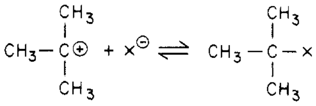
the value observed for triflic acid is 850. The reduced acidity and higher nucleophilicity[12] of the methanesulfonic acid may allow it to undergo side reactions in the polymer matrix, thus decreasing its ability to catalyze the removal of the protective group. Specifically, attack of a nucleophilic anion on the *tert*-butyl cation formed as the initial product of deprotection can result in termination and thus (Scheme III) reduce the observed catalytic length for the aliphatic acids.

Scheme III



$$(CH_3)_3C^{\oplus} + X^{\ominus} \rightleftharpoons (CH_3)_3C{-}X$$

Lithographic Evaluation. Exposure response curves were generated for ester/poly(*t*-BOCoxy-α-methylstyrene) formulations listed in Table III. Representative curves are shown in Figure 5, and sensitivity and contrast data are presented in the table. The required dose to clear large area features is 100 mJ/cm^2 for 2,6-dinitrobenzyl methanesulfonate using a PEB of 120 °C for 2 min. In contrast to this result, formulations using the same concentration (8.4 mol%) of either 2,6-dinitrobenzyl tosylate or 2,6-dinitrobenzyl benzenesulfonate, under the same processing conditions, required approximately 10 mJ/cm^2 to achieve the same effect. Substitution of the aromatic sulfonic acid ring with the electron-withdrawing NO_2 group affords an increase in sensitivity to 2 mJ/cm^2. One could expect the pentafluorobenzenesulfonate derivative **3** to be even more sensitive than the corresponding *p*-nitrobenzenesulfonate in its lithographic behavior but its low thermal stability renders it unacceptable for this application. The differences in sensitivity for the 2,6-dinitrobenzyl esters examined here result from the lowered nucleophilicity observed for the sulfonic acids and follows the sequence CH_3SO_3H < tosic < *p*-nitrobenzenesulfonic. This sequence is also consistent with the observed catalytic chain length. The nitrobenzyl ester/*t*-BOCoxy-α-methylstyrene resist is capable of high-resolution imaging with good sensitivity. Figure 6 depicts a coded 0.5 μm by 1.0 μm line/space pattern printed in a 1.0-μm thick layer of the tosylate resist formulation. These results are typical of the esters examined here.

Conclusions

The chemistry of a family of 2,6-dinitrobenzyl esters has been investigated and found to be effective acid generators for deep UV chemically amplified resists. These materials photogenerate organic acids which, upon mild heating, catalyze the removal of a *t*-BOC protecting group from poly(*t*-BOCoxy-α-methylstyrene). The thermal behavior of the esters has been examined and the quantum yield determined for selected sulfonate esters. The quantum yield is only slightly affected by the structure of the sulfonate group. A lithographic evaluation of several of the sulfonate esters when used in conjunction with poly(*t*-BOCoxy-α-methylstyrene) has been made. A correlation has been found between the nucleophilicity of the sulfonate anions and the catalytic chain lengths observed for *t*-BOC removal in the lithograhic process. These data have been shown to be related to the lithographic sensitivity of resists formulated with the esters. Sensitivities ranging from 2 to 100 mJ/cm^2 in the deep UV have been observed, and 0.5-μm resolution has been demonstrated.

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Miscibility of Copolymer Blends

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ABSTRACT: The miscibility of two homopolymer–copolymer pairs were studied. In the first pair, poly(4-hydroxystyrene) and poly(*n*-butyl acrylate-*co*-*tert*-butyl acrylate), miscible blends were obtained only when the *n*-butyl acrylate content of the copolymer was 64% or higher. In the second pair, poly(*tert*-butyl acrylate) and poly(styrene-*co*-4-hydroxystyrene), a miscibility window was found when the amount of 4-hydroxystyrene in the copolymer was between 28 and 66 mol %. The results were analyzed with the use of current theories.

Introduction

Many recent studies of the miscibility of a copolymer with a homopolymer made use of a mean-field theory, which considered the pair interaction parameters of all the components in the blend.[1-7] Analysis of experimental data with the above theory has met with success in the prediction of miscibility behaviors.

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In our studies[8,9] of the role of specific interaction in miscibility enhancement, we have found that the incorporation of a small amount of hydrogen bond donors into polystyrene rendered the modified polymer to be miscible with poly(methyl methacrylate), a hydrogen bond acceptor. Since the modified polystyrenes are, by definition, also copolymers, the motivation of this study is to test the applicability of the above theory to systems in which specific interaction contributes to miscibility.

