Binary and Ternary Blends of Polystyrene-*block*-Poly(*p*-hydroxystyrene)

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ABSTRACT: Binary and ternary blends of polystyrene-*block*-poly(*p*-hydroxystyrene) (MW = 1×10^4−1×10^4) with various homopolymers were studied. In binary blends, in which the homopolymers poly(ethylene oxide) (PEO), poly(*p*-vinylpyridine) (PVPy), and poly(*n*-butyl acrylate) (P*n*BA) had attractive interactions via hydrogen-bonding with the poly(*p*-hydroxystyrene) block but were immiscible with the polystyrene block, microphase separation played a dominant role in morphology development. The attractive interaction parameter appeared to be the major factor that influenced the phase separation mechanism. The results obtained with three different molecular weights of PEO suggested that the molecular weight effect was not important when the attractive interaction parameter was sufficiently strong. In PVPy/copolymer blends, microphase separation was also prevalent, but phase separation in P*n*BA/copolymer blends seemed to follow the macro−micro mechanism. In blends of the diblock copolymer with poly(vinyl methyl ether), which was miscible with both blocks, the latter acted as a polymeric solvent for the copolymer and gave a single-phase mixture when present in sufficient amount. The addition of the block copolymer reduced the domain size in PS/poly(ethyloxazoline) blends. In PS/poly(methyl methacrylate) and PS/poly(*n*-butyl methacrylate) blends, the morphology changed to a cocontinuous pattern upon incorporation of the copolymer.

Introduction

In recent years, there has been a growing interest in blends of an $\alpha\beta$ diblock copolymer with a homopolymer C[1−3] that has a chemical structure different from either block but has attractive interaction with one of them, e.g., β. The microphase vs macrophase relationships in such blends have been analyzed theoretically and compared with morphological observations in a number of publications, including a recent paper by Hellmann et al.[1] In their paper, the morphological features of blends A/$\alpha\beta$ and C/$\alpha\beta$ of a polymer A or C with a diblock copolymer $\alpha\beta$ were analyzed, where A was chemically identical to α while C was immiscible with α but had an attractive interaction with β. The phase relationship was predicted and schematically expressed as in Figure 1. Five steps were suggested from the initially homogeneous state (normally in a nonselective solvent) to the three possible states, i.e., microphase separation, macrophase separation, and macromicrophase separation.

Calculations of microscale and macroscale fluctuations in the still homogeneous solutions were carried out to predict blend morphologies at the onset of initial demixing as the solvent evaporated.[1] In A/$\alpha\beta$ blends, for which the weight fraction of the block copolymer is defined by f, a transition concentration f^* divides the composition scale into a range $f > f^*$, where microscale fluctuations are dominant and microphases (A + α) + β prevail, and a range $f < f^*$ where macroscale fluctuations dominate and result in macrophase formation, A + ($\alpha + \beta$). The concentration f^* varies with the chain volume ratio, λ, of the homopolymer to the diblock copolymer. These conclusions agree with the earlier theoretical predictions, which are supported by a large body of experimental data.[4,5] In $\alpha\beta$/C blends, fluctuations depend not only on f and λ but also on the magnitude of the attraction interaction ξ ($\xi < 0$) between C and β, compared to the repulsive interactions χ ($\chi > 0$) between C and α as well as between α and β. There is a critical interaction parameter ξ^* below which (more negative ξ values) microphase separation should prevail. However, secondary segregation processes may produce effects not predicted by the model.

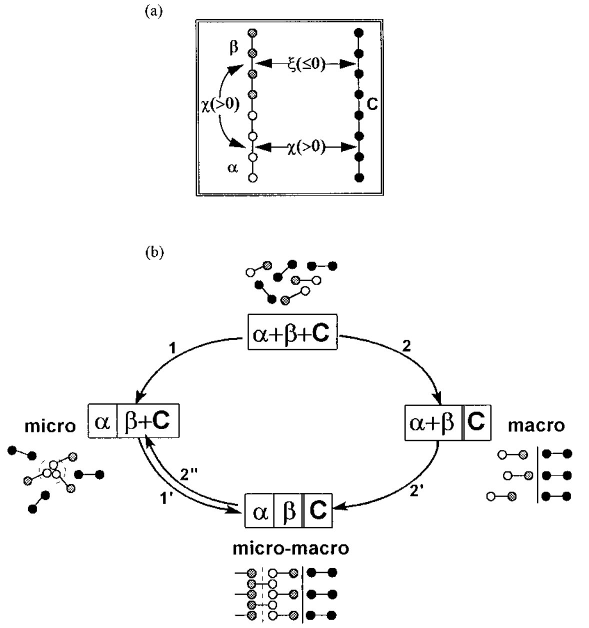

Figure 1. Schematic expression of microphase vs macrophase relationship of block copolymer ($\alpha\beta$)/homopolymer C blends: (a) interaction parameters χ and ξ, phase separation processes; (b) "+" indicating miscibility and vertical bar immiscibility.[1]

The objective of this research is to synthesize a suitable $\alpha\beta$ diblock copolymer so that its miscibility with a variety of homopolymers can be studied. The block copolymer of our choice is polystyrene-*block*-poly(*p*-hydroxystyrene) having equal block lengths of 1×10^4, which we have synthesized previously.[6] Poly(*p*-hydroxystyrene) (PHOST), the β block, is known to be miscible with at least a dozen different polymers via hydrogen-bonding interaction.[7−15] Therefore, the effect of the strength of attractive interaction between β and

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C on phase behavior can be studied by using the same diblock copolymer with a number of different homopolymers. The homopolymers so chosen were poly(*p*-vinylpyridine) (PVPy),[10] poly(ethylene oxide) (PEO),[11] and poly(*n*-butyl acrylate) (P*n*BA),[12] all of which were immiscible with polystyrene (PS) but miscible with PHOST. The strength of attractive interaction with PHOST decreases in the order, PVPy > PEO > P*n*BA, according to the heating of mixing of model compounds measured by Machado.[16] Furthermore, the glass transitions of PEO and P*n*BA are located at temperatures substantially lower than those of PHOST and PS, so that microphase or macrophase formation can be readily deduced from T_g changes. In the case of PVPy, the synergistic T_g effect of the PHOST−PVPy pair also made possible the unequivocal identification of phases.

