Heats of Mixing of Strongly Interacting Model Compounds and Miscibility of the Corresponding Polymers

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ABSTRACT: The miscibility between polystyrene polymers that contain potential hydrogen bond, or proton, donor groups and other polymers that are good hydrogen bond, or proton, acceptors is investigated. Calorimetry is used here as the primary technique to understand the thermodynamics of mixing of low molecular weight model compounds, chosen to represent the organic polymers of interest. The proton donor groups include SO_3H, CO_2H, phenol, alcohol and hexafluoroisopropyl alcohol, spanning a wide range of pK_a values. The acceptor molecules include amide (poly(*N,N*-dimethylacrylamide)) and ester (poly(methyl methacrylate)) functionalities. The results for the small molecules are shown to be useful in predicting the probability of miscibility occurring between the corresponding polymers. In blends, both of the model compounds and of the polymers, the strengths of the interactions with the acids are shown to be very different for the ester than for the amide, owing at least in part to the differences in their basicity. Stronger bases seem to be better candidates for forming miscible blends with strong, self-associating hydrogen bond donors since the stronger interaction between the acid and the base helps to break up the self-associations. Differential scanning calorimetry, along with infrared spectroscopy and optical transparency, is used to investigate the miscibility of these polymers. The morphology present in these blends is seen to be strongly influenced by the blend preparation method.

Introduction

In many cases the observed miscibility in polymer blends is a direct result of a negative enthalpy of mixing (ΔH_m) contribution to the overall free energy of mixing (ΔG_m),[1,2] the fundamental thermodynamic quantity that controls miscibility.

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1)$$

For a binary mixture the entropy can be expressed in terms of the Flory–Huggins model, which assumes that the only entropic contributions are combinatorial

$$\Delta S^{(c)} = -R\left\{\frac{\phi_i \ln \phi_i}{v_i} + \frac{\phi_j \ln \phi_j}{v_j}\right\} \qquad (2)$$

where ϕ_i and ϕ_j are volume fractions and v_i and v_j are the molar volumes of species i and j, respectively. The heat of mixing of two components depends upon the difference in cohesion energies, E_i, of the mixed and unmixed components and can be represented by the semiempirical relation, proposed by Scatchard,[3] for systems in which the cohesion is due to dispersive forces alone.

$$\Delta H_m = V\phi_i\phi_j(\delta_i - \delta_j)^2 \qquad (3)$$

The solubility parameters, δ_i and δ_j, are defined as $\delta_i = (E_i/v_i)^{1/2}$ and V is the total volume of the system.

For a blend to be a single phase the requirement that $\Delta G_m < 0$ must be fulfilled. Additionally, the second derivative of ΔG_m with composition must be zero or positive. For high molecular weight polymers (which have large molar volumes) the combinatorial entropy terms will be small. Therefore, enthalpic contributions usually dominate in polymeric systems. When only dispersive or van der Waals forces are present and the entropic contributions are considered to be negligible, the enthalpy of mixing will always be positive, or zero if δ_i and δ_j are near equal, ultimately leading to contributions to ΔG_m that are unfavorable to mixing. For many systems, however, there exist specific interactions such as hydrogen bonding or dipolar coupling, resulting in negative ΔH_m and favorable contributions to the free energy of mixing. The enthalpy of mixing can then be written in the empirical form

$$\Delta H_m/V = RT(\chi_{ij}/v^0)\phi_i\phi_j \qquad (4)$$

where χ_{ij} is the binary interaction parameter and v^0 is an arbitrary segment volume that is not easily defined for polymers. It is therefore preferable to define a normalized quantity to represent the interaction parameter.

$$\tilde{\chi}_{ij} = \chi_{ij}/v^0 \qquad (5)$$

From the above discussion, it is clear that knowledge of the enthalpy of mixing is fundamental to the understanding of polymer–polymer miscibility. Calorimetry is one of the most direct methods of determining this thermodynamic parameter. Unfortunately, the enthalpy of mixing of two high molecular weight polymers cannot be measured directly in the bulk state due to their high viscosities and low diffusion coefficients. An alternative approach (chosen for this work) is to measure the heat of mixing of low molecular weight models of the polymers in question, which contain all of the appropriate functional groups. Low molecular weight analogues of polymers have been frequently used in such experiments.[4] The choice of the structure of the model for a polymer is important since different models for the same polymer can give somewhat different results. Although this choice remains subjective, valuable insight and quantitative information can be obtained from these measurements. Typically, a model compound is chosen to have a structure that is similar to the monomeric unit of the polymer or to a dimer of this unit. Oligomers have also been used elsewhere as models for the corresponding polymers.[5]

Mixing can be done readily when the model compounds are in the melt form. Since the enthalpy of mixing results from changes in energy associated with nearest-neighbor contacts, it should be independent of molecular weight to a first approximation unless strong steric restrictions associated with the polymer are present. An interaction parameter, $\tilde{\chi}_{ij}$, between the two compounds can be obtained via these experiments (eqs 4 and 5).

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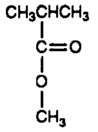
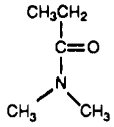
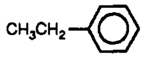
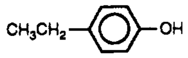
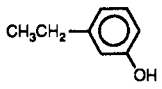
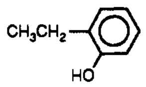
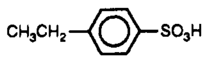
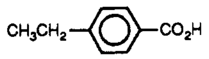
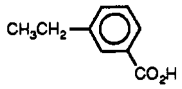
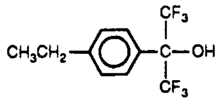
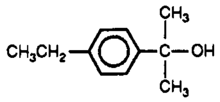
Table I
Model Compounds

chemical name (abbrevn)	structure	density,[a] g/cm^3
methyl isobutyrate (MIB)		0.856
N,*N*-dimethylpropionamide (DMP)		0.902
ethylbenzene (EBZ)		0.851
4-ethylphenol (4-EPH)		0.988
3-ethylphenol (3-EPH)		0.993
2-ethylphenol (2-EPH)		1.001
4-ethylbenzenesulfonic acid (ESA)		1.258
4-ethylbenzoic acid (4-EBA)		
3-ethylbenzoic acid (3-EBA)		0.987
α,α-bis(trifluoromethyl)-4-ethylbenzenemethanol (HFH)		1.347
α,α-dimethyl-4-ethylbenzenemethanol (HCH)		0.961

[a] Measured by pycnometer at 50 °C.

The interaction energy density, *B*, is a useful quantity for representing the data and has often been used by Paul.[6] *B* is defined in eq 6 and follows directly from eqs 4 and 5. Although several other experimental techniques are

$$B = RT\tilde{\chi}_{ij} = \Delta H_m\,(\text{cal/cm}^3)/\phi_i\phi_j \qquad (6)$$

commonly used to determine χ_{ij} values for polymers (e.g., small-angle neutron scattering, inverse GC, melting point depression), the χ_{ij} values obtained by these techniques contain both enthalpic and entropic contributions. Unlike these, heat of mixing experiments provide only the enthalpic contributions to χ_{ij}.

Experimental Section

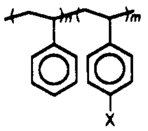
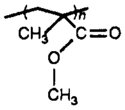
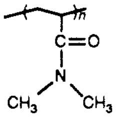
Synthesis of Model Compounds and Polymers. The molecular structures and the densities of the model compounds are listed in Table I. The structures and characterization information of the homopolymers and copolymers used are presented in Table II.

Model Compounds. Most model compounds used in the heats of mixing experiments were purchased from the Aldrich Chemical Co. or the Eastman Kodak Co. (EBZ and 4-EPH). Purification of these was done when deemed necessary; 4-ethylbenzoic acid was purified by sublimation. Three model compounds were synthesized as follows.

(a) α,α-Bis(trifluoromethyl)-4-ethylbenzenemethanol. A 250-mL three-necked round-bottom flask was fitted with a mechanical stirrer, reflux condenser, addition funnel, and argon inlet adapter. All glassware was oven-dried, assembled hot, and cooled under argon purge. The flask was charged with 4.0 g (0.16 mol) of magnesium and 50 mL of THF distilled from sodium benzophenone ketyl. Then a sufficient volume of a solution of 26.8 g (0.14 mol) of 4-(bromoethyl)benzene in 50 mL of THF was added to start the reaction. After the reaction mixture was refluxing vigorously, the remainder of the aryl bromide solution was added dropwise. Following a 3-h reflux, the water-cooled condenser was replaced with a cold finger filled with dry ice/isopropyl alcohol. The stirrer was replaced by a gas dispersion tube through which 30.7 g (0.18 mol) of hexafluoroacetone was added slowly from a lecture bottle. The reaction mixture was allowed to sit overnight, after which approximately 30 mL of a saturated aqueous ammonium chloride solution, used to hydrolyze the magnesium salts, was added slowly through the addition funnel. The clear yellow solution was decanted from residual solids, which were triturated with several portions of ethyl ether. The combined organic layers were dried briefly over $MgSO_4$ and the solvents removed on the rotary evaporator. The crude liquid product was decanted from a red-brown solid and twice distilled: yield 28.8 g (76%); bp 85–86 °C (13.5 Torr); 96% pure by GLC. The structure was confirmed by ^1H NMR and GC/mass spectroscopy.