The materials chosen for this study are butyl acrylate polymers and copolymers of styrene and 4-hydroxystyrene. Poly(*n*-butyl acrylate) and poly(*tert*-butyl acrylate) are immiscible with polystyrene, and with each other. The former is miscible with poly(4-hydroxystyrene), but the latter is not. The purpose of this investigation is 2-fold: (1) to study blends of poly(4-hydroxystyrene) with copolymers of *n*- and *tert*-butyl acrylate and (2) to determine whether a miscibility window exists for blends of poly(*tert*-butyl acrylate) and poly(styrene-*co*-4-hydroxystyrene). The choice of 4-hydroxystyrene copolymers is particularly attractive because the miscibility of the homopolymer with a large number of hydrogen bond acceptor polymers has already been investigated extensively.[10-13]

Experimental Section

1. **Materials. (a) Poly(4-hydroxystyrene) (PHS).** PHS-1 was purchased from Polysciences, Inc. The intrinsic viscosity of the polymer was determined to be 0.18 dL/g in tetrahydrofuran at 25 °C. GPC measurements indicates a broad molecular weight distribution with a M_n value of 6.3×10^3 and a M_w value of 4.6×10^4, both expressed as PS equivalent molecular weights. PHS-2 was synthesized in this laboratory by hydrolysis of poly(4-acetoxystyrene), which was prepared by the polymerization of 4-acetoxystyrene at 60 °C using azobis(isobutyronitrile) as initiator. The hydrolysis reaction was carried out in dioxane, which contained 1% hydrazine hydrate and 0.5% water.[14] After the reaction was allowed to proceed for approximately 6 h at room temperature, the reaction product, poly(4-hydroxystyrene), was isolated and purified by precipitation from THF solution into petroleum ether and then dried in vacuo at 60 °C for 1 day. The infrared spectra of this material were in good agreement with the results reported by Danusso.[15] The carbonyl group absorption at 1758 cm^{-1}, which was present in the parent polymer, disappeared completely. Instead, strong absorption bands were seen at 3532 and 3400 cm^{-1}, characteristic of the stretching frequencies of free and self-associated hydroxyl groups, respectively. The ^1H NMR spectrum exhibited broad resonances near 1.5 (aliphatic backbone), 6.54 and 7.08 (aromatic), and 9.02 ppm (hydroxyl group). The intrinsic viscosity of PHS-2 was 1.44 dL/g. The M_n and M_w values (GPC) were 1.2×10^5 and 2.5×10^5, respectively.

(b) Poly(styrene-*co*-4-hydroxystyrene). The copolymers were synthesized by copolymerization of styrene and 4-acetoxystyrene followed by hydrolysis of the acetoxy group as described above. In a separate study, we have determined the monomer reactivity ratios to be r_1 (styrene) = 0.80 and r_2 = 1.02. Therefore the two types of units are arranged in a nearly random manner along the chain. In our copolymerization experiments, conversion was limited to about 15% in each case. The compositions of the copolymers were determined by ^1H NMR spectra, which showed resonances near 1.6 (aliphatic backbone), 2.3 (methyl), and 6.4 and 6.9 ppm (aromatic). The copolymers will be designated as HS, and the approximate mole percent of the hydroxystyrene in the copolymer will be represented by a numeral after HS. The intrinsic viscosities and glass transition temperatures of the copolymers are listed in Table I. We did not perform GPC measurements for each copolymer. The M_n and M_w values for HS48 are 7.3×10^4 and 1.6×10^5, respectively.

(c) Poly(*n*-butyl acrylate) (PnBA) and poly(*tert*-butyl acrylate) (PtBA) were purchased from Polysciences, Inc. The intrinsic viscosities of the two polymers were determined in THF at 25 °C to be 0.20 and 0.34 dL/g, respectively. The M_n and M_w values are 3.3×10^4 and 5.4×10^4 for PnBA and 1.7×10^4 and 1.2×10^5 for PtBA. The glass transition temperatures of PnBA and PtBA are −42 and +30 °C, respectively.

