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Phase Behavior of Copolymer Blends

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It is generally believed that dissimilar polymers are miscible only if there is a net favorable interaction between them leading to a negative enthalpic contribution to the free energy of mixing. Phase separation of miscible blends at elevated temperatures, i.e., the lower critical solution temperature (LCST) behavior, is caused by a decrease in the magnitude of the favorable interaction to the point that it is overcome by the equation of state or free volume contribution, as the latter is always positive and increases with increasing temperature.[1-3] The LCST behavior has been observed in numerous miscible blends.

The upper consolute point (UCST) is a much less common occurrence. McMaster[4] has predicted in his calculation that a blend with a small positive exchange interaction parameter and a very small free volume term can exhibit both LCST and UCST behaviors. The two consolute points may merge to result in an hourglass-shaped phase diagram sometimes seen in polymer–solvent mixtures. The UCST behavior, however, is rare and only four cases have been reported, by Schmitt,[5] by Inoue,[6] by Ueda and Karasz,[7] and by Cong et al.[8] We wish to report in this paper hourglass-shaped cloud-point curves for a blend containing two copolymers.

The polymers used in this study were methyl methacrylate–styrene copolymers and phenol formaldehyde resins in which the hydroxyl groups had been partially methylated. In previous studies,[9,10] we found that the phenol formaldehyde resin (PHMP) was completely miscible with poly(methyl methacrylate). Extensive hydrogen bonding took place between the hydroxyl groups of PHMP and the carbonyl groups of PMMA. The favorable interaction prevailed even at high temperatures so that lower consolute points could not be detected below the decomposition temperatures of the component polymers. However, when the density of the hydrogen bond acceptors in the chain was reduced by using methyl methacrylate–styrene copolymers, LCST behavior was observed.[10] In the present study, the densities of donors and acceptors in the chains are both reduced.

The PHMP resin, with a number-average degree of polymerization of 8.8, contained methylene bridges exclusively at the ortho-ortho positions.[10,11] Methylation of the hydroxyl groups was performed by using sodium hydride and methyl iodide. The degree of methylation was determined by chemical analysis. Each sample was designated by a numeral followed by S-PHMP, with the numeral indicating the approximate percent of hydroxyl groups which had been methylated. The copolymers were designated by the symbol COP and the numeral following COP represented the weight percent MMA in each copolymer. The intrinsic viscosities of the copolymers were about 0.4 dL/g in toluene at 30 °C. Films of the blends were cast from methylene chloride/tetrahydrofuran mixture (90/10). The cast films were turbid and showed two T_g's. For example, the 80/20 blend of 50S-PHMP and COP50 had T_g's of about 60 and 100 °C. When these values are compared with the values of the 54 °C for 50S-PHMP and 105 °C for COP50, respectively, the low T_g phase can be said to be rich in 50S-PHMP and the high T_g phase rich in COP50.

Several different functional groups are involved in hydrogen bonding in these blends: (a) self-association of the hydroxyl groups, (b) bonding between the hydroxyl groups and the ether groups in S-PHMP, and (c) interpolymer bonding between the hydroxyl groups and carbonyl groups. Hence, the infrared spectra of solid films in the hydroxyl absorption region contained many broad, overlapping peaks unsuitable for analysis. But the data from model compounds served as useful guides of the relative strengths of hydrogen bonding among different species. From the FTIR spectra of phenol, 2,6-dimethylanisole (as model for 100% O-methylated PHMP), and ethyl acetate or *tert*-butyl acetate in dilute solutions of carbon tetrachloride, we identified the following absorption frequencies of the hydroxyl groups: 3606 cm^{-1} for free hydroxyl, 3342 cm^{-1} for self-associated hydroxyl, 3351 for hydroxyl group hydrogen bonded to the hindered ether group in dimethylanisole, and 3438–3449 cm^{-1} for hydroxyl group bonded to ester groups. On the basis of the enthalpy–frequency shift correlation[12] for hydrogen bonding of OH groups, it could be deduced that the strength of hydrogen bonding in the model compounds decreased in the order self association > bonding with ester group > bonding with 2,6-dimethylanisole. (The lesser strength of hydroxyl-anisole bonding is reflected in lower glass transition temperatures of the O-methylated PHMP's: 81 °C for PHMP, 54 °C for 50S-PHMP, and 16 °C for 100S-PHMP.)