Another type of homopolymer that is miscible with both blocks has also been included in the present study. Poly(vinyl methyl ether) (PVME), known to be miscible with both PS[17] and PHOST,[7] was chosen to investigate the possibility that it could act as a "nonselective polymer solvent" for the two blocks. After the results of binary blends were compared with theory, the study was extended to ternary blends with the expectation that the diblock copolymer would act as a compatibilizer for homopolymers A and C.[18−22] Preliminary results are also reported in this paper.

The primary tool used in our study was the measurement of glass transition temperatures of the phases. Although the method has its limitation, it will be seen in the following that useful information can be obtained for the systems chosen.

Experimental Section

Materials. Polystyrene-*block*-poly(*p*-hydroxystyrene) (PS-*b*-PHOST) with a molecular weight of $1 \times 10^4 - 1 \times 10^4$ was synthesized by living anionic polymerization of styrene and *p*-[(*tert*-butyldimethylsilyl)oxy]styrene followed by removing the *tert*-butyldimethylsilyl group.[6] The block copolymer showed two glass transition temperatures at 104 and 169 °C, determined by differential scanning calorimetry (DSC), corresponding to the T_g's of polystyrene and poly(*p*-hydroxystyrene) blocks, respectively.

Poly(*p*-hydroxystyrene) (PHOST) was synthesized by anionic polymerization of *p*-[(*tert*-butyldimethylsilyl)oxy]styrene with *sec*-butyllithium as initiator in THF at −78 °C, followed by removing the *tert*-butyldimethylsilyl group. The polymer ($M_n = 1 \times 10^4$) has a narrow molecular weight distribution ($M_w/M_n = 1.10$) from GPC. The glass transition of the polymer was 179 °C (DSC).

Polystyrene (PS) with molecular weights of 2.5×10^3 (designated as LPS), 5×10^3, and 5×10^4 were monodisperse polymers from Aldrich Inc. The glass transition temperature of LPS (MW = 2.5×10^4) was determined by calorimetry to be 66 °C (DSC).

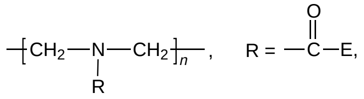
Poly(ethylene oxide) (PEO) with three different reported molecular weights of 1540, 1.8×10^4, and 1×10^5 were purchased from Polyscience Inc.

Poly(vinylpyridine) (PVPy) was synthesized by bulk free radical polymerization of vinylpyridine. The molecular weight was determined by viscometry[23] in ethanol at 25 °C to be about 1×10^5. The glass transition temperature of the polymer was 155 °C (DSC).

Poly(*n*-butyl acrylate) (P*n*BA) from Polyscience Inc., obtained as a 20% solution in toluene, was purified by precipitation of the solution into a large amount of methanol and then dried in a vacuum oven at 60 °C for 72 h. The molecular weight was determined by GPC as $M_w = 1.1 \times 10^5$ and $M_n = 8 \times 10^4$, using PS calibration. The glass transition temperature of the polymer was −50 °C (DSC).

Poly(vinyl methyl ether) (PVME) from Aldrich Inc. was obtained as a 50% water solution with a reported molecular weight of 1.8×10^4. The polymer was purified by precipitation of a methanol/H_2O solution into a large amount of *n*-hexane and dried under vacuum at 50 °C for 72 h. The glass transition temperature of the polymer was −30 °C (DSC).

Poly(ethyloxazoline) (PEOx)



$$-\!\!\left[\mathrm{CH_2}-\underset{\mathrm{R}}{\underset{|}{\mathrm{N}}}-\mathrm{CH_2}\right]_n\!\!-, \qquad \mathrm{R} = -\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{E},$$

from Dow Chemical Co. with a reported molecular weight of 5×10^4 was purified by filtration of a methylene chloride solution prior to precipitation into a large amount of *n*-hexane and dried under vacuum at 60 °C for 72 h.

Poly(butyl methacrylate) (PBMA) with a reported molecular weight of 5.0×10^4 was purchased from Aldrich Inc.

Poly(methyl methacrylate) (PMMA) from Polyscience Inc. was a monodisperse sample with a molecular weight of 5.0×10^3.

Preparation of Blend Films. Solutions (2%) of all the polymers except PEO were prepared in THF. A 2:1 mixture of THF and chloroform was used for PEO solutions. Blends of various compositions were prepared by mixing appropriate amounts of these solutions. Films of polymer blends for DSC studies and optical microscopy measurements were obtained by casting the blend solutions onto glass slides. For FTIR measurements, thin films were cast from solutions onto potassium bromide windows at room temperature. Solvents were removed slowly by evaporation at room temperature, and the films were dried in a vacuum oven at 70 °C for 72 h.

Determination of Glass Transition Temperature. A TA 2920 modulated differential scanning calorimeter (MDSC) was used for the determination of glass transition temperature.[24,25] The measurements were carried out under N_2 at a heating rate of 5 °C/min with a temperature oscillation of ±1 °C/min. Glass transition temperatures were determined in the reversing heat flow. The sample size was about 10 mg. Each sample was first scanned from a low initial temperature to 180 °C, maintained at that temperature for 0.5 min, and then slowly cooled back to the initial temperature and scanned again to 220 °C. T_g's were taken as the midpoints of the specific heat jumps observed in the second scan. The T_g values were reproducible to ±1 °C.

Infrared Spectroscopy. Fourier transform infrared spectroscopy measurements were recorded on a Perkin-Elmer 1600 FTIR spectrometer using a total of 64 scans at a resolution of 2 cm^{-1} in a N_2 atmosphere. All films were sufficiently thin to be within the absorbance range where the Beer−Lambert law was expected to be obeyed.

Optical Microscopy. Morphological observations of the ca. 10 μm film samples by optical microscopy were carried out with the use of a Nikon Optiphot microscope equipped with a Sony CCD-IRIS color video camera. The images were processed by the Global Lab Image program. Observations were made at 40× and 10× magnifications.