Table I
Compositions and Glass Transition Temperatures of Poly(styrene-*co*-4-hydroxystyrene)[a]

sample	compositn of HS, mol %	[η], dL/g	T_g, °C
HS-8	8.1	0.58	112
HS-11	11.1	0.56	113
HS-15	14.7	0.59	111
HS-22	22.1	0.56	121
HS-28	27.5	0.63	136
HS-43	43.4	0.66	147
HS-48	48.0	0.71	158
HS-62	62.2	0.77	164
HS-66	66.0	0.70	170
HS-71	71.4	0.65	173
HS-81	80.6	0.88	175
HS-87	86.9	0.73	177
PHS-1	100.0	0.18	163
PHS-2	100.0	1.44	198
PS	0.0	0.70	100

[a] Intrinsic viscosities measured at 25 °C in tetrahydrofuran solution.

Table II
Compositions and Glass Transition Temperatures of Poly(*n*-butyl acrylate-*co*-*tert*-butyl acrylate)[a]

sample	compositn of nBA, mol %	[η], dL/g	T_g, °C
BA-8	8.0	0.67	27
BA-39	38.7	0.84	16
BA-42	42.1	0.77	5
BA-51	50.8	0.69	−7
BA-54	54.3	0.72	−16
BA-57	56.3	0.73	−25
BA-61	61.2	0.66	−32
BA-64	64.0	0.53	−34
BA-69	68.8	0.75	−35
BA-70	70.0	0.60	−40
BA-80	80.1	0.72	−41
PnBA	100.0	0.20	−42
PtBA	0.0	0.34	30

[a] Intrinsic viscosities measured at 25 °C in tetrahydrofuran solution.

(d) Poly(*n*-butyl acrylate-*co*-*tert*-butyl acrylate). The copolymers were synthesized by copolymerization of the two monomers with 1% AIBN at 45 °C. They were purified by precipitation from 2-butanone solution into methanol, followed by drying in vacuo at 60 °C for 3 days. The compositions of the copolymers were determined from ^1H NMR spectra, which showed resonances at 0.91 (methyl group of nBA) and 1.45 ppm (methyl group of tBA) and broad peaks near 1.55 (aliphatic backbone and $-CH_2CH_2-$ group of nBA) and 4.06 ppm ($-OCH_2-$ of nBA). The monomer reactivity ratios of this pair were not determined in this study since polymerization proceeded rapidly to ~40% conversion. (The copolymer composition and the feed composition, however, did not appear to be widely disparate.) The acrylate copolymers are designated as BA, with the numeral following the symbol representing the approximate mole percent of *n*-butyl acrylate. Their intrinsic viscosities and T_g values are listed in Table II. Again, we did not carry out GPC measurement for each copolymer. The M_n and M_w values for BA54 are 5.3×10^5 and 6.8×10^5, respectively.

(e) Preparation of Blend Films. Films were cast from THF solutions and dried in a vacuum oven at 60 °C for 3 days. For infrared studies, thin films were cast onto potassium bromide windows and dried by the same procedure.

2. **Infrared Spectroscopy.** Fourier transform infrared spectroscopy measurements were made with the use of a Digilab FTS-60 FTIR spectrometer. A total of 60 scans at a resolution of 2 cm^{-1} were signal-averaged and stored on a disk. The frequency scale was calibrated with a reference helium–neon laser

Table III
Glass Transition Temperatures of Blends of Poly(4-hydroxystyrene) with Poly(*n*-butyl acrylate-*co*-*tert*-butyl acrylate) and Hydrogen-Bonding Interactions[a]

copolym	T_g, °C exptl		T_g, °C wt av	A_b/A_T, at 60 °C
BA-8	32	163		0.04
BA-39	18	153		0.04
BA-42	8	152		0.06
BA-51	2	154		0.10
BA-54	-9	157		0.12
BA-61	-13	144		0.11
BA-64	149		65	0.28
BA-69	159		64	0.25
BA-70	155		62	0.27
BA-80	126		61	0.31
PnBA	123		61	0.37

[a] Blend composition is 50/50 by weight in each sample.

to an accuracy of 0.2 cm^{-1}. The temperature of the sample chamber was controlled to ±1 °C. Infrared spectra were recorded at 20 °C intervals after the preselected temperature was maintained for 3 min. The area of the hydrogen-bonded carbonyl peak, at 1708 cm^{-1}, was determined by subtraction from the total carbonyl absorption, by the use of Digilab Quant 32 program. The uncertainty in the calculated fraction of bonded carbonyl groups was estimated to be ±0.02–0.03.