Table I
Phase Behavior of O-Methylated PHMP and Poly(methyl methacrylate-*co*-styrene) Blends[a]

O-Me-PHMP	poly(MMA-*co*-St)	25 °C	170 °C	200 °C
20S-PHMP	PMMA	I	M	M
	COP60	I	M	M
	COP50	I	M	M
	COP40	I	I	I
50S-PHMP	PMMA	I	M	M
	COP60	I	M	M
	COP50	I	M	I
	COP40	I	I	I
80S-PHMP	PMMA	I	I	I
	COP60	I	I	I
	COP50	I	I	I
	COP40	I	I	I

[a] Blend composition 80/20: I = immiscible; M = miscible (single T_g).

The multitude of interactions among different functional groups led to complex phase behaviors which were summarized in Table I. As shown in the table, miscible regions were observed only when the hydrogen bond donor or acceptor groups were present in at least 50% of the segments in each polymer. The cloud points, determined by microscopy at a heating of 2 °C/min, are shown in Figure 1 for blends of 50S-PHMP with COP50 and COP60. When the weight percent of the copolymer is less than 50% in the blends, two phase transformation temperatures were detected for each blend, one at 125–145 °C and the other one at 190–210 °C. For blends containing 50–95% copolymers, heterogeneity persisted throughout the temperature range of our investigation. The phase boundary had the shape of a distorted hourglass.

We noted that the miscible region was larger for COP60 blends than for the COP50 blends; i.e., when the carbonyl content of the copolymer increased, miscibility was enhanced. This observation was supported by infrared results of a higher degree of intermolecular hydrogen bonding in COP60 blends, to be discussed in a later section. Photomicrographs (Figure 2) of blends in the miscible and immiscible regions showed that the domain size became larger when (a) the degree of O-methylation increased and (b) the amount of the copolymer increased in the blend.

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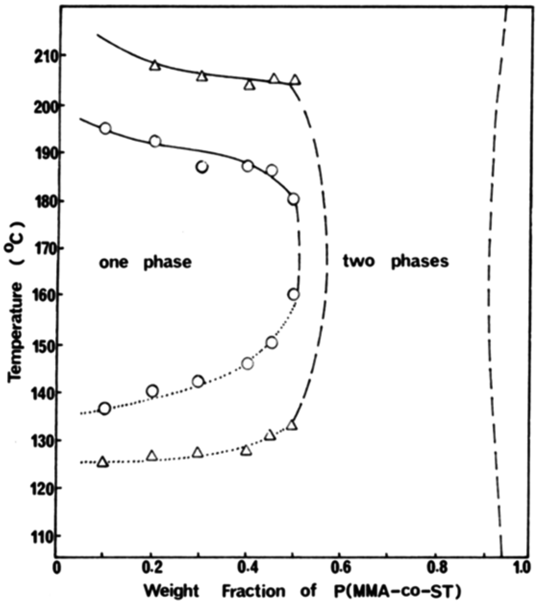

Figure 1. Cloud-point curves of blends of 50S-PHMP with COP50 and COP60. Broken lines on the right represent estimated boundary. Dotted lines represent UCST.