(b) α,α-Dimethyl-4-ethylbenzenemethanol. The procedure was the same as that for the hexafluoro analogue, except the ketone used was anhydrous acetone: yield 68%; bp 110–113 °C (11 Torr); 99.5% pure by GLC.

Table II
Polymers

name and structure	X-containing monomer, mol %	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
			
poly(vinylphenol) (PVPh) X = OH	100	35.0K	1.7
poly(styrene-*co*-vinylphenol) X = OH			
p(S-VPh(22))	22	95.6K	2.0
p(S-VPh(42))	42	157.0K	2.4
p(S-VPh(82))	82	356.0K	4.0
poly(styrene-*co*-styrene-4-carboxylic acid) X = CO_2H			
p(S-CA(5))	5	318.0K	4.5
p(S-CA(25))	25	58.4K	2.0
p(S-CA(54))	54	32.0K	2.0
poly(styrene-co-styrene-4-sulfonic acid) X = SO_3H			
p(S-SA(2))	2	241.0K	3.0
p(S-SA(12))	12	241.0K	3.0
polystyrene (Styron 666) (PS) X = H		241.0K	3.0
poly(methyl methacrylate) (PMMA) 		93.0K	2.0
poly(*N*,*N*-dimethylacrylamide) (PDMA) 		490.0K	broad

(c) 3-Ethylbenzoic Acid. Part 1. Synthesis of 3-(Bromoethyl)benzene.[7] A 2-L three-necked round-bottom flask fitted with a mechanical stirrer and reflux condenser was charged with 200 g (1.0 mol) of 3-bromoacetophenone, 170 g (3.0 mol) of KOH, 1.4 kg of ethylene glycol, and 170 mL (175 g, 3.5 mol) of hydrazine hydrate. The mixture was heated slowly (ca. 3 h) to 130 °C and refluxed at this temperature for 2 h. A distillation head was attached and approximately 500 mL of distillate collected, which separated into two layers, a clear upper aqueous layer and a cloudy lower organic layer. The top layer was washed twice with 150 mL of ether, and the ether washings were combined with the bottom layer. The distillation residue was similarly washed with ether, and the ether fractions were combined as before. This ether solution was dried over first $MgSO_4$ and then molecular sieves, concentrated on a rotary evaporator, and then distilled, affording 137 g (73.9%) of a clear colorless distillate [bp 84–85 °C (15.5 Torr); lit.[7] bp 85–86 °C (20 Torr)]. Infrared and NMR spectroscopic data were consistent with the expected structure.

Part 2. Synthesis of 3-Ethylbenzoic Acid. A 2-L three-necked round-bottom flask was fitted with a mechanical stirrer, cryogenic cold finger, and pressure-equalized addition funnel. The apparatus, which had been oven dried and assembled hot under a nitrogen purge, was charged with 13.4 g (0.55 mol) of Mg and then flamed out. On cooling, 50 mL of a solution of 92.5 g (0.5 mol) of 3-(bromoethyl)benzene in 650 mL of anhydrous ether was added. The reaction began within 5 min, after which the aryl halide solution was added at a rate to maintain gentle reflux. On completion of the addition, the reaction mixture was refluxed for 2 h. The mixture was cooled in an ice bath and dry CO_2 bubbled through the solution from a cannula for 1.5 h, and then the mixture was neutralized with 10% aqueous HCl. The layers were separated, the upper ether layer was washed twice with 100 mL of H_2O (pH 3 and 4) and dried over $MgSO_4$, and the ether was removed on a rotary evaporator. The benzoic acid was obtained by reduced pressure distillation [bp 86–88 °C (0.001 Torr)] followed by extraction with 5% aqueous NaOH and subsequent neutralization: yield 30%; 98.5% pure by GLC.

Polymers. Poly(*N*,*N*-dimethylacrylamide) was purchased from Polysciences. The polymer was purified by dissolving it in water and filtering the solution through Celite to remove insoluble gel. The solution was then freeze-dried, followed by drying at 90 °C for 24 h under vacuum. The molecular weight was determined by size-exclusion chromatography (SEC) using PW gel columns in a 5% polyethylene glycol in water solution. The molecular weights are reported as polysaccharide equivalent molecular weights. Poly(methyl methacrylate) was purchased from Aldrich. The molecular weight information was provided by the manufacturer. The polystyrene used was Dow Styron 666.

(a) Poly(styrene-*co*-styrene-4-carboxylic acid). Monomers. Small samples (2–6 g) of 4-vinylbenzoic acid[8a] were carefully recrystallized[8b] from 70:30 water/ethanol heated to 40–45 °C (mp soft. 140; 141.5–142 °C) (lit.[8b] mp 143–144 °C). Attempts to purify larger batches resulted in contamination by polymer. Because this monomer is so prone to self-polymerize in the solid state, purified samples were used immediately. Inhibitor was removed from styrene by passing commercial material through a short column of neutral alumina. AIBN was recrystallized several times from methanol.

Polymerizations. The monomers and AIBN (0.5 mol %) were mixed in desired relative amounts in a polymerization bottle, which was sealed and subjected to three freeze–thaw cycles under vacuum. Samples with 10 mol % or less carboxylic acid monomer were polymerized in bulk. Others were carried out in 10% THF solutions. After being stirred in a 60–70 °C constant-temperature bath for 16–84 h, the clear or slightly cloudy samples were diluted with several milliliters of THF and the polymer was precipitated into a large excess of heptane in an explosion-proof blender. The samples were filtered, washed well with fresh hexanes, and dried in an 80 °C vacuum oven for at least 72 h: yields 50–70%.

Characterization. The composition of the copolymers was determined by titration in methanol with dilute standard NaOH solution, by ^1H NMR analysis, and by elemental analysis. The molecular weights were determined by SEC on the ester derivatives of the copolymers and are reported in polystyrene equivalents.

Poly(styrene-*co*-4-vinylphenol). Monomers. (*tert*-Butyloxycarbonyl)styrene (tBOC-styrene) was obtained from the Synthetic Chemicals Division, Eastman Kodak Co., and used as received. Inhibitor was removed from styrene by passing the commercial material through a short column of neutral alumina. AIBN was recrystallized several times from methanol.

Polymerizations. The monomers and AIBN (0.5 mol %) were mixed in desired relative amounts in an Ace Glass polymerization tube and subjected to three freeze–thaw cycles under vacuum. After immersion in a 70 °C constant-temperature bath for 25–240 min, the viscous samples were dissolved in THF and the polymer precipitated into a large excess of methanol in an explosion-proof blender. The samples were filtered, washed well with fresh hexanes, and dried in a 60 °C vacuum oven for at least 72 h: yields 55–75%.

Deprotection. In a three-necked round-bottom flask equipped with mechanical stirrer, reflux condenser, and argon inlet tube, the tBOC copolymer was dissolved under argon in sufficient *p*-dioxane to make a 15–20% solution. Then trifluoroacetic acid was added and the solution refluxed 15 h. The clear reaction mixture was precipitated into a large excess of water, and the white polymer was filtered and washed well with water until the pH of the washes was 6. Samples were then dried in a vacuum oven at 75 °C for at least 72 h.

Characterization. The composition of the tBOC copolymers was determined by ^{1}H NMR spectroscopy (CDCl$_3$) and corroborated by elemental analysis. Completion of the deprotection reaction was confirmed by analysis of the ^{1}H NMR spectra (DMSO-d_6 or *p*-dioxane-d_8) and by IR analysis. The molecular weights of the copolymers were determined by SEC on the protected polymers and are expressed as polystyrene equivalents. The absolute molecular weight of poly(vinylphenol) homopolymer was determined by SEC, with viscosity detection and a universal calibration curve, on the deprotected polymer and is reported in Table II. The absolute molecular weight of the protected homopolymer is almost twice that of the deprotected homopolymer.

Poly(styrene-*co*-styrene-4-sulfonic acid).[9] In a 500-mL Erlenmeyer flask, 52.1 g (0.500 mol of monomer units) of commercial polystyrene (Dow Styron 666) was dissolved in 250 mL of 1,2-dichloroethane with stirring and heated to 50 °C. Then a known volume of a fresh 1 M solution of acetyl sulfate in 1,2-dichloroethane[9] was added, and the reaction mixture was stirred at 50 °C for 70 min (1 mol of acetyl sulfate was added for each mole of sulfonic acid desired). After 25 mL of absolute ethanol was added to terminate the reaction, the reaction mixture was added slowly to ca. 3 L of rapidly boiling water to strip the solvent and precipitate the sulfonated polymer. The white mass was broken up in a blender, filtered, washed well with fresh water, and dried. The dry polymer was dissolved in THF and reprecipitated in water to remove traces of acetic and sulfuric acids.