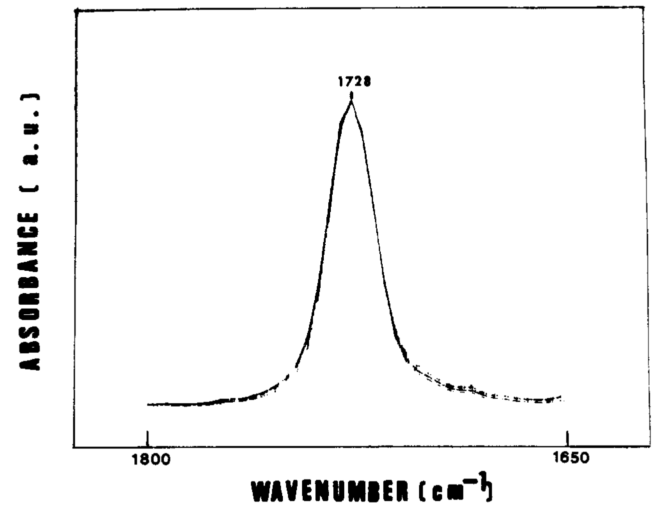
3. **Thermal Analysis.** A Du Pont 1090 thermal analyzer equipped with a differential scanning calorimeter (Model 1090) was used for the determination of glass transition temperatures. The sample size was between 10 and 15 mg. Each sample was heated from room temperature to 200 °C at a heating rate of 10 °C/min and maintained at 200 °C for 5 min. It was then quenched to -100 °C and reheated at 20 °C/min. The glass transition temperature (T_g) was taken as the midpoint of the specific heat jump observed in the second scan. The accuracy of T_g determined was ±1 °C.

4. **Intrinsic Viscosity.** All intrinsic viscosity measurements were carried out at 25 °C in tetrahydrofuran using a Ubbelohde viscometer.

Results

1. **Homopolymer Blends.** Among the four homopolymers, polystyrene (A), poly(4-hydroxystyrene) (B), poly(*n*-butyl acrylate) (C), and poly(*tert*-butyl acrylate) (D), only the BC pair forms miscible blends. The other five blends are immiscible, and each blend shows two distinct T_g's characteristic of the values for the component polymers respectively.

2. **Copolymer Blends.** The compositions and T_g values of the two sets of copolymers, one from styrene/4-hydroxystyrene and the other from *n*-butyl acrylate/*tert*-butyl acrylate, are listed in Tables I and II. When the acrylate copolymers were blended with poly(4-hydroxystyrene), only the ones containing 64% or more of *n*-butyl acrylate were miscible with PHS-1 (Table III). The infrared spectra of the immiscible blends in the carbonyl absorption region consisted of primarily the absorption due to "free" carbonyl groups at 1728 cm^{-1}. The absorption at 1708 cm^{-1}, assigned to carbonyl groups hydrogen bonded to the hydroxy groups of PHS-1, had low intensity in each of the immiscible blends, but the intensities were much higher in miscible blends (Figure 1). The absorption of the bonded carbonyl groups decreased in intensity in the miscible blends at high temperatures as the hydrogen bond underwent extensive dissociation but was still discernable even at 200 °C. The fraction of bonded carbonyl groups, expressed as the ratio of the area of the 1708-cm^{-1} peak to the total absorption, A_b/A_T, was given for each blend in Table III. It is seen that there is a large increase in the bonded fraction from 0.11 for the immiscible BA-61 blend to 0.28 for the miscible BA-64 blend.



