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# Miscibility Control by Hydrogen Bonding in Polymer Blends and Interpenetrating Networks

**Hyung-Il Kim, Eli M. Pearce, and T. K. Kwei***

*Department of Chemistry and Department of Chemical Engineering, Polytechnic University, Brooklyn, New York 11201.* *Received September 26, 1988; Revised Manuscript Received January 13, 1989*

ABSTRACT: Interpenetrating polymer networks (IPNs) were synthesized from miscible blends of poly[(1-hydroxy-2,6-methylene)phenylene] and poly(methyl methacrylate) by using two types of cross-linking agents at different temperatures. The extent of hydrogen bonding in the blends and IPNs was controlled by changing the temperature of the cross-linking reaction and by reducing the density of the hydrogen bond acceptor groups in the chain, using copolymers of methyl methacrylate and styrene. Fourier transform infrared spectroscopy was employed to measure the extent of hydrogen bonding. A critical value of hydrogen bonding interaction was needed for miscibility to be maintained in these blends and IPNs.

## Introduction

The miscibility of dissimilar polymers is favored by exothermic intermolecular interactions. Of the many different types of interactions commonly encountered, hydrogen bonding has been the subject of many recent investigations[1-6] because the formation of hydrogen bonds lends itself in many cases to quantitative spectroscopic measurements, and a wealth of information in the literature on hydrogen bonding between small molecules can be used as guides for polymer studies. More recently, the theory of hydrogen bonding in polymer blends has been formulated so that thermodynamic quantities can be evaluated and phase diagrams calculated from these quantities.[7]

The aim of this research is to study the minimum amount of interpolymer hydrogen bonding needed to maintain a single phase. Our approach consists of varying the density of interacting groups in the chain, determining the fraction of hydrogen bonded groups, and correlating the extent of interaction to phase behavior.

A second objective of our investigation concerns hydrogen bonding in interpenetrating networks (IPNs) derived from miscible blends. Hydrogen bonding formation and dissociation in polymers are thermally reversible.[8] However, if the cross-linking reaction for IPN synthesis takes place at an elevated temperature at which a large proportion of hydrogen bonds have dissociated, it is conceivable that the restricted segment mobility in the network may hinder the full recovery of hydrogen bonds upon cooling. If the temperature is further increased to the point at which the remaining hydrogen bonds is no longer sufficient to maintain the blend as a single phase, it is an open question whether the network formed in the heterogeneous state is able to revert to the miscible state, upon cooling, through the reestablishment of hydrogen bonds. This aspect of IPN properties has been addressed, in part, by Coleman and co-workers.[9] It constitutes a primary element of our study.

To answer the above questions, we have chosen the pair poly(methyl methacrylate) (PMMA) and a phenol–formaldehyde resin, *o,o*-poly[(1-hydroxy-2,6-methylene)phenylene] (PHMP). The two polymers are miscible over the entire range of blend compositions, and spectroscopic evidence of hydrogen bonding between the hydroxyl group of PHMP and the carbonyl group of PMMA has already been reported.[8] The density of the hydrogen bond acceptors in the chain was varied by using a series of methyl methacrylate copolymers containing styrene units. Styrene was selected as the comonomer because the solubility parameter of polystyrene, 9.05, is very close to that of PMMA, 9.24. Consequently, the "copolymer" contribution to miscibility change[10] is expected to be small, and as a first approximation, the styrene segment in the copolymer can be considered as a diluent for the carbonyl group to reduce the number of available interaction sites.

## Experimental Section

**Materials.** (a) Poly[(1-hydroxy-2,6-methylene)phenylenes] (PHMP) were synthesized from phenol and formaldehyde at 165 °C in the presence of calcium hydroxide as catalyst.[11] The reaction condition results in highly specific ortho–ortho methylene linkages without noticeable amounts of side reactions,[12] as confirmed by infrared spectra and by chemical shifts in proton and carbon-13 NMR spectroscopy.

(b) Copolymers of methyl methacrylate and styrene were synthesized by radical polymerization at 70 °C, using azobis(isobutyronitrile) as initiator. The reaction was allowed to proceed to about 10% conversion, and the polymer was isolated and purified by precipitation from methyl ethyl ketone solution into hexane twice. The composition of the copolymer was determined by UV spectrophotometry, using the absorption at 262 nm for the styrene units. The 13 copolymers are designated as COP90 (83.5), 80 (79.2), 70 (72.2), 60 (60.7), 50 (48.9), 40 (37.2), 38 (36.3), 36 (35.6), 34 (34.3), 32 (31.7), 30 (30.4), 20 (16.9), and 10 (9.3), with the weight percent MMA indicated by the number in parentheses. The intrinsic viscosities of these copolymers were determined in toluene at 30 °C. The values increase systematically from 0.359 dL/g for COP90 to 0.516 for COP10. As points of reference, PMMA with an intrinsic viscosity of 0.327 has a viscosity-average molecular weight of 147 000, while PS with an intrinsic viscosity of 0.528 has a calculated molecular weight of 135 000. The 13 copolymers have similar $T_g$ values, about 100 °C.

