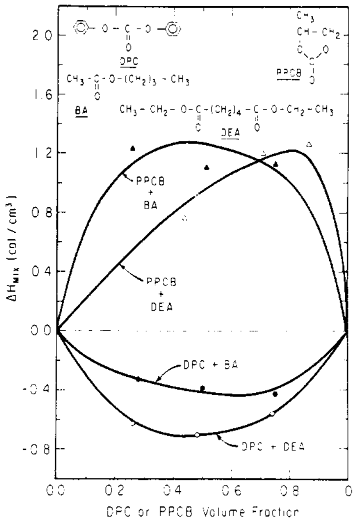


Figure 2. Heats of mixing of aliphatic esters with an aromatic carbonate (DPC) and an aliphatic carbonate (PPCB).

The exothermic heats of mixing found for the DPC–ester pairs in Table V suggest the existence of a specific interaction between the ester group and the DPC molecule. In order to learn more about this interaction, a variety of structurally similar esters and carbonates were studied with the calorimeter.

Figure 2 illustrates the finding that heats of mixing of aliphatic carbonate–ester pairs are endothermic rather

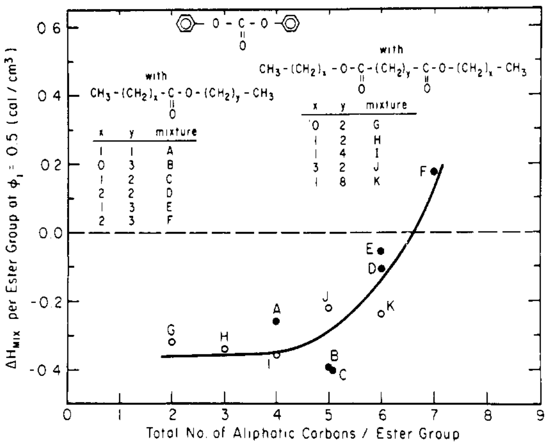


Figure 3. Effect of ester group content on the observed heats of mixing of aliphatic esters with DPC.

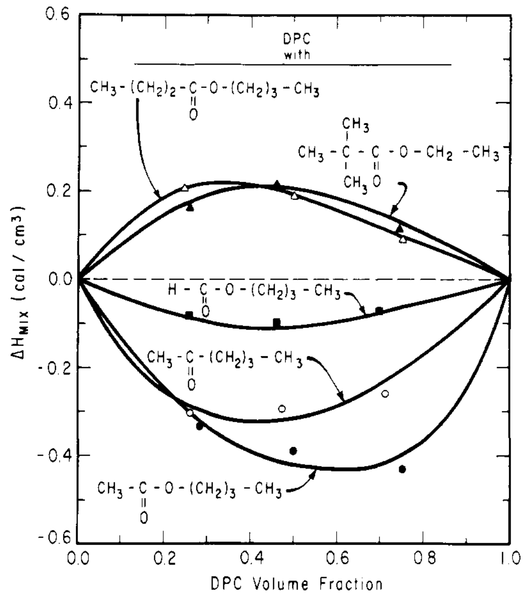


Figure 4. Effect of structure of aliphatic carbonyl containing compounds on the heats of mixing with DPC.

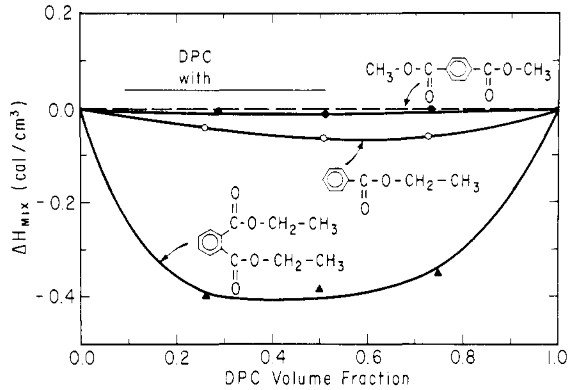


Figure 5. Heats of mixing of some aromatic esters with DPC.

than exothermic. Similar results were found for dimethyl carbonate. This result strongly suggests that the aromaticity of the DPC molecule is a very important factor for the existence of a specific interaction between it and esters. Grollier et al.[22] have observed similar behavior for mixtures of esters and hydrocarbons (endothermic) and for benzene–ester mixtures (exothermic), and they suggest that there may be an n–π complex formation between free electrons of the ester group and the aromatic ring. The role of the carbonate moiety is somewhat unclear from these results, and further study is needed.