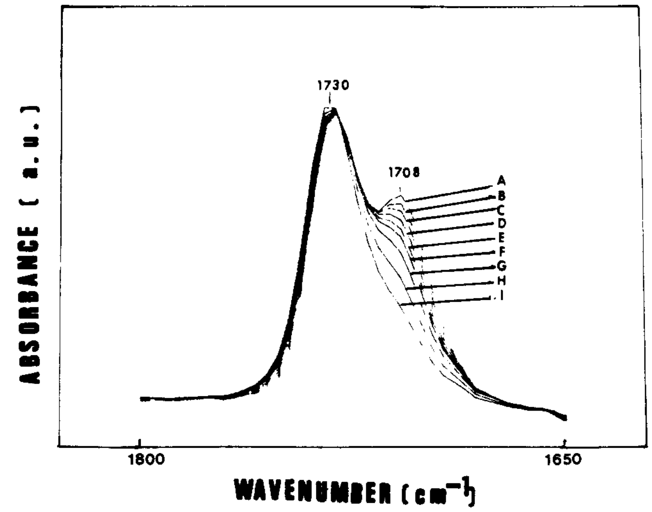


Figure 1. FTIR spectra in the carbonyl absorption region for, top, a 50/50 immiscible blend of PtBA with PHS-1, at 40–200 °C and, bottom, a 50/50 miscible blend of BA-80 with PHS-1 at 40 (curve A) to 200 °C (curve I) at 20 °C intervals. Absorbance in arbitrary units.

Although neither polystyrene nor poly(4-hydroxystyrene) was miscible with poly(*tert*-butyl acrylate), a miscibility window was found for the styrene copolymers and PtBA. Copolymers containing 22 mol % or less 4-hydroxystyrene units exhibited two T_g's in their blends with PtBA. When the amount of 4-hydroxystyrene was 71 mol % or higher, the blends also had two T_g's. Copolymers having intermediate compositions, however, were miscible with PtBA (Table IV). The FTIR spectra of representative miscible blends are shown in Figure 2. The calculated A_b/A_T values were about 0.15 in miscible blends but were much smaller in magnitude, about 0.02–0.03, in immiscible blends (Table IV).

The bonded carbonyl fractions were determined at different temperatures for a typical immiscible blend and three miscible blends of HS-28. The bonded fraction for the immiscible blend of PtBA and HS-8 had the same value of about 0.03 from 40 to 180 °C (Figure 3). For each of the three miscible blends of HS-28 the A_b/A_T value was higher at 40 °C and remained at that value until about 100 °C. The bonded fraction decreased at

Table IV
Glass Transition Temperatures of Blends of Poly(*tert*-butyl acrylate) with Poly(styrene-*co*-4-hydroxystyrene) and Hydrogen-Bonding Interactions[a]

copolym	T_g, °C exptl		T_g, °C wt av	A_b/A_T, at 60 °C
HS-8	57	111		0.02
HS-11	57	113		0.02
HS-15	53	111		0.03
HS-22	55	119		0.03
HS-28	132		83	0.15
HS-43	140		88	0.16
HS-48	156		94	0.16
HS-66	152		100	0.16
HS-71	57	175		0.02
HS-81	55	172		0.02
HS-87	50	155		0.02

[a] Blend composition is 50/50 by weight in each sample.

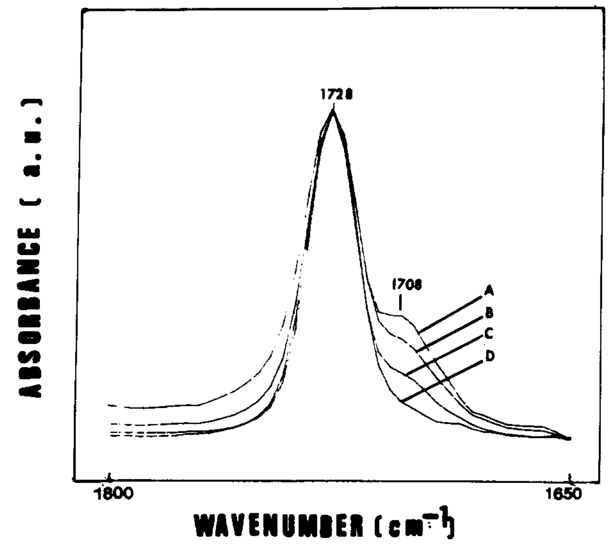


Figure 2. FTIR spectrum in the carbonyl absorption region for miscible blend of PtBA with HS-48 at 40 °C. Curves: A, 75/25 by weight; B, 50/50; C, 25/75; D, PtBA.

temperatures above the T_g of the blend, as was observed in other miscible blends having hydrogen-bonding interactions.[11,16] The change in the slope of each curve occurred at ~115 °C, close to the T_g of the blend. These results lend support to the identification of the miscible region.