Results and Discussion

1. Blends of Polystyrene-*block*-poly(*p*-hydroxystyrene) with Low Molecular Weight Polystyrene.

Since T_g measurements were used in this study to identify phases, it was important to verify first that the measurement was indeed capable of providing information about micro- or macrophases in agreement with literature results. Therefore, the diblock copolymer was blended with a low molecular weight polystyrene (LPS, MW = 2500), similar to the ones used by Roe[26] or by Hashimoto[27] in their studies of phase relationships in block copolymer/homopolymer blends. The solubilization of LPS in the polystyrene microphases was well documented by these authors. Swelling of the PS microphase by LPS in PS-*b*-PHOST/LPS blends therefore should result in changes in the T_g's of the microphases from which the compositions of the swollen phases can be estimated.

Table 1. Glass Transition Temperatures (°C) of Polystyrene-*b*-poly(*p*-hydroxystyrene) (αβ) and Low Molecular Weight Polystyrene (A) Blends

f^a	PS		PHOST block
1.0	$104_{(\alpha)}$		$169_{(\beta)}$
0.8	$89_{(A+\alpha)}$		$169_{(\beta)}$
0.6	$78_{(A+\alpha)}$		$165_{(\beta)}$
0.4	71		$161_{(\beta)}$
0.2	$70_{(A+\text{disordered }\alpha\beta)}$	$86_{(\alpha+A)}$	$161_{(\beta)}$
0	$66_{(A)}$		

[a] *f* denotes the weight fraction of the block copolymer in the blend.

However, before the above line of reasoning for the analysis of experimental data can be applied, a comment about the T_g of the PS microphase, which was determined to be 104 °C, is in order. The value 104 °C was higher than that measured for a styrene homopolymer of the same molecular weight, namely, 96 °C. Both values were reproducible; and DSC experiments conducted in a standard mode without imposed temperature oscillation also gave the same results. Furthermore, the value 96 °C for a monodisperse PS standard agreed with literature reports. The T_g value of 104 °C for the PS microphase was in variance with the results of Krause on polystyrene-*b*-poly(dimethylsiloxane), a glass–rubber copolymer, which showed a T_g lower than expected for the PS phase.[28] Our first instinct was that phase separation was incomplete under the experimental conditions; as a result, the PS block was contaminated with some high-T_g segments. While phase mixing cannot be ruled out, the elevation of the T_g of the PS block from 96 to 104 °C would require the incorporation of 12% (by weight) HOST units in the PS domain according to the Fox equation, which seemed excessive because the interaction parameter between styrene and hydroxystyrene units was at least 1.5 per styrene unit, calculated from the heat of mixing of model compounds.[7,16] In the following, we offer an alternative explanation. In the free volume theory of glass transition, the free volume of a homopolymer chain can be considered as consisting of contributions from the two end groups and from the internal bonds. The relative contribution of the two end groups to the total free volume is significant when the molecular weight of the chain is low. (This explains the well-known dependence of T_g on molecular weight.) In our block copolymer, one end of the PS chain is anchored to the high-T_g PHOST block and loses its mobility normally associated with end groups. The deprivation of the free volume contribution of one of the end groups would therefore raise the T_g of the PS phase. This immobilization was often used to explain the high T_g of mineral-filled polymers. By the same reasoning, the linkage of one end of the PHOST chain to a "soft" PS phase at temperatures above 110 °C may conceivably result in an increase in the free volume contribution of that end and hence a lowering of the T_g of the PHOST phase. This is indeed what we have observed. The T_g of 169 °C for the PHOST phase is to be compared with the value of 179 °C for the homopolymer having the same molecular weight. This explanation also rationalizes Krause's findings, because the PS block was linked to a soft phase.

The T_g data of the cast films determined from the second scans are summarized in Table 1. Two clear T_g's were seen for the $f = 0.8$ blend, one at 89 °C and the other at 169 °C. The upper T_g was readily identified with the poly(*p*-hydroxystyrene) block while the lower one, located between the T_g values of the PS block and the LPS homopolymer, was obviously associated with a mixed phase of A and α. The 60% copolymer blend also showed two T_g's at 78 and 165 °C, which could be assigned respectively as before to a mixed (A + α) phase and a PHOST phase. The T_g of the mixed phase was lowered further to 74 °C in the $f = 0.4$ blend and the upper T_g was lowered to 161 °C. For the $f = 0.2$ blend, the thermogram revealed, in addition to the two transitions at 70 and 161 °C, a small third transition at 86 °C. Since the specific heat increment accompanying the third transition at 86 °C was small, the sample was annealed at 85 °C for 15 min in hopes that the transition might become sharper. This was indeed the case, but the specific heat increment was still less than 10% of the total for all three transitions, suggesting the presence of only a minor amount of the material (Figure 2).

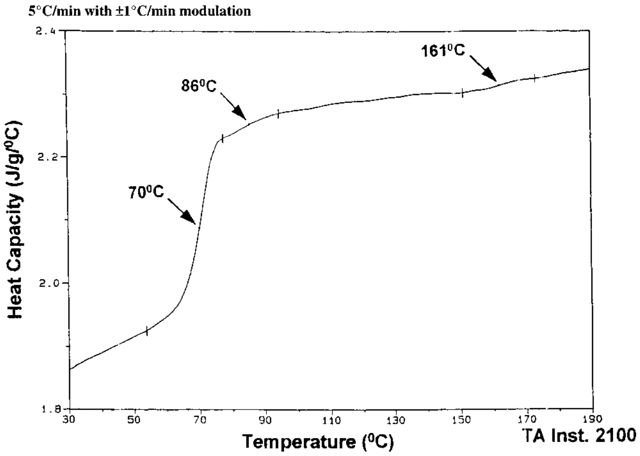


Figure 2. DSC thermogram of PS-*b*-PHOST/LPS blend at $f = 0.2$.