Characterization. The molecular weight of the copolymer is the same as that of the polystyrene starting material (determined by SEC and reported in polystyrene equivalents). The mole percent of sulfonic acid was determined by titration of a solution of the polymer in a 90:10 THF/methanol solution with dilute NaOH standard. Elemental analysis corroborated the titration results.

Preparation of Blends. The polymer blends were prepared by dissolving each component in a common, good solvent at a level of 5 wt %. The solutions were combined in the appropriate amounts. Most of the solutions were cast into shallow dishes, and the solvent was removed very slowly to obtain equilibrium morphology (method I). Other preparation techniques were utilized to examine the effects of solvent and the preparation method on the resulting morphology of the blends. Some of the blend solutions were precipitated into a 10 to 1 excess of hexane (method II). Others were coated onto an inert substrate using a doctor blade (method III); this produced thin films that were on the order of 25 μm thick and allowed for rapid evaporation of the solvent. Samples for FTIR measurements were spin coated from solution onto KBr disks (method IV). Due to limited quantities of the modified polystyrenes, melt blending was not, in general, a viable alternative to solvent casting of the blends.

Table III
Blend Preparation and Results

blend components	solvent	method of preparation[a]	blend appearance
PDMA/PS	pyridine	I, IV	opaque film
PDMA/PVPh	pyridine	I, IV	clear film
	DMF	III	clear film
	MEK	I	clear gel
PDMA/p(S-VPh(22))	pyridine	I, IV	clear film
PDMA/p(S-VPh(42))	pyridine	I, IV	clear film
PDMA/p(S-VPh(82))	pyridine	I, IV	clear film
PDMA/p(S-CA(5))	pyridine	I, IV	opaque film
	MEK	I	translucent film
PDMA/p(S-CA(25))	MEK	I	clear gel
PDMA/p(S-CA(54))	pyridine	I, IV	clear film
PDMA/p(S-SA(2))	pyridine	I, IV	opaque film
PDMA/p(S-SA(12))	pyridine	I, IV	opaque film
	MEK	I	clear gel
PMMA/PVPh	pyridine	I, IV	opaque film
	THF	I	opaque film
	THF	II	white powder
	MEK	I	clear film
	MEK	II	white powder
		V	clear film
PMMA/p(S-VPh(22))	pyridine	I, IV	clear film
PMMA/p(S-VPh(42))	pyridine	I, IV	opaque film
PMMA/p(S-VPh(82))	pyridine	I, IV	opaque film
PMMA/p(S-CA(5))	pyridine	I, IV	opaque film
	MEK	I	translucent film
PMMA/p(S-CA(25))	MEK	I	clear film
PMMA/p(S-CA(54))	pyridine	I, IV	opaque film
PMMA/p(S-SA(2))	pyridine	I, IV	opaque film
PMMA/p(S-SA(12))	pyridine	I, IV	opaque film
	MEK	I	clear film

[a] See the Experimental Section for the method description.

However, due to the abundance of contradicting data on the miscibility of PMMA and PVPh,[10-13] a 50:50 wt % blend of this pair was prepared by using a single-screw ($^1/_4$ in.) Microtruder laboratory extruder, set at 238 °C and a screw speed of 75 rpm (method V). The details concerning the preparation of the individual blends are reported in Table III.

The blend samples were dried under vacuum from ambient temperature to a temperature that is close to the glass transition temperature (T_g) of the blend (if single phase) or to that of the component with the highest T_g. The maximum drying temperature was, however, kept below 170 °C to prevent degradation. When pyridine was used as a solvent, it could not completely be removed by this drying process and it was necessary to extract the residual solvent via displacement with a more volatile solvent. The solvents used were either pentane or ether, and the samples were extracted at ambient temperature for 7–8 days until no traces of pyridine in the washings were detected by GLC. This was followed by vacuum drying as detailed above.

Experimental Techniques. The enthalpies of mixing were obtained using a Setaram C-80 calorimeter. A reversing mechanism ensures proper mixing of the two compounds. These are placed in separate chambers arranged as concentric cylinders with the top of each cell open to a small common vapor space. Some measurements were also made under conditions where the vapor spaces were isolated from each other, thus preventing the vapors from mixing prior to the experiment. No differences in the measured enthalpy values were observed. Typically, the total sample volume used was 2 mL. The calorimeter is temperature controlled. All of the measurements were performed at a common temperature of 50.0 ± 0.1 °C, chosen so that all components are in the melt form and have a low viscosity.

When literature values were not available, the densities of the components were measured in the melt state (50 °C) using calibrated pycnometers.

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 calorimeter. The heating rate used was 20 °C/min, and the glass transition temperature is taken as the midpoint in the change in heat capacity with temperature.

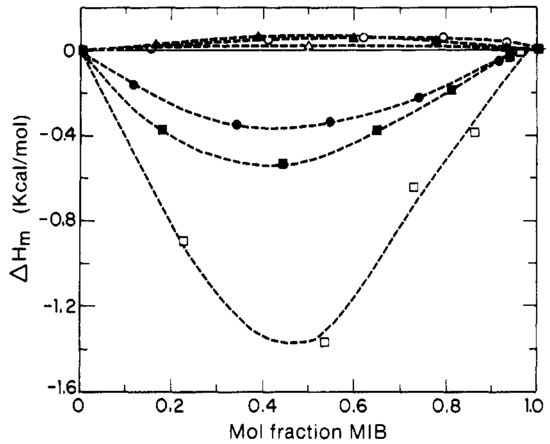


Figure 1. Composition dependence of the heats of mixing for mixtures of MIB with (△) EBZ, (○) HCH, (▲) 3-EBA, (●) 4-EPH, (■) ESA, and (□) HFH at 50 °C.

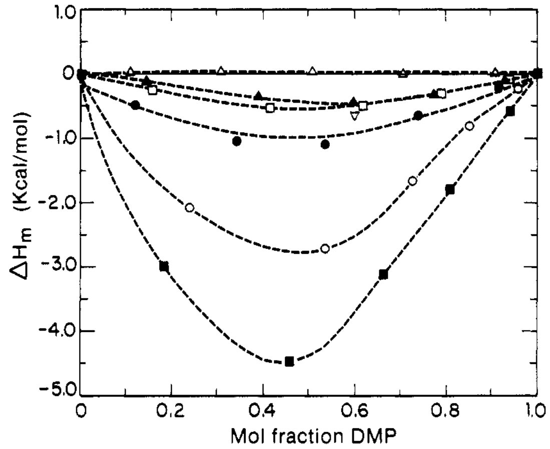


Figure 2. Composition dependence of the heats of mixing for mixtures of DMP with (△) EBZ, (□) HCH, (▲) 3-EBA, (▽) 4-EBA, (●) 4-EPH, (○) HFH, and (■) ESA at 50 °C.

FTIR spectra were obtained by using either a Bio-Rad (Digilab Division) FTS-7 spectrometer (3240-SPC) or a Nicolet 60SX FTIR spectrometer. The resolution used was 4 cm^{-1}.

Since optical clarity is used herein as one criterion for miscibility, the refractive indices (n_i) of the functionalized polystyrenes were measured to ensure that these were sufficiently different from those of PMMA and PDMA to produce scattering of light from different phase domains. These were measured by the method of index matching using the Becke line method and calibrated liquid standards. In all cases, $n_1 - n_2$ was greater than 0.07.

Experimental Results

Heats of Mixing. Two classes of polymers that are viewed as potential hydrogen bond (or proton) acceptors were chosen for this study. These were an ester, PMMA, and an amide, PDMA. The model compounds chosen to represent these are methyl isobutyrate (MIB) and *N,N*-dimethylpropionamide (DMP), respectively. The heats of mixing for each of these models with a series of modified ethylbenzene compounds containing hydrogen bond (or proton) donating groups of varying acid strength (to represent the acid-modified polystyrenes) were measured. These results, shown in Figures 1 and 2, illustrate the composition dependence of the enthalpy of mixing, in kilocalories per mole. The dashed lines are simply spline fits through the data. With a few exceptions [both mixtures with ethylbenzene (EBZ) and mixtures of MIB with the aryl isopropyl alcohol (HCH) and with ethylbenzoic acid (3-EBA)], the various combinations result in large, exothermic enthalpies of mixing, some of which are found to be as great as −4.5 kcal/mol. In general, the interactions between the amide DMP and each acid are much stronger than the interactions between the latter and the ester MIB. To a first approximation, it would appear that, as the acidity of the modified ethylbenzene increases, the magnitude of the measured enthalpy of mixing increases. The picture is actually not that simple and will be discussed in more detail below.