Discussion

1. Glass Transition Temperatures of Copolymer Blends. Each of the immiscible blends of PSH-1 and acrylate copolymers showed two glass transition temperatures (Table III). One transition occurred at a temperature 2–5 °C higher than the T_g of the copolymer, while the other occurred at a temperature 6–19 °C lower than the T_g of PHS-1. The locations of the two transition temperatures suggest the coexistence in the blend of a polyacrylate-rich phase and a poly(4-hydroxystyrene)-rich phase. The four miscible blends all had T_g values much higher than the calculated weight averages. The differences were 62–74 °C. Deviation of the same magnitude was noticed for the miscible blend of PHS-1 and PnBA. Large positive deviations of T_g's from the weight-average values were also found in several other blends in which hydrogen-bonding interaction was operative.[13,17]

As mentioned above, copolymers of styrene with 4-hydroxystyrene are miscible with PtBA only when the content of 4-hydroxystyrene lies between 28 and 66 mol %. Copolymers having compositions outside this range are immiscible with PtBA. Of the immiscible blends, each shows two glass transition temperatures, one located at 55 ± 2 °C and the other at a temperature very nearly the same as the T_g of the copolymer. (The only exception is the HS-87 blend, which has lower T_g values.) The T_g at 55 °C, when compared to the value of 30 °C for PtBA, can be assigned to a PtBA-rich phase. The high-temperature T_g, which corresponds very closely to the values for the copolymer, is, at first thought, suggestive of a phase containing essentially only the copolymer. However, this conclusion may be unwarranted in view of the unusual T_g characteristics of the miscible blends. In Figure 4, the glass transition temperatures of blends of PtBA/HS-28 and PtBA/HS-43 are shown as a function of blend composition. It is seen that in both sets of blends the glass transition temperatures of the blends change very little with composition as long as the copolymer content is larger than 25%. Hence, it is not possible to deduce from the two T_g values of an immiscible blend the approximate composition of each phase. The unusually high T_g values for the miscible blends of PtBA/HS copolymers and PHS/butyl acrylate copolymers constitute a convincing manifestation of the effect of hydrogen-bonding interaction on physical properties.

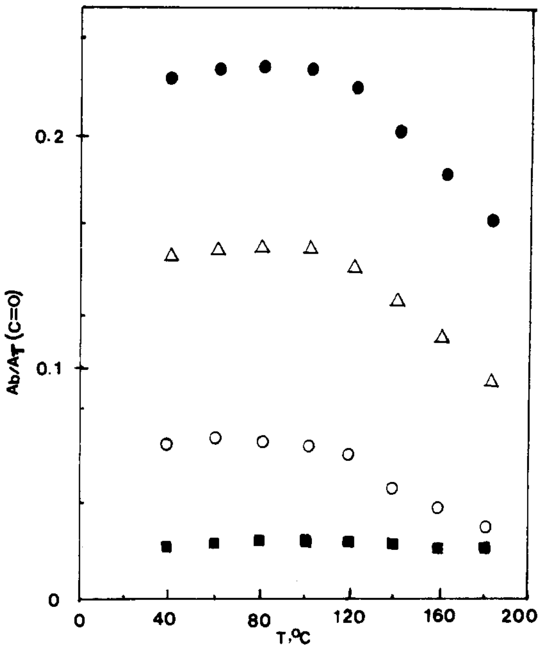


Figure 3. Fractions of bonded carbonyl groups, expressed as A_b/A_T, for a 50/50 immiscible blend of PtBA and HS-81 (■) and for miscible blends of PtBA with HS-28: (○) 25/75, (△) 50/50, and (●) 75/25.

2. Phase Behaviors. The miscibility of copolymers has been analyzed by several research groups with the use of a mean-field theory mentioned above. For binary mixtures of homopolymer B with copolymer C_yD_{1-y}, the expression for the free energy of mixing is given by eq 1, in which three interaction parameters are involved. In

$$\Delta G/RT = (\phi_1/m_1)\ln\phi_1 + (\phi_2/m_2)\ln\phi_2 + \phi_1\phi_2[y\chi_{BC} + (1-y)\chi_{BD} - y(1-y)\chi_{CD}] \quad (1)$$

eq 1, m_1 and m_2 are the degrees of polymerization of the two polymers and ϕ_1 and ϕ_2 their volume fractions in the blend, respectively. When eq 1 is used to analyze the miscibility of PHS-1 (B) with copolymers of *n*-butyl acrylate (C) and *tert*-butyl acrylate (D), it is recognized that χ_{BC} is negative while χ_{BD} and χ_{CD} are both positive. The magnitude of χ_{CD} can be estimated from the