According to theoretical predictions and the experimental results of Roe[26] and Hashimoto,[27] LPS is expected to be completely absorbed into the PS block at $f = 0.8$. If this is the case, the T_g of the (A + α) phase can be estimated with the use of the Fox equation,

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \tag{1}$$

where W is the weight fraction of the component in the mixed phase and subscripts 1 and 2 denote A and α, respectively. The T_g value of 104 °C is used here for the PS block and 66 °C for LPS. The calculated value of 90 °C is in excellent agreement with the experimental value of 89 °C. For the $f = 0.6$ blend, the calculated T_g of 81 °C is to be compared with the experimental result of 78 °C. For blends containing larger amounts of LPS, morphological changes to cylindrical or spherical domains are likely to occur and simple calculations as the ones given above may no longer be appropriate.[27]

Now let us return to the question of the small third transition of $f = 0.2$ blend. The thermogram of the blend is shown in Figure 2. The glass transition of the PHOST (β) block is located at 161 °C and has a heat capacity change $\Delta C_p \cong 0.02$ (J/g)/°C. From the reported ΔC_p of 0.42 (J/g)/°C for PHOST,[29] the amount of PHOST in this phase is certainly less than 10%. Apparently, a substantial amount of PHOST is not accounted for in this phase. The major transition at 70 °C is obviously related to LPS and has a $\Delta C_p \cong 0.255$ (J/g)/°C. The amount of material in this phase is more than 80%, since the ΔC_p of PS has been reported to be ~0.30 (J/g)/°C.[30] The excess material is believed to come from disordered block copolymer "dissolved" in the LPS

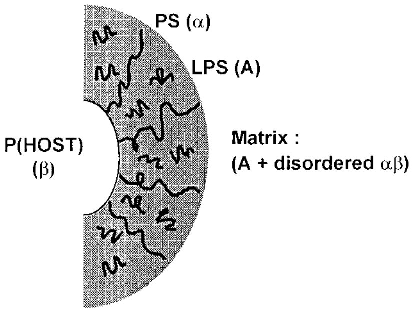


Figure 3. Schematic diagrams of micellar aggregation for the PS-*b*-PHOST/LPS blend at $f = 0.2$.

Table 2. Compositions of Micellar Structure of PS-*b*-PHOST/LPS (20/80) Blend

	composition (wt %)				T_g (°C)	
	total	LPS	PS	PHOST	expt	calc
core (high T_g phase)	7	0	0	7	161	
matrix (A + disordered $\alpha\beta$)	83.5	77.5	3	3	70	70
corona (interphase)	9.5	2.5	7	0	86	87

Table 3. Glass Transition Temperatures of Polystyrene-*b*-poly(*p*-hydroxystyrene) ($\alpha\beta$) and Poly(ethylene oxide) (C) Blends ($f = 0.8$)

	MW	T_{g_1} (°C)	T_{g_2} (°C)
PEO1	1540	$95_{(\alpha)}$	$46_{(\beta+C)}$
PEO2	1.8×10^4	$95_{(\alpha)}$	$53_{(\beta+C)}$
PEO3	1×10^5	$90_{(\alpha)}$	$50_{(\beta+C)}$

matrix. This would account for the “lost” PHOST in the 161 °C transition. According to the studies of Roe,[26] Hashimoto,[27] and Hellmann,[1] the morphology of the blend in this composition range is expected to be micellar or spherical. We adopt their interpretation and assign the small transition at 86 °C as arising from the material in the corona in which some LPS is mixed with the PS block (Figure 3). The amount of the material is estimated to be ~10%, from a simple consideration of material balance. We then proceed to estimate the compositions of the matrix (LPS + disordered block copolymer) and of the corona (PS + LPS) that would be consistent with the overall material balance and with their respective T_g values. The T_g of each phase was calculated with the use of the Fox equation, and the results are given in Table 2. The matrix is estimated to contain about 93% LPS and 7% disordered block copolymer in which the corona is composed of about 74% styrene block and 26% LPS.

Although the $f = 0.4$ blend showed two clear glass transitions, annealing at 85 °C produced a faint third transition at ~90 °C. The ΔC_p associated with this transition, however, is too small to justify an estimate of the amount and composition of the corona. The morphology in this blend is without doubt more complicated than a simple two-phase system, in view of Roe’s findings.

We then attempted to compare the calculated solubility of LPS in the corona with theoretical predictions. The thermodynamic model by Paul,[31] for examining the extent to which free chains (component B, LPS) can be solubilized into a “brush” of grafted chains (component A, α block) forming the corona, appears to be particularly suited to our situation and is briefly described below. The chemical potential of the free chain is given by

$$\frac{\Delta\mu_B}{RT} = \frac{B_{AB}}{RT}(1-\phi_B)^2 + \frac{\rho_B}{M_B}(1-\phi_B+\ln\phi_B) + \frac{\rho_A}{M_A}\left(\frac{L_0}{R_0}\right)^2\frac{1}{(1-\phi_B)} - \frac{\rho_B}{M_B}\left(\ln K - \phi_B\frac{\partial \ln K}{\partial \ln x}\right) \quad (2)$$

where

$$x = \frac{R_g}{\alpha} = \frac{R_g}{(L/2)} = \frac{2\phi_A R_g}{L_0} \quad (3)$$

$$K = \frac{8}{\pi^2}\sum_{m=0}^{\infty}(2m+1)^{-2}\exp\left\{-(2m+1)\left(\frac{\pi^2}{4}\right)\left(\frac{2\phi_A R_g}{L_0}\right)\right\} \quad (4)$$

In the equations, B_{AB} is the interaction energy density, which is zero in the present case, L_0 is the corona thickness, R_0 is the perpendicular unperturbed end-to-end distance of a single graft chain (α), R_g is the radius of gyration of the penetrating polymer (LPS), ρ is the density, and ϕ the volume fraction. The saturation of the corona with the homopolymer corresponds to the condition $\Delta\mu_B = 0$. Although there was no assurance that the condition was met under the experimental conditions, we nevertheless thought the calculation to be instructive. Since R^2 and L^2 scale with molecular weight, their ratio can be readily calculated. For the PS-*b*-PHOST/LPS (20/80) blend, the corona becomes saturated with the homopolymer at $(\phi_B)_s = 0.22$ (LPS fraction of 0.22) which compares favorably with the estimated ϕ_B value of 0.26 from Table 2.

2. Diblock Copolymer/Poly(ethylene oxide) Blends. Poly(ethylene oxide) (PEO) was miscible with poly(*p*-hydroxystyrene) (PHOST) where the hydrogen bonding interaction between the phenol groups of PHOST and the ether groups of PEO had been documented.[11] Blends of the block copolymer with PEO are examples of $\alpha\beta$/C systems for which the ξ parameter is negative and large in magnitude.