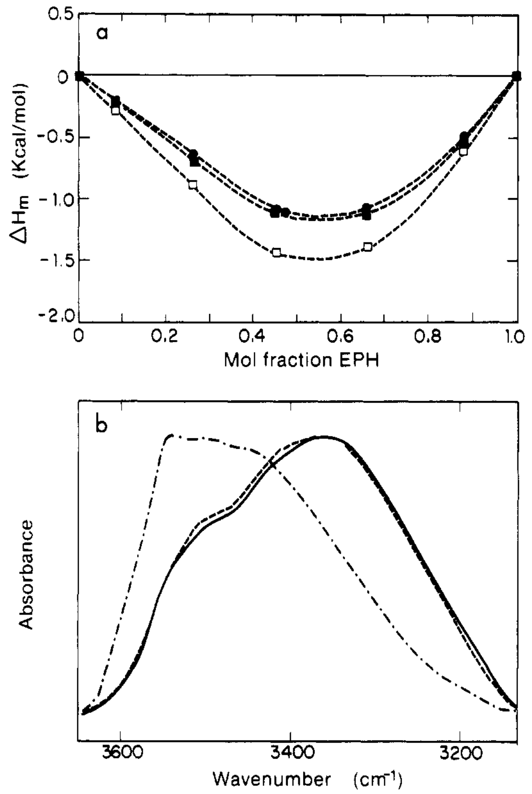


Figure 3. (a) Composition dependence of the heats of mixing for mixtures of DMP with (□) 2-EPH, (■) 3-EPH, and (●) 4-EPH at 50 °C. (b) Hydroxyl stretching region of the infrared spectra for pure melts of (– · –) 2-EPH, (- - -) 3-EPH, and (—) 4-EPH at 50 °C.

The methods used to obtain heats of mixing for mixtures containing ethylbenzoic acid (EBA) deserve some additional explanation. Carboxylic acids are highly self-associated and usually exist as dimers. Many also have relatively high melting points (T_m). The choice models for this study would be 4-ethylbenzoic acid (4-EBA) or 4-isopropylbenzoic acid. Their respective melting points are 112 and 117 °C, which prohibited their use in the mixing experiments at 50 °C. In addition, since MIB has a boiling point of 90 °C, a common mixing temperature for that case could not be found. Two alternative methods were thus used to determine the heats of mixing between the benzoic acid model and the hydrogen bond acceptors. The first consisted of using an isomer, 3-ethylbenzoic acid (3-EBA), which has a melting temperature of 47 °C. The second method involved measuring the heats of mixing of the ester (or amide) with premixes of 4-EBA and EBZ of varying 4-EBA content and from these deducing the result for the pure 4-EBA. Both methods are detailed below.

It was felt that using the 3-EBA in lieu of the 4-EBA would result in very similar magnitudes for ΔH_m since the carboxylic acid groups in the two isomers have similar steric environments and similar pK_a values. To add support to this argument, the heats of mixing between DMP and various isomeric forms of ethylphenol were measured. These are shown in Figure 3a. The results obtained for 4-EPH and 3-EPH with DMP are essentially identical throughout the composition range. The heats of mixing of DMP with 2-EPH are more exothermic than with the other isomers. This is probably the result of less self-association in the pure 2-EPH than in the 3-EPH or 4-EPH rather than a stronger interaction with DMP. It is reasonable to expect less self-association with the 2-isomer, owing to a certain amount of steric hindrance about the oxygen atom caused by the ortho ethyl group. One must remember that the measured value for the enthalpy is the sum of the heat required to break any self-association between individual components (always endothermic) and the heat of formation of new associations between the unlike species. This point is illustrated in Figure 3b, in which the hydroxyl (OH) stretch regions of the FTIR spectra for neat 2-EPH, 3-EPH, and 4-EPH at 50 °C are compared. The OH band is quite broad and can be deconvoluted into several overlapping bands (not shown). The band that occurs at higher wavenumbers (ca. 3525–40 cm^{-1}) is due to "free" hydroxyls, and the lower frequency bands are due to hydrogen-bound hydroxyls. It is immediately apparent that there is a much larger fraction of free OH groups (ca. 30%) in 2-EPH than in the other isomers, 3-EPH and 4-EPH being almost identical and having only ca. 15% free hydroxyls. On the other hand, the infrared spectra (hydroxyl and carbonyl regions) are virtually identical for mixtures of DMP with each of the isomers. A comparison of the infrared spectra (carbonyl region) of 3-EBA and 4-EBA reveals that they are self-associated to essentially the same degree. In conclusion, one should be able to obtain representable heats of mixing values for 4-EBA by using 3-EBA. It is these results that are plotted in Figures 1 and 2.

The second approach is based on the application of the binary interaction model[14,15] and consists of using the following equation for the net interaction energy density for mixing a homopolymer (here modeled by DMP) with a random copolymer (modeled by the EBZ/4-EBA mixtures)

$$B = B_{23}\phi_2' + B_{13}\phi_1' - B_{12}\phi_1'\phi_2' \qquad (7)$$

where 1 = EBZ, 2 = 4-EBA, and 3 = DMP. The volume fraction of components 1 and 2 in the copolymer are ϕ_1' and ϕ_2', respectively. By measuring the heat of mixing of component 3 with premixes of components 1 and 2 and varying the ratio of 1 to 2, the overall value of B is obtained. If B_{13} and B_{12} can also be measured, then B_{23} can be extracted rigorously from the slope of a plot of Y against ϕ_2' where

$$Y = B - B_{13}\phi_1' + B_{12}\phi_1'\phi_2' \qquad (8)$$

However, in the present system B_{12} cannot be measured directly at 50 °C for the same reasons impeding the measurement of B_{23}. If it is assumed that B_{13} and B_{12} are small in comparison with B_{23}, which is a reasonable assumption for these strongly interacting compounds, then eq 7 can be reduced to

$$B \simeq B_{23}\phi_2' \qquad (9)$$

and a plot of B against ϕ_2' will give B_{23} as the slope. As a test of this method, a system where all the values of B can be determined experimentally was studied. The enthalpies of mixing were measured when premixes of EBZ (component 1) and 4-EPH (component 2) were mixed with DMP (component 3). Figure 4 shows the dependence of the interaction energy density on the volume fraction of 4-EPH in the premixes, in the form of both the complete eq 7 and the approximate eq 9. These give almost identical results, and the values of ΔH_m calculated from the slopes are −9.1 and −9.2 cal/cm^3, respectively. These agree with the measured value of −9.3 cal/cm^3 for a 50:50 mixture of 4-EPH with DMP. Figures 5 and 6 show plots of the measured value of B as a function of volume fraction 4-EBA in the EBZ/4-EBA mixtures for mixing with DMP and MIB, respectively, at 50 °C. Only mixtures of low 4-EBA

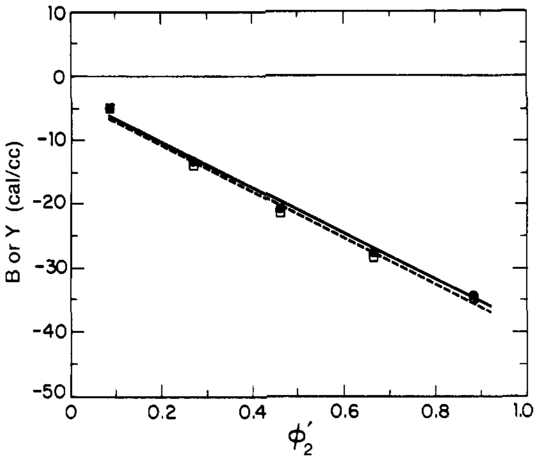


Figure 4. Interaction parameters for mixing DMP with premixes of EBZ and 4-EPH as a function of the volume fraction of 4-EPH in the EBZ/4-EPH mixtures, ϕ_2', (–●–) in the form of the complete eq 7 and (–□–) in the approximate form given by eq 9. The temperature was 50 °C.

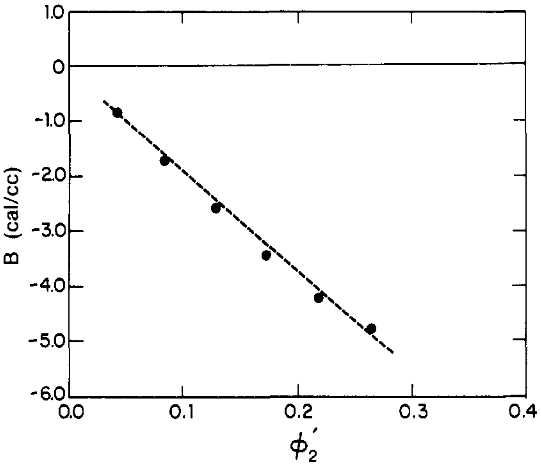


Figure 5. Interaction parameters for mixing DMP with premixes of EBZ and 4-EBA as a function of ϕ_2' at 50 °C in the form of eq 9.

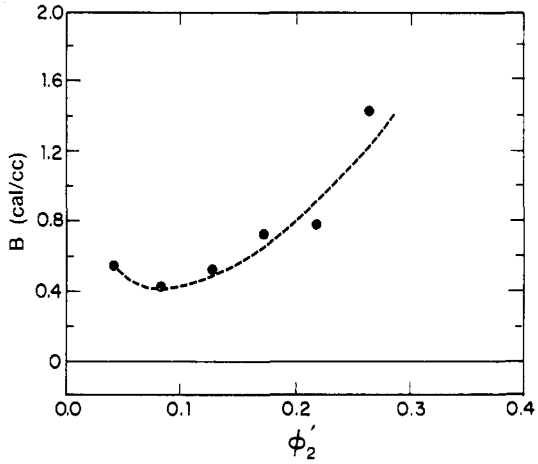


Figure 6. Interaction parameters for mixing MIB with premixes of EBZ and 4-EBA as a function of ϕ_2' at 50 °C in the form of eq 9.