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(c) Interpenetrating polymer networks: Two cross-linking agents, hexamethylenetetraamine (HMTA) and 1,3-dioxolane (DIOXO), were used to react with PHMP to form cross-linked networks. They were chosen because the reactivities of the two reagents were widely different. PHMP reacted with dioxolane at 60–70 °C, but the reaction with HMTA proceeded at an appreciable rate only at temperatures above 140 °C. In our procedure, PHMP was allowed to react with an equal amount of dioxolane containing 0.5 wt % of *p*-toluenesulfonic acid at 60–70 °C for 24 h in a closed mold, but the reaction with HMTA (4 wt %) took place at 180 °C for 2 h. These conditions were chosen because the resulting networks had similar chemical structures and physical properties.

We have also synthesized full IPNs by dissolving PHMP and HMTA (or DIOXO) in a mixture of methyl methacrylate and either ethylene glycol dimethacrylate or trimethylolpropane trimethacrylate. The hydrogen bonding characteristics of the full IPNs, however, are qualitatively similar to those found for semi-IPNs. Therefore, only the semi-IPN data will be reported in the paper.

(d) Sample preparation: All the blend samples were prepared by casting from a 2% solution of methylene chloride/tetrahydrofuran (90/10) and dried at 50 °C in a vacuum oven for 72 h. The same solvent mixture was used for HMTA cross-linked semi-IPN. When dioxolane was used, it served both as cross-linking agent and solvent for the ingredients.

**Infrared Spectroscopy.** In the preparation of specimens for infrared measurements, a thin film of the blend or IPN was coated on a reflective aluminum plate and dried or cross-linked. Infrared spectra were obtained with the use of a Digilab FTS60 FTIR spectrometer. The aluminum reflectance plate was mounted on a Wilks specular reflectance apparatus equipped with a cartridge heater, and spectra were obtained in an external reflectance absorption mode. Temperature was controlled to an accuracy of ±1 °C by using an Omega 4001 KC temperature controller. At least 64 scans were signal-averaged at a resolution of 2 $cm^{-1}$. Spectra in the region 1500–1900 $cm^{-1}$ were recorded at 20 °C intervals during heating and cooling cycles to monitor changes in the absorption of the carbonyl group. The area of the hydrogen bonded carbonyl peak was determined by subtraction, with the use of Digilab Quant 32 program.

**Glass Transition Temperature.** A differential scanning calorimeter, Perkin-Elmer 7, was used to determine the glass transition temperatures of the polymers. Samples were first heated to 160 °C and then quenched by dry ice. Thermograms were recorded at a heating rate of 10 °C/min. under nitrogen atmosphere. $T_g$ was taken as the extrapolated onset of the abrupt increase in the specific heat of the sample. (We chose not to use the midpoint of $C_p$ change because the temperature ranges of transitions were very broad, about 40 °C, for the semi-IPNs.) Each sample was scanned several times to ensure reproducibility. Results from duplicate or triplicate samples indicate an accuracy of ±1.2 °C for un-cross-linked polymers. The range of uncertainty is larger for cross-linked materials, about ±2 °C, due to the broad transitions.

**Dynamic Mechanical Properties.** The dynamic Young's modulus and loss tangent were measured with the use of a Du Pont 982 dynamic mechanical analyzer. Sample dimension were 25 mm × 10 mm × 1.2 mm. A heating rate of 5 °C/min was used.

**Microscopy.** Thermally induced phase separation was detected by monitoring the change in the intensity of the transmitted light through the sample under a microscope.[13] A heating rate of 2 °C/min was used throughout the experiments. Photomicrographs of phase-separated samples were recorded to examine their morphological features.