Three different PEO samples having molecular weights of 1540, 1.8×10^4, and 1×10^5, respectively, were used to examine the effect of molecular weight. Only one blend composition, $f = 0.8$, was studied because high molecular weight PEO underwent crystallization in PEO-rich blends. The T_g of the PEO samples were all below −70 °C. (The detection of the T_g of the 1×10^5 molecular weight sample was handicapped by the high crystallinity of the material, but literature values were −70 to −60 °C.) The blend films were clear, but two T_g’s were observed for each blend (Table 3). The T_g at about 95 °C was that of the PS microphase and was insensitive to PEO molecular weight. The second T_g, near 50 °C, was associated with the PHOST microphase swollen with PEO. The microphase morphology $\alpha + (\beta + C)$ deduced from T_g data is in full agreement with predictions for strong β/C interactions, regardless of molecular weight.

The infrared spectra in the hydroxyl stretching region are shown for the block polymer and its blends (Figure 4). The spectra of the block copolymer, and of PHOST, showed shoulders at 3525 cm^{-1}, ascribed in the literature to the stretching vibration of the dimeric OH group, and a large broad peak centered at 3350 cm^{-1}, attributable to “self-associated” hydroxyl groups.[7] The 3350 cm^{-1} absorption overlaps the absorption of the hydroxyl end group of PEO, and shifts in this region are not useful as an indicator for a phenol−ether interaction. However, the 3525 cm^{-1} peak diminished in intensity

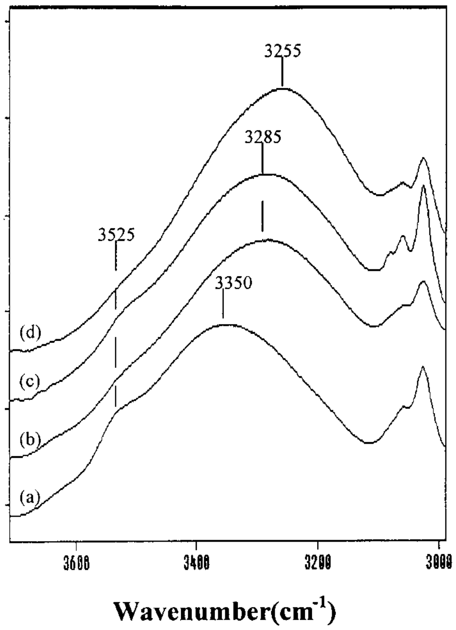


Figure 4. FTIR spectra of 80/20 ($f = 0.8$) PS-*b*-PHOST/PEO blends in the hydroxyl streching vibration region: (a) pure copolymer; (b) PEO3 (MW = 1×10^5); (c) PEO2 (MW = 1.8×10^4); (d) PEO1 (MW = 1540).

Table 4. Glass Transition Temperatures of Polystyrene-*b*-poly(*p*-hydroxystyrene) (αβ) and Poly(*p*-vinylpyridine) (C) Blends

f	T_{g_1}(°C)	T_{g_2}(°C)
1	$104_{(\alpha)}$	$169_{(\beta)}$
0.8	$99_{(\alpha)}$	$192_{(\beta+C)}$
0.6	$97_{(\alpha)}$	$186_{(\beta+C)}$
0.5	$97_{(\alpha)}$	$181_{(\beta+C)}$
0.4	$97_{(\alpha)}$	$175_{(\beta+C)}$
0.2	$100_{(\alpha)}$	$159_{(\beta+C)}$
0		$155_{(C)}$

and could hardly be seen in the blends. Thus, all three PEO samples had achieved high degrees of intimate mixing with the PHOST block via hydrogen bonding.

3. Diblock Copolymer/Poly(vinylpyridine) Blends. Poly(vinylpyridine)[10] (PVPy, MW = 1×10^5) has also been reported to be miscible with PHOST, and the glass transition temperatures of such blends are synergistic. The pyridine moiety is a stronger hydrogen bond acceptor than the ether group,[16,32] and the interaction parameter ξ should be more negative. Blend films cast from THF were clear.

The synergistic glass transition temperature data (Table 4 and Figure 5) are similar to those reported for homopolymer blends of PVPy and PHOST[10] and appear to confirm the dominance of microphase separation in the *entire* composition range, in agreement with Hellmann's predication for a chain length ratio λ of 5 and a very negative ξ. However, one would think that swelling of the β phase by PVPy must eventually induce morphological changes and the dissolution of some disordered block copolymer in PVPy. Thus the phase assignment for the $f = 0.2$ blend may be questionable. Nonetheless, there is little doubt that PHOST and PVPy segments are intimately mixed in all cases.

4. Diblock Copolymer/Poly(*n*-butyl acrylate) Blends. Poly(*n*-butyl acrylate) (P*n*BA) having a MW of 5×10^4 was reported to be miscible with PHOST.[12] The ester group is a weaker hydrogen bond acceptor than the pyridine or the ether group[16] and thus provides a case for examining the effect of a less negative ξ on phase behavior. A P*n*BA sample having a molecular weight of 1.1×10^5 was used because the λ value of about 6 was close to the λ value of 5 used in theoretical calculations. Three T_g's were observed for each composition (Table 5), which could be assigned respectively to the PS block (α), PHOST block (β), and a third phase that, judged by its T_g, must contain P*n*BA and disordered copolymer, that is, (C + αβ). The T_g of the mixed phase decreased progressively toward the value for pure P*n*BA as the copolymer content in the blend decreased; i.e., the mixed phase became richer in P*n*BA.