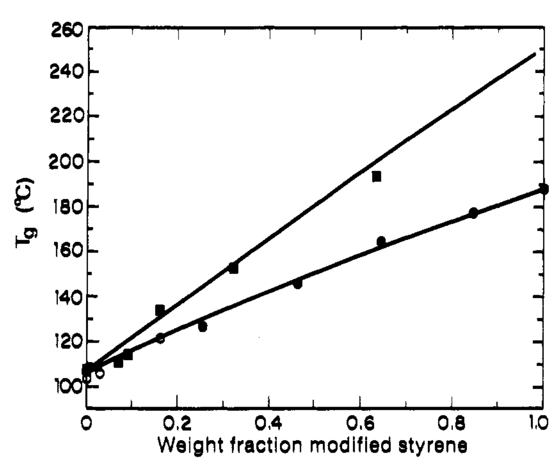


Figure 7. Glass transition temperature of the modified polystyrene copolymers as a function of weight percent of the modified styrene unit in the copolymer: (●) p(S–VPh), (■) p(S–CA), and (○) p(S–SA). The solid curves are fits to the Couchman equation.

compositions could be used due to the limited solubility of the benzoic acid in EBZ. The mixing of DMP with an equal quantity of the EBZ/4-EBA premixes results in a linear relationship between B and the volume fraction of 4-EBA in the premix (Figure 5). The slope of the curve gives a value for the overall interaction energy density between DMP and 4-EBA at a 50:50 weight composition of $B = -18.0$ cal/cm^3. The enthalpy of mixing can then be calculated, giving $\Delta H_m = -4.5$ cal/cm^3 (−0.6 kcal/mol) at a composition of 60 mol % DMP. This result is slightly more exothermic than was found by mixing DMP with 3-EBA directly where $\Delta H_m = -3.5$ cal/cm^3 (−0.45 kcal/mol) for the same composition. The results obtained by both methods are shown in Figure 2. The difference is minor relative to the entire picture.

The above analysis also reveals that when strongly interacting molecules are involved, the addition of an essentially inert moiety (such as in a copolymer) behaves to a first approximation as a diluent for the interactions.

The determination of B for mixing MIB with EBZ/4-EBA was not as successful. The measured values of B are all endothermic and do not show a linear relationship when plotted as a function of the volume fraction of 4-EBA in the premix (Figure 6). In fact, they seem to go through a minimum at a composition of about 10 wt % 4-EBA and then become increasingly more endothermic. As for mixing the other isomer 3-EBA with MIB, the ΔH_m values were found to be endothermic at all compositions. These results reflect once again the strongly self-associated nature of these carboxylic acids. Either the weaker base MIB is not strong enough to break these up or any new interactions formed with the acid do not result in a large enough negative enthalpy to offset the endothermic contribution.

Polymer Blends. The glass transition temperatures for each of the modified polystyrene copolymers are shown in Figure 7. The strong increase in T_g as a function of the incorporation of acidic groups has been reported in the past[16] and is evidence of strong self-association among the polymer chains. The poly(styrene-4-carboxylic acid) homopolymer is reported to have a T_g value of ca. 250 °C.[17] The composition dependencies of the T_g for the vinylphenol (S–VPh) and vinylbenzoic acid (S–CA) copolymers follow the Couchman equation[18] reasonably well; the value of 250 °C was used for calculating the S–CA curve. PMMA and PDMA had T_g values of 110 and 123 °C, respectively.

A summary of the miscibility results for the blends is presented in Table IV. The presence of a single, sharp, composition-dependent glass transition temperature, as determined by DSC, is indicative of phase homogeneity, at least on the distance scale of the experiment (ca. 100 Å). In some cases, the T_g values of the individual components were too close to enable conclusions to be drawn as to their phase miscibility. In those instances, optical clarity (which detects heterogeneity on a scale of ca. 1000 Å) of the film and the presence or absence of evidence of hydrogen bonding in the FTIR spectra were used as the criteria for miscibility.

The composition dependencies of the T_g for several of the blends are shown in Figures 8–10. It is extremely useful to fit this type of data to the Kwei equation[20,21]

$$T_g = (w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2) + q w_1 w_2 \qquad (10)$$

in that it provides an indication of the excess stabilization energy present in the blends due to molecular interactions. In consideration of the fact that only a few compositions were studied for each blend series, giving limited T_g data, it is deemed more appropriate to fit these data with only one adjustable parameter, q. Thus, the simplified version of the Kwei relation[20] where k is set equal to unity is used.

Table IV
Summary of Blend Miscibility Results

	polymer 2	
polymer 1	PDMA	PMMA
PS	immiscible (1, 2)	immiscible[a]
p(S-VPh(22))	miscible (1, 2, 3)	miscible (1, 2, 3)
p(S-VPh(42))	miscible (1, 2, 3)	immiscible[b]
p(S-VPh(82))	miscible (1, 2, 3)	immiscible[b]
PVPh	miscible (1, 2, 3)	miscible (1, 2, 3)
p(S-CA(5))	immiscible (1, 2)	immiscible (2)
p(S-CA(25))	miscible (1, 2)	miscible (1, 2)
p(S-CA(54))	miscible (1, 2)	immiscible (1, 2)
p(S-SA(2))	immiscible (1, 2)	immiscible (2)
p(S-SA(12))	miscible (2)	miscible (1, 2)

Criteria for Miscibility

(1) The presence of a single, composition-dependent T_g for the blend indicates a miscible system, and the presence of two distinct T_g values indicates immiscibility.
(2) Optical transparency indicates miscibility.
(3) The observation of shifts in the FTIR absorbance spectra are attributed to hydrogen bonding between blend components.

[a] See ref 19. [b] These polymer pairs were found to be phase separated under the conditions used in this study. However, on the basis of the results obtained with PVPh and p(S-VPh(22)), they are most likely to be miscible under other conditions.

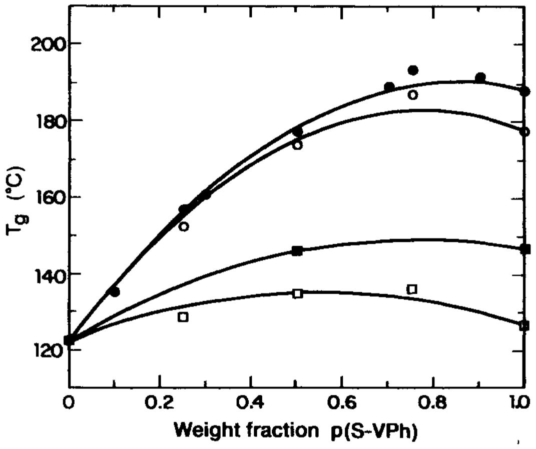


Figure 8. Composition dependence of the glass transition temperature for blends of PDMA with (●) PVPh, (○) p(S-VPh(82)), (■) p(S-VPh(42)), and (□) p(S-VPh(22)). The solid curves are fits to the Kwei equation (eq 11) with q = 94, 101, 46, and 42 for the above blends, respectively.

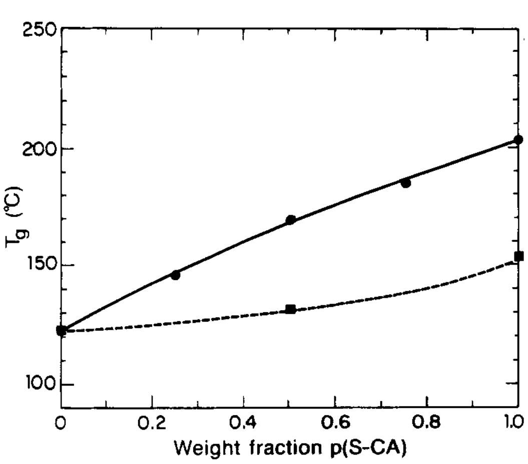


Figure 9. Composition dependence of the glass transition temperature for blends of PDMA with (●) p(S–CA(54)) and (■) p(S–CA(25)). The solid curve for the former is the Kwei equation (eq 11) with $q = 21$; no fit was performed on the latter (dashed curve).