## Results and Discussion

**Characterization of PHMP.** $^{13}C$ NMR spectra provide pertinent information about the position of the methylene bridge in PHMP. The spectra of 2,2′-, 2,4′-, and 4,4′-dihydroxydiphenylmethanes showed distinct peaks for the individual methylene units at 31.0, 35.8, and 40.1 ppm, respectively.[14] In the NMR spectra of our PHMP, the chemical shifts of the methylene group occurring at 26–32 ppm are believed to indicate that ortho–ortho isomeric structures are present, to the virtual exclusion of ortho–para or para–para linkages. In the proton NMR spectra, the chemical shift for the methylene protons was observed at 3.89 ppm, in good agreement with literature values for ortho–ortho linkages. Furthermore, there was no evidence of chemical shift at 4.47–4.48 ppm which would correspond to oxymethylene bridges.[15,16]

Infrared absorption in the region between 1500 and 1400 $cm^{-1}$ is related to deformation vibrations of the C–H bonds in the methylene bridge.[17] This region also provides information about the oxymethylene bridge, which would show an absorption at 1410 $cm^{-1}$. In the infrared spectra of our PHMP, no evidence of a 1410-$cm^{-1}$ absorption was found, and absorption at 1455–1468 $cm^{-1}$ indicated ortho–ortho linkages.[18] There was also no absorption at 1150 $cm^{-1}$ which would suggest the presence of $-H_2C-O-CH_2-$ groups. When taken together with the NMR results, the IR spectra offer strong evidence of the aromatic rings being linked by methylene bridges exclusively at ortho–ortho positions.

The number-average molecular weight of PHMP was determined by vapor-phase osmometry to be 934, or a degree of polymerization of 8.8. The glass transition temperature is 81 °C.

**Cross-Linking of PHMP.** Although HMTA is widely used for cross-linking phenolic resins, the reaction mechanisms remain poorly understood. Recent studies[19] using CP/MAS $^{13}C$ NMR revealed that the curing reaction resulted in methylene cross-links and these methylene bridges originated from the methylene carbon of HMTA. The infared spectra of the HMTA cross-linked PHMP show absorption peaks that are similar to those of the PHMP and are in agreement with NMR results. The reaction between 1,3-dioxolane and PHMP is initiated by a protolytic attack of the acid on the cyclic formal resulting in the release of formaldehyde. After reaction with DIOXO, the infrared spectra of cured PHMP again show peaks similar to those of the original PHMP. The DIOXO absorptions at 1157 $cm^{-1}$ for cyclic C–O–C stretching and at 912 $cm^{-1}$ for cyclic out-of-plane C–H bending were no longer detectable. It is believed that cross-linking proceeds in this case also by methylene bridge formation, and side reactions are not significant under the conditions employed in this study.

The glass transition temperature of the HMTA cross-linked network is 124 °C, and the swelling ratio is 1.80–2.35 in tetrahydrofuran. (The large error incurred in the determination of swelling ratio was caused by small pieces of the polymer fractured and broken off.) The $T_g$ of the DIOXO cross-linked PHMP is 122 °C, and the swelling ratio is 1.64–2.12. As a first approximation, the two networks can be considered to have comparable cross-link densities.

**PHMP/PMMA Blends.** Hydrogen bonding interaction in PHMP/PMMA blends occurs between the hydroxyl group of PHMP and the carbonyl group of PMMA. There are two areas of interest in the infrared spectra of the blend, one in the hydroxyl stretching region from 3600 to 3200 $cm^{-1}$ and the other in the carbonyl stretching region from 1800 to 1650 $cm^{-1}$. In the former region, the absorption of the "free" hydroxyl group occurs at 3510 $cm^{-1}$, the "self-associated" hydroxyl group at 3279 $cm^{-1}$, and the hydroxyl group engaged in hydrogen bonding with ester groups at about 3380 $cm^{-1}$.[20] Due to the complicated nature of the hydroxyl group interactions, infrared absorption in this region was not suitable for assessing the extent of interpolymer hydrogen bonding. The carbonyl region was therefore chosen to monitor changes in hydrogen bonding