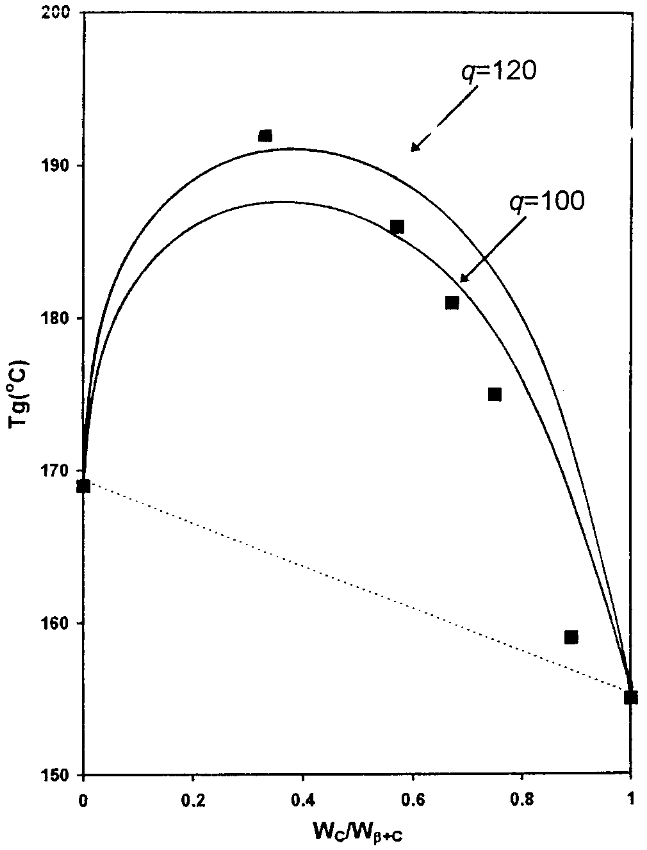


Figure 5. Glass transition temperture behaviors of the (β + C) main phase in PS-*b*-PHOST/PVPy blends, β and C representing HOST and VPy, respectively. The two curves are drawn in accordance with the equation by Kwei,[37] $T_g = W_1T_{g1} + W_2T_{g2} + qW_1W_2$ with q values of 100 and 120.

Table 5. Glass Transition Temperatures of Polystyrene-*b*-poly(*p*-hydroxystyrene) (αβ) and Poly(*n*-butyl acrylate) (C) Blends

f	T_{g_1}(°C)	T_{g_2}(°C)	T_{g_3}(°C)
1.0	$104_{(\alpha)}$	$169_{(\beta)}$	
0.8	$101_{(\alpha)}$	$165_{(\beta)}$	$16_{(C+\beta)}$
0.6	$91_{(\alpha)}$	$162_{(\beta)}$	$-19_{(C+\beta)}$
0.5	$87_{(\alpha)}$	$165_{(\beta)}$	$-32_{(C+\beta)}$
0.4	$87_{(\alpha)}$	$164_{(\beta)}$	$-40_{(C+\beta)}$
0.2	$96_{(\alpha)}$	$164_{(\beta)}$	$-36_{(C+\beta)}$
0			$-50_{(C)}$

The existence of a third phase composed largely of P*n*BA conforms to Hellmann's prediction of macrophase separation for weak βC interactions followed by microphase separation of the block copolymer. The opacity of the cast films also supports this interpretation. However, the continuous change of T_g of the macrophase with blend composition is more difficult to understand. Whether the inclusion of the block copolymer in P*n*BA is a result of incomplete phase segregation due to kinetic reasons or solubility of the block copolymer in P*n*BA, or both, cannot be ascertained at present, but we are inclined to regard kinetic considerations as a significant

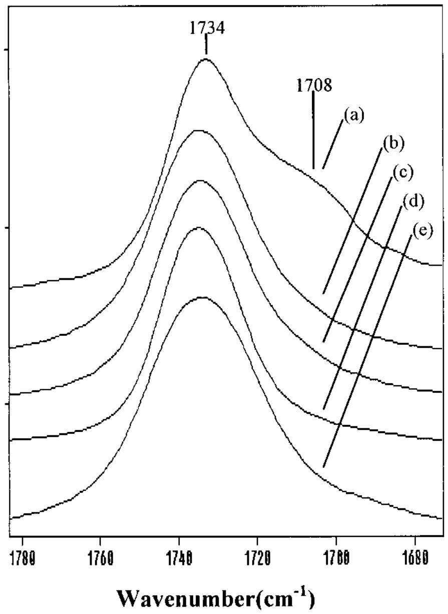


Figure 6. FTIR spectra of PS-*b*-PHOST/P*n*BA blends in the carbonyl stretching vibration region: (a) $f = 0.8$; (b) $f = 0.6$; (c) $f = 0.4$; (d) $f = 0.2$; (e) PnBA.

factor in view of the larger variation of the compositions of the macrophases.

The FTIR spectra of the blends (Figure 6) in the carbonyl stretching region were also examined. The carbonyl group of P*n*BA absorbs strongly at 1734 cm^{-1}. In blends of poly(methacrylates) and poly(acrylates) with PHOST, the peak for the bonded carbonyl[7,12] usually appeared at around 1720−1710 cm^{-1}. When P*n*BA was present in a small amount, the absorption by the bonded carbonyl was seen as a shoulder at 1708 cm^{-1}. With decreasing copolymer content in the blend, the shoulder became very weak and was identifiable only by the curve subtraction method for $f = 0.6$ and $f = 0.4$. The infrared results are consistent with the conclusion from T_g measurements that only small amounts of PHOST are present in the mixed phases at small f values.

5. Blends of the Diblock Copolymer with Poly(vinyl methyl ether). Poly(vinyl methyl ether) (PVME) is known to be miscible with both PS[16] and PHOST.[8] Hence the blends were classified as αβ/D to differentiate them from those already described. The purpose of the present investigation was to explore the possibility of PVME acting as a common solvent for both blocks.

All the solution-cast films were clear. For the 90% copolymer blend, two T_g's were observed, at 100 and 133 °C, respectively (Figure 7 and Table 6). Since PVME was miscible with both blocks, it was expected that it could dissolve in both microphases and lower their respective glass transition temperatures. The T_g results for the $f = 0.9$ blends, however, indicated a clear preference for the phenol−PVME interaction while hardly any PVME was incorporated into the PS domain. When the PVME content was increased to 20% in the blend, only a single but broad endothermic event with a large ΔC_p was detected between 80 and 100 °C. It is believed that the T_g of the swollen PHOST microphase has, by coincidence, dropped to the same temperature range as that of the PS microphase and the two transitions could not be resolved. The explanation seems to have merit because two T_g's were again observed in the $f = 0.7$ blend at 90 and 61 °C, and in the $f = 0.6$ blend at 85 and 46 °C, respectively. Although it is not possible to ascertain the identities of the microphases responsible for the two T_g's in the $f = 0.7$ and $f = 0.6$ blends, the 61 and 46 °C data seem to belong to the group of data associated with the PHOST microphases whereas 90 and 85 °C seem to belong to the group associated with the PS microphases if a plot of the T_g values against blend compositions is made. By comparing the T_g results with those of PS−PVME homopolymer blends, the PVME content in the PS microphase was estimated to be about 15% in the $f = 0.6$ blend;[33] a material balance calculation then gave the weight percent of PVME in the PHOST phase as 53%. If the T_g assignments for this blend is reversed, that is, 46 °C for the T_g of the (PS + PVME) phase instead of 85 °C, the PVME content would be 25% in the PS microphase and, by difference, 50% in the PHOST microphase.