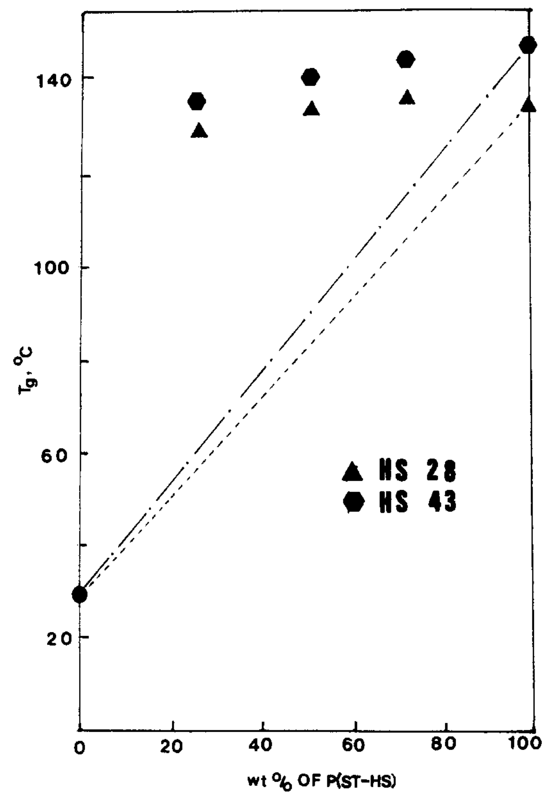


Figure 4. Glass transition temperatures of miscible blends of PtBA with HS-28 (▲) and HS-43 (●).

solubility parameters of the two acrylate polymers, using Hoy's group contribution factor,[18] to be 0.07. The critical value of y for miscibility is 0.64 from our experimental data. By inserting these values and m_1, m_2, ϕ_1, and ϕ_2 into eq 1, it becomes apparent that the absolute magnitude of χ_{BD} is larger than that of χ_{BC}. If we further assume that χ_{BC} is -0.1, then $\chi_{BD} = 0.24$.

The miscibility data for poly(*tert*-butyl acrylate) (D) and copolymer $A_{1-x}B_x$, where A stands for styrene and B for 4-hydroxystyrene, can be analyzed in a similar manner. The miscibility window indicates two critical values of x, 0.28 and 0.66. If one of the three interaction parameters in eq 1 is known, the other two can be calculated from two simultaneous equations of eq 1, using the two critical values of x. For example, if χ_{AD} is estimated from the solubility parameters of polystyrene and poly(*tert*-butyl acrylate) to be 0.086, then $\chi_{AB} = 0.45$ and $\chi_{BD} = 0.11$. Therefore it is clear that $\chi_{AB} > \chi_{AD}$ or χ_{BD}. We believe that these results offer confirmation of the repulsion force between comonomer units as being a significant factor in copolymer miscibility, in addition to hydrogen-bonding interaction, which is present in the blends.

In the above calculation, the contribution of hydrogen-bonding interaction was not dealt with separately but was included in the χ parameter. A method to account for hydrogen-bonding interaction in an explicit manner was given by Painter and Coleman.[19-22] The free energy, ΔG_H, of hydrogen-bonding interaction was evaluated separately and added to eq 1. Recently, they have extended their calculation to blends of poly(styrene-*co*-4-hydroxystyrene) with poly(alkyl methacrylates).[23] The calculated results agreed very well with experimental data.[9] The method used by these authors has two important advantages: (1) because ΔG_H is calculated separately, the component of χ, which is exclusive of hydrogen bonding, can be estimated from appropriate solubility parameters, and (2) the temperature dependence of hydrogen bonding interaction can be predicted through the ΔG_H term. By using Painter and Coleman's method with χ_{AB} estimated from solubility parameters, we obtained the following χ values, which predicted critical copolymer compositions in good agreement with experimental data, $\chi_{AB} = 0.68$, $\chi_{AD} = 0.25$, and $\chi_{BD} = 0.54$.

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Registry No. 4-hydroxystyrene (homopolymer), 24979-70-2; (*n*-butyl acrylate)(*tert*-butyl acrylate) (copolymer), 110215-28-6; *tert*-butyl acrylate (homopolymer), 25232-27-3; (styrene)(4-hydroxystyrene) copolymer), 24979-74-6.

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