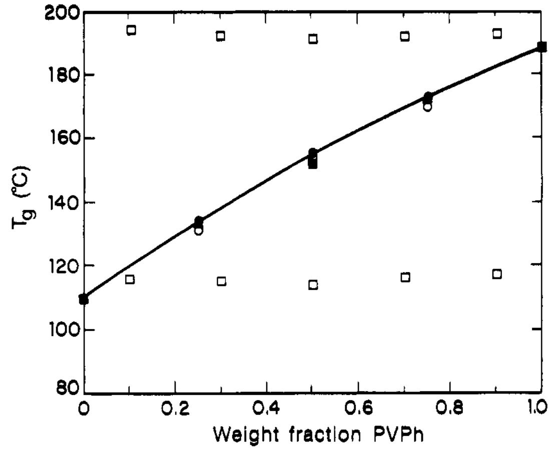


Figure 10. Composition dependence of the glass transition temperature for blends of PMMA with PVPh (□) cast from pyridine, (○) cast from MEK, (△) precipitated from MEK, (●) precipitated from THF, (■) melt blended at 238 °C. The solid curve is a fit to the Kwei equation (eq 11) with $q = 25$.

$$T_g = w_1T_{g1} + w_2T_{g2} + qw_1w_2 \qquad (11)$$

Discussion

The experimental study of strongly interacting polymers is encumbered by several effects whose manifestation is enhanced by these interactions. Two of these have been encountered extensively in the present study. The first is the unusually strong binding of basic solvent molecules to the acidic polymers, making it extremely difficult to remove all traces of the solvent and obtain true values for the glass transition temperatures of the blends. One must keep in mind that, in order to dissolve polymers with relatively high concentrations of polar functional groups in the first place, the solvent must be at least moderately interactive with the polymer. The second is solvent-induced phase separation that results from what is usually termed as the ΔX effect,[22,23] where preferential solvation of one polymer over the other occurs. This could also be thought of as one polymer interacting more strongly with the solvent than with the other polymer, resulting in the latter being excluded from the solution phase of the former as the concentration of the solution increases during the drying of the film. This second effect in particular may seriously obscure the "true" equilibrium phase behavior of the blends.

This work shows that in many instances heats of mixing of model compounds can be useful in predicting phase behavior in the blend, which can be otherwise obscured by these effects. The heats of mixing results also provide evidence that the extent of hydrogen bonding with a given acceptor is not exclusively determined by the acidity of the donor. The basicity of proton acceptor also plays an important role. Other more subtle interactions may also be at work; for example, the heat of mixing for MIB with HFH is larger than that with ESA, the latter being the stronger acid. Also the enthalpy of mixing results are dramatically different for the amide and the ester. The interactions between the acids and the amide, which is a stronger base than the ester, are substantially stronger than the corresponding interactions with the ester. The pK_a values for this series of acids, estimated from linear free energy arguments,[24] decrease in the following order, indicating increasing acid strengths:

$$pK_a = 15 \text{ (HCH)} > 10 \text{ (4-EPH)} > 7.4 \text{ (HFH)} > 5 \text{ (4-EBA)} > 0.6 \text{ (ESA)}$$

The magnitudes of the exothermic enthalpies of mixing with DMP increase as

HCH < 4-EBA < 4-EPH < HFH < ESA

which is essentially the same order as the acid strength with the exception of the benzoic acid. The results obtained for mixing with MIB, however, do not follow the same trend. The ΔH_m values become more exothermic in the order

EBA ≅ HCH < 4-EPH < ESA < HFH

Here the interactions are strongest with the HFH, and MIB does not interact strongly enough with the benzoic acid to compensate for its self-association, resulting in an endothermic heat of mixing. Similarly, the mixing of MIB with the alcohol HCH results in an endothermic ΔH_m value.

The heats of mixing can be expressed as interaction parameters for the model compounds as described by eqs 4 and 5. These are shown in Figure 11. It is apparent that the interaction parameters are composition dependent, particularly so for the more exothermic enthalpies. The composition dependence of χ reflects the difference in the heat that is given off when a few molecules of the proton donor are added to a sea of acceptor molecules as compared to the heat evolved when a few molecules of the acceptor are added to a sea of donors, the latter being the most exothermic in most cases studied herein.

The stronger interaction of the amide with the acids is also reflected by the data for the polymer systems in that it is much easier to form single-phase blends of the proton donor polymers with PDMA than with PMMA. This is apparent looking at the summary of the blend miscibility results presented in Tables III and IV. There was much less effect of solvent-induced phase separation with the PDMA systems, although it was observed to occur for the PDMA/p(S–SA(12)) blend. The solvent effect on the phase behavior is more profound in the case of PVPh or the p(S–VPh) copolymers with PMMA than with PDMA. Blends with PVPh or random copolymers of PS and PVPh are observed to be miscible with PDMA when cast from pyridine where the solvent is allowed to remain in the sample for a long equilibration time. Single-phase blends are also obtained from DMF. Under these same conditions (cast from pyridine or THF), PMMA phase separates from the PVPh homopolymer and from the copolymers with high phenol content. The only copolymer composition that did not phase separate under these conditions was p(S–VPh(22)), containing 22 mol % VPh. However, if the blend preparation conditions are changed (the use of

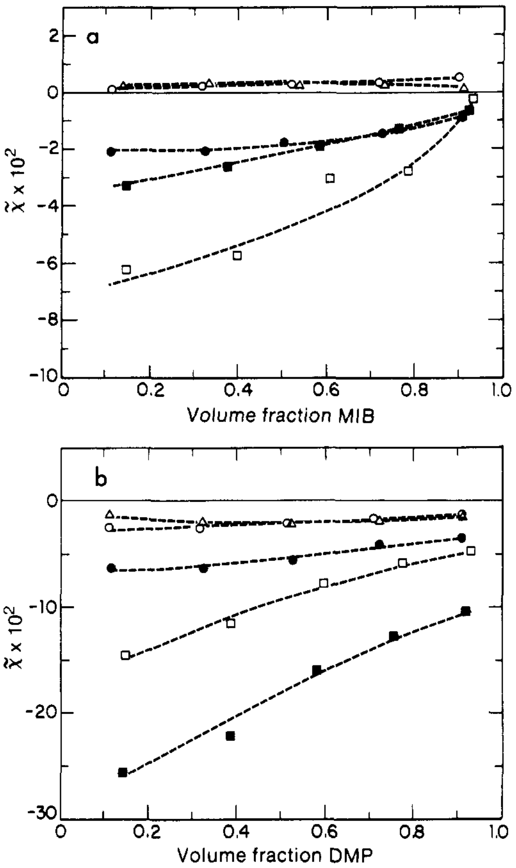


Figure 11. Composition dependence of the interaction parameters for mixtures of (●) 4-EPH, (■) ESA, (△) EBA, (○) HCH, and (□) HFH with (a) MIB or (b) DMP at 50 °C.

MEK as a casting solvent, preparation via precipitation), single-phase blends are obtained between PMMA and PVPh. The intermediate copolymer compositions would most likely also be miscible with PMMA under the appropriate preparation conditions.

The heats of mixing values obtained for the corresponding mixture of MIB and EPH were indeed large and exothermic and would predict that the polymer pair should be miscible. The larger ΔH_m values measured for the DMP/EPH system, however, would suggest that the stronger interaction of PDMA with the VPh unit may lead to a lower probability of occurrence of solvent-induced phase separation.

The PVPh/PMMA blend (using low molecular weight PVPh: $\bar{M}_w = 1500$) has been examined in the past by several groups. The question as to whether or not the two high molecular weight polymers are miscible was not totally resolved. Several studies have shown these two polymers to be immiscible;[11,12] however, Coleman and Painter have predicted, via free energy calculations, that these are miscible at room temperature.[10] In addition, the Penn State group has previously discussed the importance of solvent-induced phase separation in these systems.[25] In order to totally eliminate possible solvent effects, a melt blend of a 50:50 by weight composition of PVPh (high molecular weight) and PMMA was prepared in this work. This resulted in an optically clear film with a T_g value that is intermediate between those of the pure components (Figure 10), indicating that the two are indeed miscible. One may argue about the possibility of cross reactions, cross-linking of the PVPh, or degradation of the PMMA at this high processing temperature (238 °C). Size-exclusion chromatography of the melt blend did indeed reveal a slight shoulder on the PVPh peak on the high molecular weight side, suggesting a small amount of branching. No change in the molecular weight or MW distribution of the PMMA was observed.

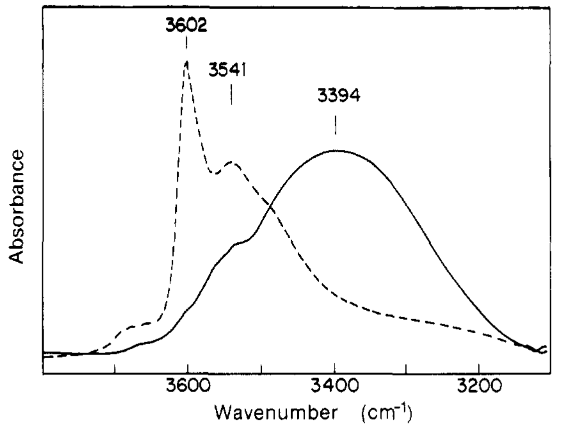


Figure 12. Hydroxyl stretching region of the infrared spectra for the pure components (—) HCH and (- -) HFH.