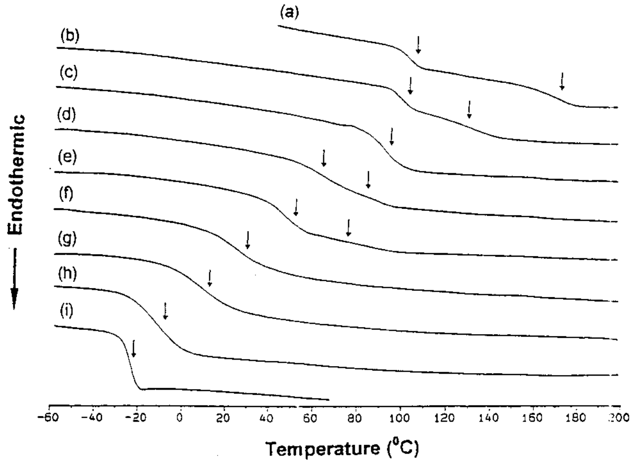


Figure 7. DSC thermgrams of PS-*b*-PHOST/PVME blends: (a) PS-*b*-PHOST; (b) $f = 0.9$; (c) $f = 0.8$; (d) $f = 0.7$; (e) $f = 0.6$; (f) $f = 0.5$; (g) $f = 0.4$; (h) $f = 0.2$; (i) PVME.

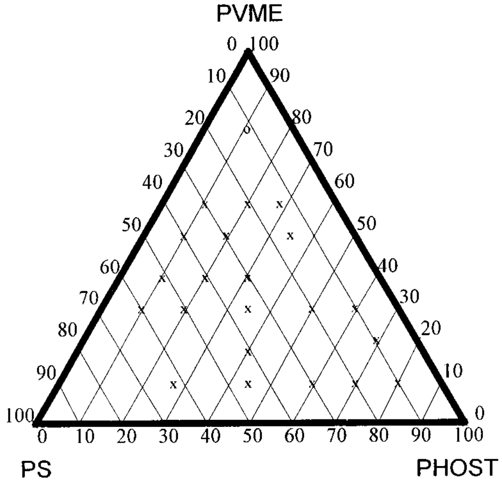


Figure 8. Experimental phase diagram of PS/PHOST/PVME blends, (x) indicating immiscibility and (o) miscibility.

Table 6. Characteristics of Polystyrene-*b*-poly(*p*-hydroxystyrene) (αβ) and Poly(vinyl methyl ether) (D) Blends

f	film appearance	T_g (°C)		
1.0		$104_{(\alpha)}$		$169_{(\beta)}$
0.9	clear	$100_{(\alpha)}$		$133_{(\beta+D)}$
0.8	clear		$92_{(overlap)}$	
0.7	clear	$90_{(\alpha+D)}$		$61_{(\beta+D)}$
0.6	clear	$85_{(\alpha+D)}$		$46_{(\beta+D)}$
0.5	clear		$25_{(\alpha+\beta+D)}$	
0.4	clear		$8_{(\alpha+\beta+D)}$	
0.2	clear		$-12_{(\alpha+\beta+D)}$	
0			$-30_{(D)}$	

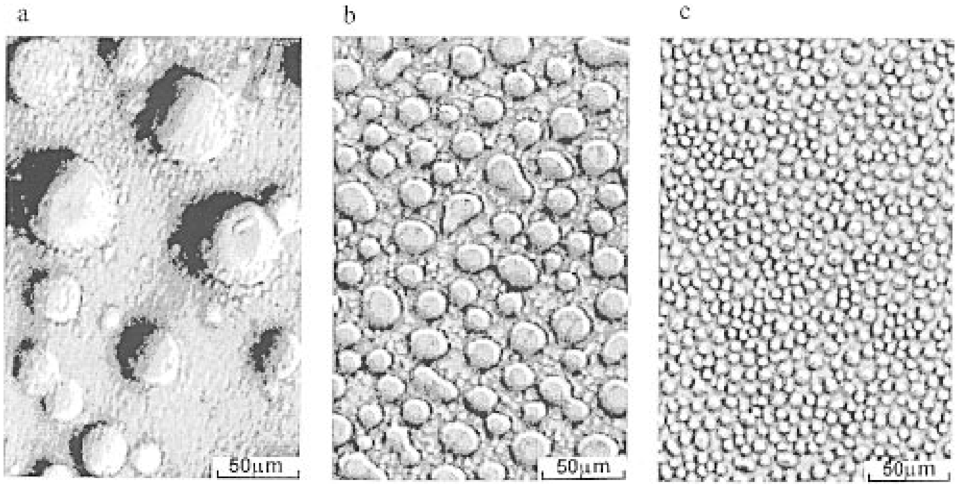


Figure 9. Optical micrographs of 50/50 PS/PEOx (MW = $5 \times 10^4/5 \times 10^4$) blends: (a) without PS-*b*-PHOST; (b) with 5% copolymer; (c) with 10% copolymer.

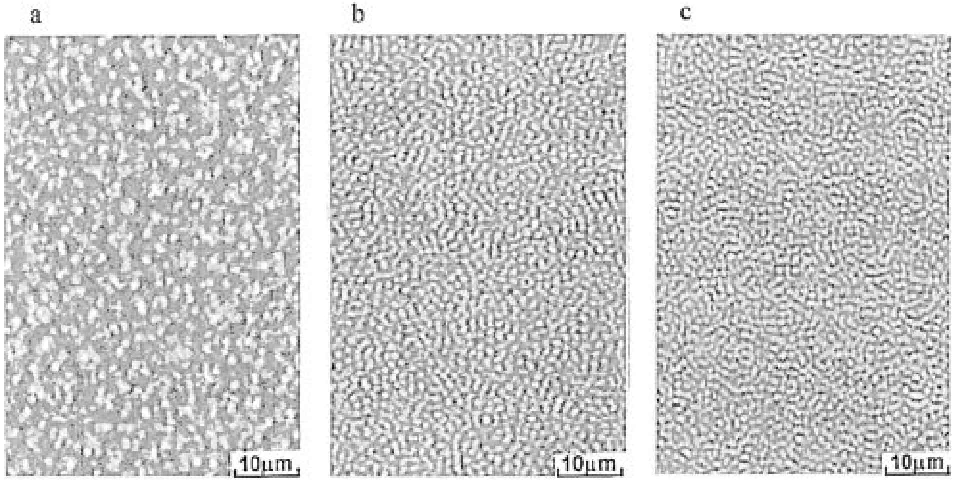


Figure 10. Optical micrographs of 50/50 PS/PMMA (MW = $5 \times 10^3/5 \times 10^3$) blends: (a) without PS-*b*-PHOST; (b) with 5% copolymer; (c) with 10% copolymer.