The exothermic heats of mixing of alkyl dicarboxylic acid esters with DPC are found to be roughly twice the magnitude of that obtained when alkyl monocarboxylic acid esters are mixed with DPC. This suggests that the specific interaction involves the ester moiety. One would further expect that as the aliphatic ester assumes greater hydrocarbon-like nature caused by increasing its alkyl content, the heat of mixing must eventually become endothermic. A reasonable way to guage these effects of ester structure is to plot the heat of mixing for 50/50 vol % mixtures of DPC and the ester vs. the number of aliphatic carbons per ester group as shown in Figure 3. Here it is seen that substantial exotherms on mixing indicative of strong pair interactions occur when the ester content is high but that this interaction decreases as ester content decreases until the interaction disappears and weak dispersive interactions predominate for aliphatic carbon to ester group ratios of 7 or greater. Interestingly, those aliphatic polyesters found to be miscible with polycarbonate at all compositions—poly(ethylene succinate), poly(ethylene adipate), poly(1,4-butylene adipate), and poly(ε-caprolactone)—have ester analogues with between two and five aliphatic carbons per ester group. Poly(hexamethylene sebacate), PHS, shows partial miscibility with polycarbonate, but its analogue, a dicarboxylic acid ester containing seven aliphatic carbons per ester group, was unavailable. Butyl butyrate, a monocarboxylic ester with seven aliphatic carbons per ester, gives a positive heat of mixing, but this compound may not be a good analogue of PHS because of the possible shielding of the ester group by its long aliphatic branches.

Some effects of ester structure on the heat of mixing with DPC can be seen in Figure 4. Of the five esters shown here, butyl acetate shows the largest negative heat of mixing. The heat of mixing observed for methyl butyl ketone is quite comparable to that for butyl acetate suggesting, again, that the specific interaction may involve the dipole–induced dipole, n–π interaction between the carbonyl group on the ester and the aromatic ring. The much reduced exothermic heat of mixing of butyl formate relative to butyl acetate results from the well known inductive effect of the methyl group on the electron density of adjacent carbonyls.[23] Removal of the methyl group lowers the polarization of the carbonyl and thus lowers the intensity of the interaction.

Figure 4 also shows that ethyl pivalate exhibits a positive or endothermic heat of mixing with DPC. Evidently this occurs because the methyl groups shield the carbonyl and prevent its exothermic interaction with DPC. This observation is relevant to the behavior of branched aliphatic esters in blends with polycarbonate summarized in Table III. Apparently the methyl groups adjacent to the carbonyl in PPL cause similar shielding and preclude any miscibility with PC. However, moving the pendant methyl groups further down the chain from the carbonyl as in PDPS reduces the shielding effect and thus leads to partial miscibility of the blend.

As indicated in Table IV, several aromatic polyesters have been found to be miscible or partially miscible with polycarbonate. One might thus expect that aromatic esters would show heats of mixing with DPC that are comparable in sign and magnitude to those obtained with aliphatic esters. Figure 5 shows that DPC does mix exothermically with diethyl orthophthalate, the analogue of poly(ethylene orthophthalate), PEOP, and with ethyl benzoate and dimethyl terephthalate, both reasonable analogues of poly(ethylene terephthalate), PET. However, PEOP and PET are only partially miscible with PC. Whereas the