The LCST behavior was thermally reversible. But the UCST behavior was not. (The use of the terms LCST and UCST should be qualified here in that we have not actually identified the critical compositions.) Once a single phase was formed by heating to above 130 °C, it did not revert to the immiscible state by lowering the temperature to below the phase boundary. In this respect, our blends behaved differently from the other systems.[5-8] Several factors may contribute to the apparent irreversibility: (a) the nonequilibrium state of hydrogen bonding during film formation, (b) the $\Delta\chi$ effect,[13,14] and (c) kinetic restriction to phase transformation. The hydrogen bond competing solvents, CH_2Cl_2 and THF, could conceivably interfere with interpolymer interaction so that the blend was unable to maintain a single phase during the nonequilibrium film-forming process. The $\Delta\chi$ effect could also be responsible for heterogeneity. Last, the transformation from the miscible state to the heterogeneous state could be hindered for kinetic reasons. In order to ascertain whether kinetic considerations played a major role in thermal irreversibility, the single-phase material, after being cooled to 25 °C, was exposed to solvent vapors in the hope that the plasticizing effect of the solvent vapor might increase segment mobility and induce phase separation. When a solvent mixture of CH_2Cl_2 and THF was used, the single-phased films did undergo phase separation. But this experiment still could not differentiate the three possible causes. Therefore, a second experiment was carried out by using carbon tetrachloride as the solvent. Being nonpolar and a poor solvent for both polymers, CCl_4 vapor was expected to exert its influence primarily through the plasticizer effect. Indeed, the CCl_4 vapor treatment also resulted in phase separation. Once the single-phased material became heterogeneous by vapor treatment, drying and heating transformed it again into a single phase. The

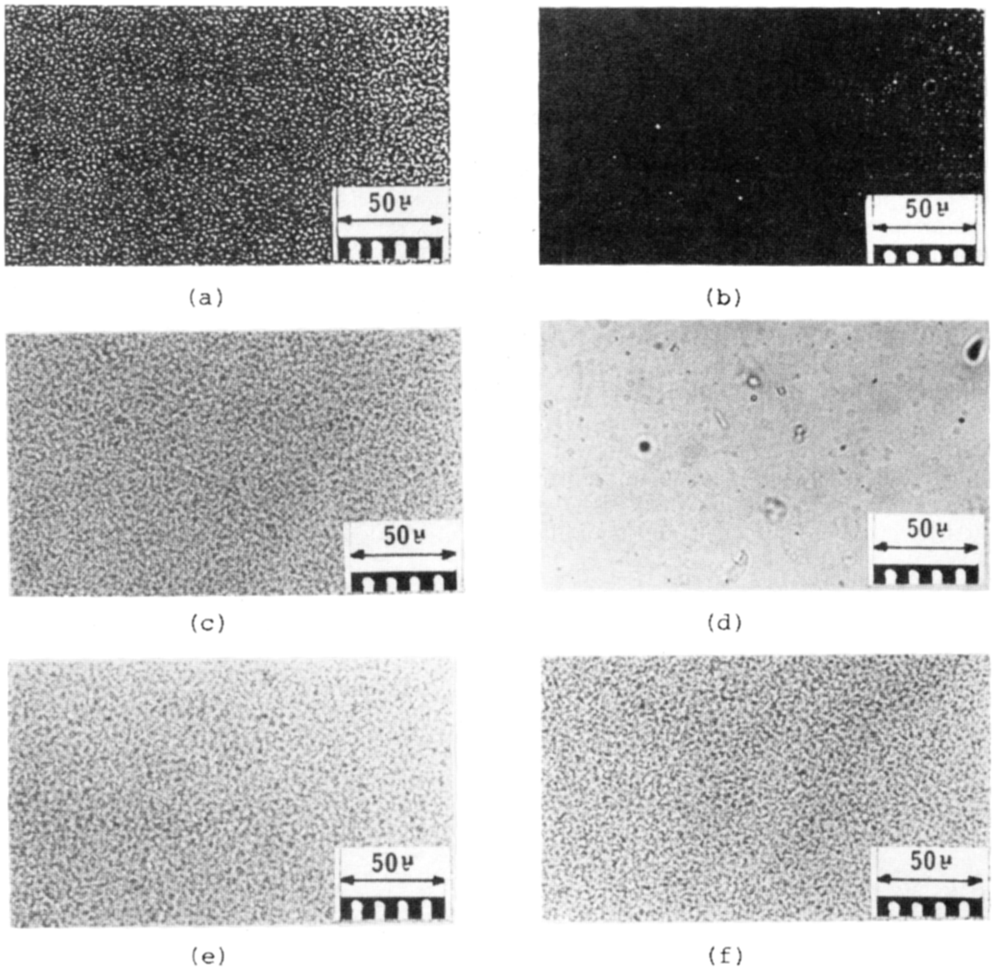

Figure 2. Photomicrographs of 50S-PHMP/COP blends: (a) 20% COP at 80 °C; (b) 20% at 180 °C; (c) 45% COP at 80 °C; (d) 45% COP at 180 °C; (e) 60% at 80 °C; (f) 60% at 180 °C. Photomicrographs were taken after each temperature was maintained for 10 min.