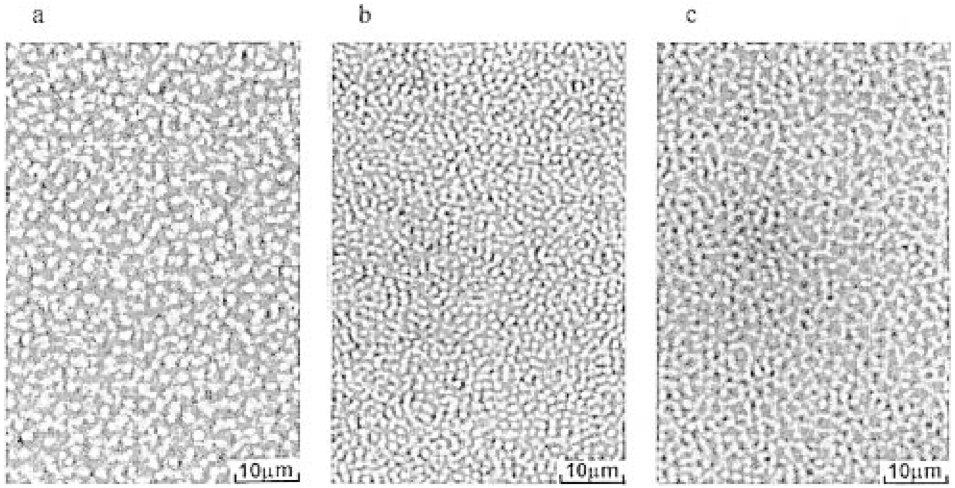


Figure 11. Optical micrographs of 50/50 PS/PBMA (MW = $5 \times 10^4/5 \times 10^4$) blends: (a) without PS-*b*-PHOST; (b) with 5% copolymer; (c) with 10% copolymer.

When the amount of PVME was increased to 50%, a single T_g was observed at 25 °C. The T_g of the $f = 0.4$ blend was located at 8 °C, and that of the $f = 0.2$ blend, at −12 °C. Since it is unlikely that the two swollen microphases in each of the three blends have coincidentally the same T_g, the single T_g's are construed by us as an indication of a single ($\alpha + \beta + D$) phase in each case. If the interpretation is correct, the results demonstrate the ability of PVME to act as a common solvent (or in a sense, a compatibilizer) for the two blocks when present in sufficient amounts.

The T_g results in Table 6 afford an interesting comparison with the miscibility of ternary mixtures of PS, PHOST, and PVME homopolymers. For the homopolymer mixtures, the cast films were transparent only when the mixtures contained 80% or more PVME. We attempted to estimate the interaction parameter between PS and PHOST by applying Scott's equation[34] to the ternary phase diagram (Figure 8). The interaction parameter between PVME and PS, χ_{S-VME}, has been reported to be a small negative number, about -0.04.[35] From the Painter−Coleman association method,[7] the interaction parameter between PVME and PHOST was calculated to be -2.5 for the 50/50 composition, by using an equilibrium constant of 88.6 for the ether−phenol interaction. It then becomes necessary to use a very large positive value of χ_{S-HOST} of about 10 to reproduce the experimental ternary phase diagram. The seemingly unreasonable χ value discouraged us from undertaking additional calculations, but we note in passing that large positive χ values have been used by Iruin and co-workers[36] to fit their miscibility results.

6. Ternary Blends. Based on the results obtained for binary blends, preliminary morphological experiments on ternary blends, A/$\alpha\beta$/C, in which A was polystyrene (PS) and C was poly(ethyloxazoline) (PEOx),[13] poly(methyl methacrylate) (PMMA),[14] or poly(*n*-butyl methacrylate) (PBMA)[15] were carried out. The three C polymers were selected because of their known miscibility with PHOST. The optical micrographs are shown in Figures 9−11. The addition of 5% block copolymer to a 1:1 PS−PEOx blend caused a notable reduction in the size of the spherical domains; the domain size was further decreased when 10% block copolymer was added. In PS−PMMA and PS−PBMA blends, the morphology changed from discrete domains to a cocontinuous pattern upon the incorporation of the copolymer (Figures 10 and 11). These preliminary observations on the development of cocontinuous structures call for additional work in this area.

Conclusion

Although T_g measurements had limitations in the study of micro−macro phase transitions in block copolymer blends, they can provide useful information in selected systems.

In $\alpha\beta$/C blends, in which the homopolymers PEO and PVPy have strong attractive interactions via hydrogen bonding with the β block but are immiscible with the α block, microphase separation was the dominant mechanism. The attractive interaction parameter ξ appeared to be the major factor that influenced phase separation. The results obtained with three different molecular weights of PEO (1540, 1.8×10^4, and 1×10^5) suggest that the molecular weight effect is unimportant when ξ is sufficiently negative. In PVPy blends, the microphase separation mechanism dominated whereas phase separation in P*n*BA/copolymer blends seemed to follow the macro−micro mechanism.

Poly(vinyl methyl ether), known to be miscible with both PS and P(HOST), dissolved preferentially in the PHOST block when the PVME content was low. When the amount of PVME was increased to 50% or higher, it acted as a common solvent for the two blocks to arrive at a single phase. Ternary blends of PS, PHOST, and PVME homopolymers are transparent only at a PVME content of at least 80%.

The block copolymer reduced the domain size in PS/PEOx blends. In PS/PMMA and PS/PBMA blends, the morphology was changed to a cocontinuous pattern upon the incorporation of the copolymer.

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