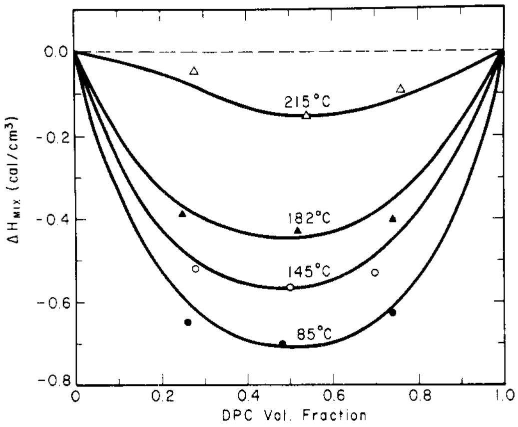


Figure 6. Effect of temperature on the heat of mixing of diethyl adipate and diphenyl carbonate.

heats of mixing are small enough for the analogues of PET to suggest that PET may be only partially miscible with PC, one would expect, based on the strong exotherm shown by the diethyl orthophthalate–DPC system, that PEOP would be completely miscible with PC. Steric restrictions to interaction between the polymer repeat units may again be responsible for the partial miscibility shown by this system. Interestingly, the strength of the exothermic interaction seen in Figure 5 appears to be related to the asymmetry of ring substitution.

All of the heat of mixing data described above were measured at a single temperature, 85 °C in the case of mixture with DPC. It is of interest to know how temperature affects the heat of mixing for systems which have specific interactions. Thus, some limited studies of this type were done for the system diethyl adipate–DPC, and the results are shown in Figure 6. The heat of mixing was found to become less exothermic as the temperature increased and to approach athermal behavior. One might expect the intensity of orientation dependent specific interactions to decrease as the molecular segments gain mobility and as the system expands thermally. This should be an important factor in any thermodynamic analysis which attempts to explain high temperature LCST behavior in blends such as that observed previously for the poly(ϵ-caprolactone)–polycarbonate system.[14]

Summary and Conclusions

This work and a growing body of information from other sources[24] generally indicate that polymer pair miscibility requires that the pair interact strongly to yield negative heats of mixing. Should this occur, single amorphous phase behavior may still not result, perhaps because the system is above its lower critical solution temperature.[25] However, endothermic interaction virtually guarantees immiscibility because the configurational entropy of mixing is so small.

The basic problem confronting those who seek miscible polymer blends is the lack of reliable methods for predicting which polymer pairs will interact to give negative heats of mixing. The good correlation demonstrated between the state of polymer blend miscibility and the signs of the heats of mixing of corresponding model compounds suggests that this experimental approach to the problem could be a useful way to screen potentially miscible polymers. Polymer pairs whose low molecular weight analogues show negative heats of mixing are likely to form miscible or partially miscible mixtures, depending on the extent to which the specific interactions between the model compounds are capable of being realized between the polymer repeat units. Polymer pairs whose analogues show endothermic or positive heats of mixing, on the other hand, are invariably immiscible.

Owing to the complexity of the specific interaction between PC and polyesters, interpretation is somewhat difficult. Based on the model compound studies presented here, it appears that the interaction leading to negative heats of mixing is probably the result of n–π complex formation between the electrons of the ester carbonyl and the aromatic ring of the carbonate molecule. To effectively promote miscibility of polyesters with polycarbonate, at least one carbonyl for every seven dispersive carbon atoms in an aliphatic polyester repeat unit structure is required, subject to the constraints that the ester carbonyl not be shielded from interaction by adjacent moieties and that carbonyls in the polymer chain be sterically able to interact with the polycarbonate repeat unit. Additional work with aromatic polyesters and their analogues is required before a clear understanding of their structural–miscibility relationships with polycarbonate will emerge.

Acknowledgment. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their partial support of this research. The support provided C. A. Cruz by the Consejo Nacional de Cience y Technologia (CONACYT) of Mexico is also gratefully acknowledged.

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