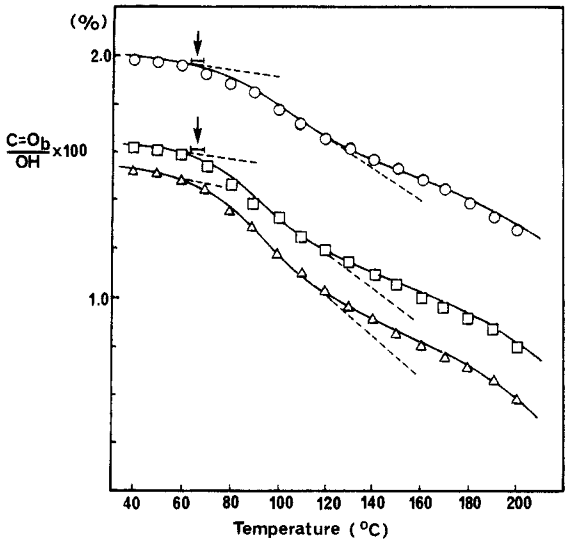

Figure 3. Percent hydrogen-bonded carbonyl group as a function of temperature. (○) 50S-PHMP/PMMA; (□) 50S-PHMP/COP60; (△) 50S-PHMP/COP50. Each sample contains 90% S-PHMP. Arrows indicate changes in the slopes of the curves.

phase transformation temperature coincided with the original UCST value. The process could be repeated many times. The CCl_4 experiment, while suggestive of kinetic restriction as one of the important factors, likewise cannot provide an unequivocal answer. Besides lowering the T_g, the presence of a third component will in itself change the phase diagram. In addition, it is not all clear why kinetic constraints persists at temperatures much higher than the T_g of the blend. At present, we are unable to offer a convincing explanation.

The extent of hydrogen bonding with the carbonyl group was expressed as the ratio of bonded carbonyl to the total hydroxyl concentration, $(C{=}O)_b/(OH)$. This ratio was used because the copolymers had different MMA contents and the amount of bonded carbonyl groups needed to be normalized in order to compare results from different samples.[10] Typical results for the copolymers were shown in Figure 3 in which the data for PMMA blends are also displayed. The ratio $(C{=}O)_b/(OH)$ decreased systematically when the MMA content of the polymer was reduced. A change in the slope of each curve occurred at about 70 °C, which was slightly higher than one of the two T_g's of the blends, 60 °C. The correspondence between the temperature of slope change and T_g was also observed in miscible blends.[9,10] The increase in the temperature coefficient of hydrogen bond dissociation above the T_g of a polymer was attributed to increased segment mobility, which allowed the rapid establishment of association–dissociation equilibrium.[9,10,15] The same explanation seems to be applicable to the low T_g phase in question, that is, the S-PHMP rich phase. A second change in the slope of the curve occurred near 120–130 °C, which coincided with the UCST and was about 20–30 °C above the T_g of the copolymer rich phase. A point worthy of note here was that the concentration of the bonded carbonyl decreased more slowly with temperature in the 120–180 °C range than in the 70–120 °C region. At temperatures above 180 °C, the LCST, there were indications that the $(C{=}O)_b/(OH)$ ratios for the two copolymer blends again decreased rapidly with temperature. The reason for the slower rate of decrease in $(C{=}O)_b/(OH)$ ratios in the miscible regions is not clearly understood. A possible contributing factor is that the two component polymers now reside in the *same* phase and the effective concentrations of the interacting groups in the miscible region are different from the values in the individual phase in the heterogeneous regions.

Lastly, Coleman[16] and co-workers have performed theoretical calculations of phase behaviors of hydrogen-bonded polymer blends and predicted hourglass phase diagrams for certain systems.

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Registry No. (MMA)(S) (copolymer), 25034-86-0.

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