On the basis of these studies and others in the literature, it would seem that it is easier to form single-phase blends (via solvent casting) of these acidic polymers with the basic polymers as the basicity of the proton acceptor becomes larger. Many such donor–acceptor blends have been reported to be miscible when other relatively strong basic polymers such as poly(vinylpyridine)[26] or poly(*N*-vinylpyrrolidone)[27] are involved.

The heats of mixing results also predict that strong interactions occur between the hexafluoroisopropyl alcohol (HFIP) containing model (HFH) and those for PMMA and PDMA. These interactions are much weaker if HCH is used in lieu of HFH. Pearce and Kwei have observed miscibility in blends of the corresponding fluoro-modified polymer with PMMA and with many other polymers.[28] Such miscibility has also been observed by others.[29] It has also been reported that blends of the HFIP-modified PS with poly(ethylene oxide) (PEO) are much more compatible than blends of PEO with the proton analogue (i.e., isopropyl alcohol modified PS).[30] This enhanced miscibility was attributed to the inductive effects that arise from the proximity of two strong electron-withdrawing substituents (CF_3) adjacent to the hydroxyl group, resulting in a lower pK_a compared to the hydrogenous material. These observations for the polymer blends are in agreement with our heats of mixing results. Although the pK_a is important, one must also consider the basicity of the hydrogen bond donor, since this will affect the extent of self-association. As demonstrated above, self-association contributes endothermically to ΔH_m and competes with heteroassociation between the donor and the target acceptor functional groups. (In fact, two or more acceptor types are always present in systems such as this. One results in self-association and the other in heteroassociation.) Besides increasing the acid strength of HFH, the strong electron-withdrawing effect of the trifluoromethyl groups reduces the base strength of HFH compared to HCH, significantly reducing the extent of self-association. Thus, HFH will exist predominantly in a form where the hydroxyl groups are free and ready to associate with a proton acceptor such as an ester or amide. This is readily seen in Figure 12, where the hydroxyl stretching region of the infrared spectra for neat samples of the HCH and HFH model compounds are compared. Unlike HCH, the hydroxyls of HFH are primarily nonassociated, even to a greater extent than ethyl phenol (see Figure 3b). This suggests that HFIP-modified polymers would be better candidates than nonsterically hindered phenolic polymers (such as PVPh) for forming miscible blends with basic polymers.

Determination of the lower limit of how many interactions are needed to effectively miscibilize an immiscible polymer pair is not the focus of the present study. Rather, we have concentrated on blends where the polymers contain a high mole percent of functional groups. Chen and Morawetz[13] have studied the miscibility of a series of modified polystyrenes containing hydroxyl, HFIP, carboxylic acid, and sulfonic acid functionalities (similar to the ones studied herein) with acrylate polymers via fluorescence techniques. They found that only a few mole percent of the proton-donating group is required to obtain miscibility of the PS with the acrylate and that the phenol and HFIP units are more efficient than the carboxylic or sulfonic acids in achieving this result. They also observed strong effects of the casting solvent on the miscibility of the polymers.

One must not forget that other factors that affect the efficiency of the acid–base interactions in addition to the self-association of the acid (which must be broken up before new intermolecular interactions are formed; this is particularly evident with carboxylic acid containing polymers) are dispersive forces and noncombinatorial entropic contributions. The latter are prominent driving forces against mixing and are significant in blends of strongly interacting polymers where the interactions formed are very directional. Walsh and Higgins have introduced an interaction entropy parameter (Q_{12}) into their analysis of enthalpy of mixing data in order to adequately generate the spinodal curve for the phase diagram.[31] It would seem that the greater exothermic enthalpies of mixing measured for the amide relative to the ester model compounds imply that, for the polymers, this additional favorable force will aid in compensating for the loss in noncombinatorial entropy.

Information concerning the relative strengths of these interactions can also be acquired from the infrared spectra of the blends and from the q values obtained from fitting the composition dependence of the glass transition temperature to the Kwei equation. The hydroxyl absorbance regions of the infrared spectra for 50:50 wt % mixtures of the model compounds for PVPh with PMMA and PDMA are compared in Figure 13. Those for the polymers are shown in Figure 14. The frequency difference between the free hydroxyl (phenol) absorbance (ca. 3520 cm^{-1}) and that of the hydrogen-bound form is a measure of the relative strengths of the hydrogen-bonding interactions. A linear relationship has been shown to exist between $\Delta\nu$(OH) and the enthalpy of hydrogen bond formation for several monomeric systems.[32,33]

For both the model compounds and the polymers, the strength of the interaction between the phenol and the amide is stronger than the strength of the interaction of the phenol with itself. With the amide, a large shift of the peak to lower wavenumbers is observed. When MIB is mixed with 4-EPH, the maximum in the H-bound hydroxyl stretching peak shifts to higher wavenumbers. This indicates that the interactions between the ester and the phenol are weaker than the self-interaction of the phenol. The same phenomenon is observed for the single-phase blend of PVPh and PMMA. In both systems, the magnitudes of the shifts observed for the model compounds are almost identical with those observed for the blends.

The glass transition temperature of a blend is affected by the interactions that occur between the individual components. Strong interactions often lead to large positive deviations of T_g from the weight-average values.

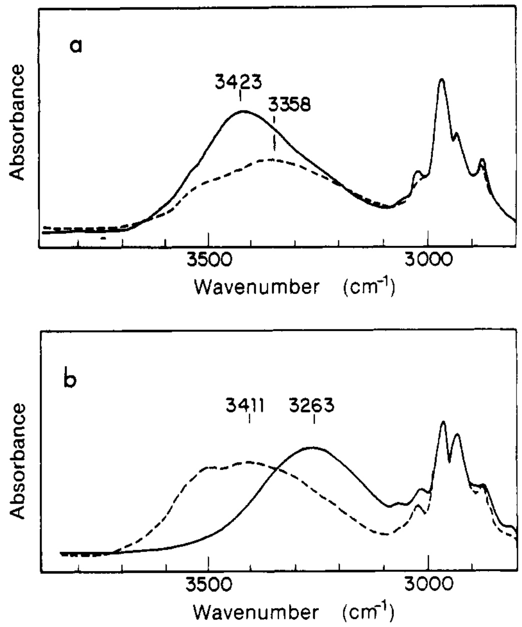


Figure 13. Hydroxyl stretching region of the infrared spectra for 50:50 wt % mixtures of (a) 4-EPH with MIB and (b) 4-EPH with DMP at 50 °C. The dashed curves are the spectra for a digital addition of the spectra of the pure components.

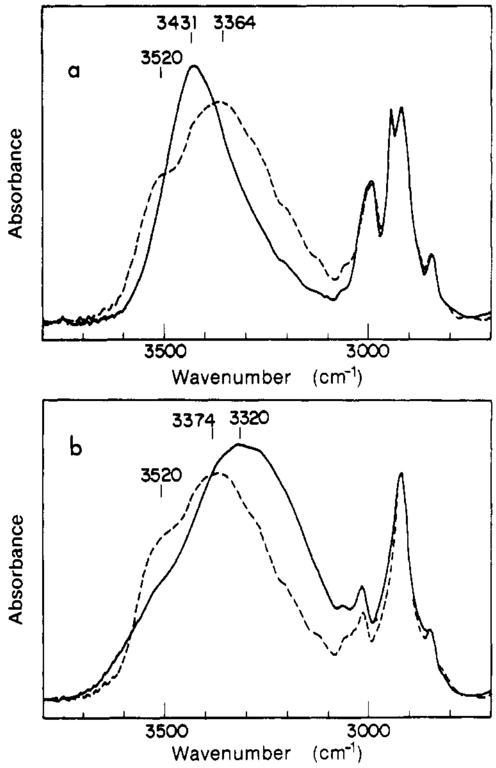


Figure 14. Hydroxyl stretching region of the infrared spectra for 50:50 wt % miscible blends of (a) PVPh with PMMA and (b) PVPh with PDMA. The dashed curves are the spectra for a digital addition of the spectra of the pure components.

One can examine this further by fitting the composition dependence of T_g to the Kwei equation (eq 10) or the simplified version (eq 11). The parameter q thus obtained (actually Rqw_1w_2, where R is the gas constant) is a measure of the excess stabilization energy in the blend system. The magnitude of Rqw_1w_2 can be attributed to both the strength of the heteroassociation relative to its initial state and, since the sources of the backbone stabilization are the specific contact points where interactions occur, to the number of these contacts.[20,21]

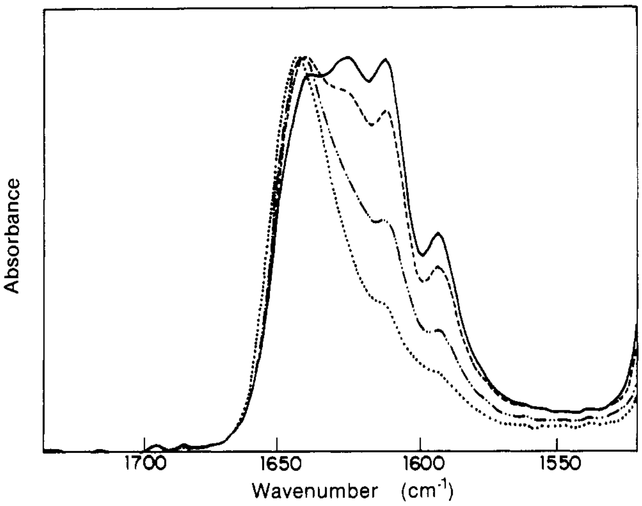


Figure 15. Carbonyl stretching region of the infrared spectra for 50:50 wt % blends of PDMA with (—) PVPh, (- - -) p(S-VPh(82)), (– · · · –) p(S–VPh(42)), and (· · ·) p(S–VPh(22)).

The data for the PDMA/PVPh and copolymer blend series shown in Figure 8 illustrate the second of the two. The value determined for q for each blend set is quite large, indicating a strong interaction between the PDMA and the phenol. However, as the number of interaction sites decreases, so does the value of q (considering the values of q for PVPh and for p(S-VPh(82)) to be similar). The strength of the interactions should be the same for PDMA with a 100% substituted PS as with a 22% substituted PS. Examination of the infrared spectra shows this to be the case. Figure 15 shows the carbonyl stretching region for the blends. The peak at ca. 1643 cm^{-1} is due to the free carbonyls, and the peak at 1626 cm^{-1} arises from the carbonyls that are hydrogen-bound. The two peaks at 1612 and 1592 cm^{-1} arise from a ring vibration in poly(vinylphenol) where the dipole of the ring is enhanced by the hydroxy substituent. The magnitude of the frequency shift of the hydrogen-bound carbonyl relative to that of the free carbonyl of PDMA is the same for all the copolymer blends. The same conclusions are derived from a qualitative examination of the hydroxyl region of the infrared spectra for these blends. On the other hand, the relative fraction of hydrogen-bound carbonyls is seen to decrease as the phenolic content of the copolymer decreases.

The manner in which differences in the energy of interaction between unlike species affect the value of q is illustrated by comparing the PDMA/PVPh and the PMMA/PVPh miscible blends. The former pair, shown by FTIR and calorimetry of the model compounds to interact with each other much more strongly than do the latter pair, exhibits a much stronger positive deviation from linear additivity in the composition dependence of T_g and thus is fit by a much larger value of q, 94 for PDMA/PVPh versus 25 for PMMA/PVPh. It is interesting to note that the ratio of the magnitudes of ΔH_m for the model compounds compares reasonably well to the ratio of Rqw_1w_2 obtained for the above two polymer blends ((PDMA/PVPH)/(PMMA/PVPh)). At a 50:50 wt % composition, values of 3.2 and 3.8 are obtained for these ratios, respectively. An indication of the relative number of interactions present can be calculated by bandfitting the carbonyl region of the infrared spectrum and obtaining relative peak areas for bound and free carbonyls. The peak areas are then corrected for differences in absorptivities, a_f (free) and a_{hb} (hydrogen-bound). Figure 16a,b shows that, at ambient temperature, a slightly larger fraction of carbonyls is hydrogen-bound to the PVPh in the PDMA/PVPh 50:50 wt % blend (47%) than in the PMMA/PVPh 50:50 wt % blend (40%). The values for the absorptivity ratio a_{hb}/a_f used in these calculations are 1.5 for the PMMA/PVPh blend[34] and 1.38 for the PDMA/PVPh blends. The latter ratio was measured for blends of the model compounds DMP with 4-EPH. This is detailed elsewhere.[35] The PMMA/PVPh and PDMA/PVPh blend samples were solvent cast, dried, and annealed at 165 or 175 °C for 14 h under nitrogen, respectively, prior to acquiring the infrared spectra at ambient temperature. The relative peak areas for the hydrogen-bound and free carbonyls were then found to be reversible when the sample was heated to 200 °C (well above the T_g of the blend) and cooled back down and are believed to represent equilibrium values.

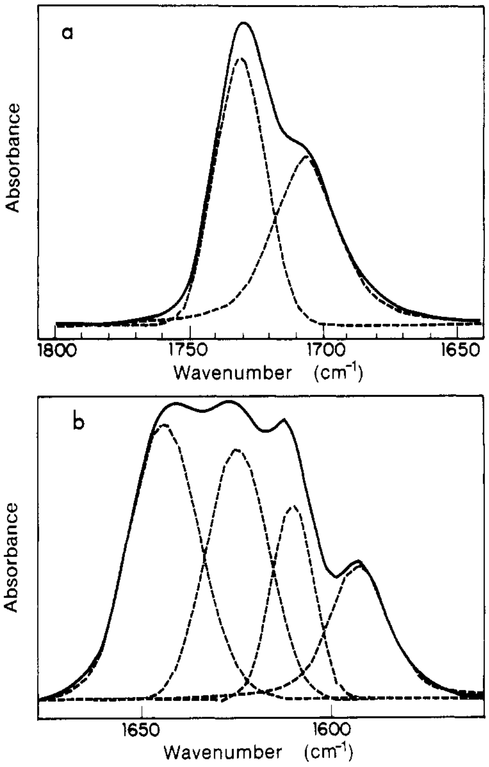


Figure 16. Band fit of the carbonyl stretching region of the infrared spectra for 50:50 wt % miscible blends of (a) PVPh with PMMA and (b) PVPh with PDMA.

Another concept considered by the Kwei theory[21] is the idea that the component with the higher T_g undergoes a loss in stabilization energy upon mixing, which is reflected by a lowering of the q value. This may very well occur in the p(S-CA) blends with PDMA, particularly when the CA composition is high as that in p(S–CA(54)). It has been shown by the enthalpy of mixing studies that it is very difficult to break up the self-association within the carboxylic acid. This would translate into a high level of destabilization of the polymer when it is molecularly mixed with another polymer. The value of q obtained for the p(S-CA(54))/PDMA blend (q = 21) is much smaller than those obtained for the p(S-VPh)/PDMA blends of similar acid content (q = 46–101).

Conclusions

A number of low molecular weight organic molecules were selected as models for repeat units in functionalized addition polymers. Heats of mixing were measured for the model compounds and compared with the miscibility of the corresponding polymers. Functionality included potential hydrogen bond acceptors such as poly(methyl methacrylate) and poly(*N,N*-dimethylacrylamide). Proton donors spanned a range of pK_a values and included polystyrene units containing sulfonic acid, carboxylic acid, phenol, alcohol, or HFIP groups. The results of the heats of mixing experiments with small molecules, as well as FTIR results, closely parallel observations of miscibility of the polymers. Thus, by studying carefully chosen model compounds, one can frequently predict phase behavior in a polymer blend. Interactions between the proton donors and *N,N*-dimethylacrylamide groups are generally stronger than those between the donors and methacrylate units.

Although several studies have shown that the incorporation of as little as a few mole percent H-donating groups is required to miscibilize the immiscible blend of PS with PMMA,[13] when the degree of acid modification to the PS is increased several practical problems are encountered. Solvent-induced phase separation is observed for several blends that were found to be miscible under other circumstances. Self-association of the acid-modified polystyrenes presents an additional barrier (endothermic contribution to ΔH_m), which must be overcome if a miscible blend is to be formed. Thus in some cases, obtaining a miscible polymer blend depends upon the method of preparation. For example, a blend of poly(vinylphenol) and PMMA appears to be immiscible if prepared by casting a film from a THF or pyridine solution. On the other hand, a miscible blend can be obtained by evaporating a MEK solution, by coprecipitating a solution of the two polymers into a nonsolvent, or by melt blending.

One could reason that the strength of the interactions between a series of hydrogen bond donors and a given acceptor should approximately increase as the pK_a of the donor decreases. However, as illustrated by the results in this work, this simple approximation does not take into account the tendency for self-association of the donor, which can compete with or overwhelm heteroassociation with the target acceptor. For example, carboxylic acids tend to form strong networks of hydrogen bond dimers (or higher polymers). Although a relatively strong acid (p$K_a \sim 5$) compared with a phenol (p$K_a \sim 10$), the carboxylic acid group is less likely to form strong hydrogen bonds with a comparatively weak base (i.e., an amide) than is a phenol. The carboxylic acid is itself a reasonably strong base. This reasoning could explain why polystyrene functionalized with hexafluoroisopropyl alcohol groups is miscible with such an unusually large range of acceptor polymers.[28,36] This functional group has a low pK_a value ($\sim$7.4) and exhibits weak self-association, owing to the electron-withdrawing effect of the trifluoromethyl groups. It is both a relatively strong acid and a weak base.

FTIR is also a very effective technique for studying the relative strengths of hydrogen-bonding interactions in many functional groups. For the systems studied in this work, both the direction and the magnitude of band shifts for the model compounds are almost identical with those observed for the blends.

From the work presented herein, it is difficult to ascertain exactly what the mechanism of interaction is between the polymers that form miscible blends in a few of the systems studied. In particular, blends of PDMA with the sulfonic acid and carboxylic acid modified polystyrenes have the potential of forming complexes via proton transfer. These ideas are currently under investigation.

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