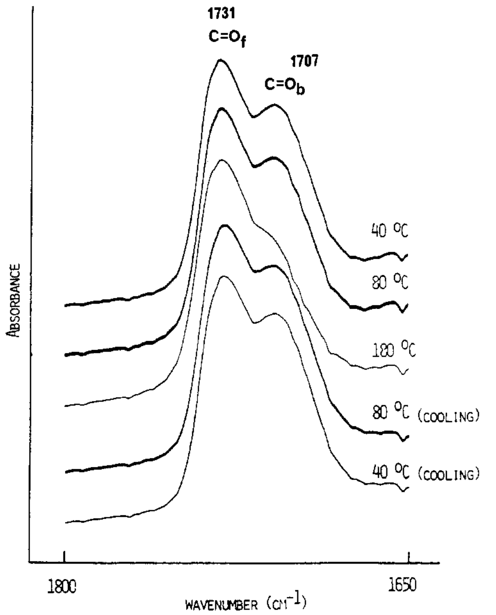

**Figure 1.** Carbonyl band in PHMP/PMMA blend (80/20 by weight) at various temperatures.

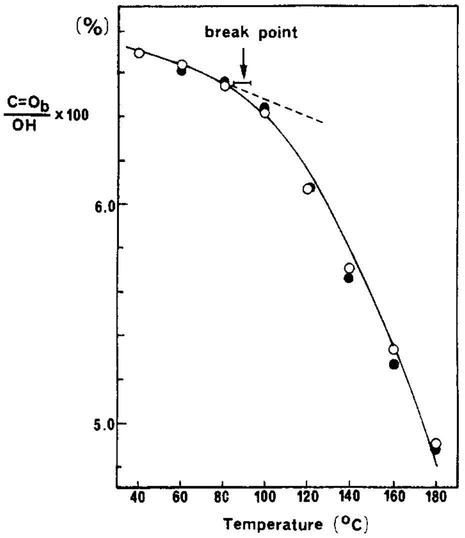

**Figure 2.** Variations of the extent of hydrogen bonding with temperature for PHMP/PMMA blend (80/20 by weight). Open and closed circles are for cooling and heating cycles, respectively.

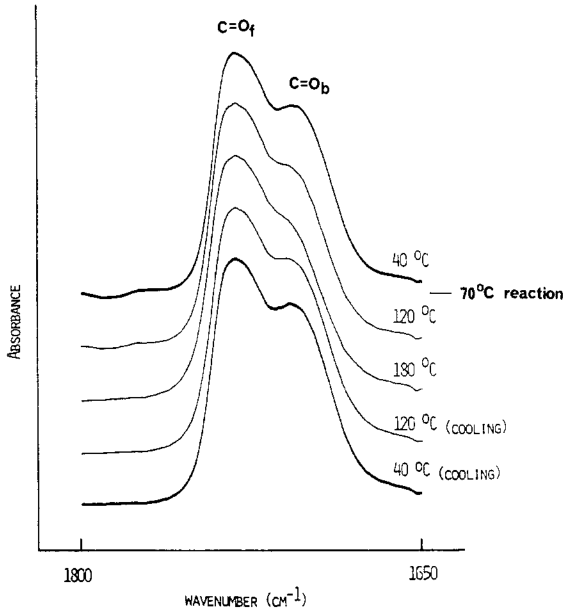

**Figure 3.** Carbonyl band in PHMP(DIOXO)/PMMA semi-IPN (80/20 by weight) at various temperatures. Cross-linking was carried out at 70 °C.

interaction.[6-8] The absorption due to free carbonyl $(C{=}O)_f$ was observed at 1731 cm$^{-1}$, while the absorption due to hydrogen bonded carbonyl $(C{=}O)_b$ was seen at 1707 cm$^{-1}$ (Figure 1). The absorptivity ratio of the bonded to free carbonyl groups was determined by the method described by Coleman and co-workers[6] to be 1.6 ± 0.1, in good agreement with their values. In the course of our study, we found the blend containing 80% PHMP to be most suitable for spectroscopic measurements. This blend composition was used throughout our study.

As temperature increased, two major effects were observed, and both were relevant to the subject of miscibility. The first observation was the constancy of the free carbonyl peak at 1731 cm$^{-1}$ in the temperature range 40–180 °C, but there was a gradual shift of the bonded carbonyl band from 1707 cm$^{-1}$ at 80 °C to 1714 cm$^{-1}$ at 180 °C. The second observation was the decrease in the fraction of bonded carbonyl group with increasing temperature (Figure 2). Note that the bonded carbonyl was expressed as $(C{=}O)_b/(OH)$ instead of the fraction of the total carbonyl groups. The choice was made to facilitate comparison of PMMA data with copolymer results. When copolymers were used, the total amount of carbonyl groups in the blends depended on copolymer composition. As the carbonyl content in the copolymer decreased, the ratio of bonded carbonyl group to the total carbonyl increased but the absolute value of the number of bonded carbonyl group actually decreased. Therefore, the ratio $(C{=}O)_b/(OH)$ was a more appropriate term, rather than the fraction of total carbonyl, for comparison of experimental results because the same blend composition, 80% PHMP, was used throughout this study.

In acquiring the data depicted in Figure 2, we noticed that the results obtained in the first heating cycle were slightly different from those in the cooling cycle. However, subsequent heating and cooling always reproduced the measurements of the first cooling cycle. Henceforth, only the results obtained during the cooling cycle were given.

The curve in Figure 2 was characterized by two distinct regions. In the low-temperature region, there was only a gradual change of the concentration of the bonded carbonyl group with temperature. But the change became much larger at temperatures above 90 °C. The general shape of the curve was reported 30 years ago by Longworth and Morawetz[21] for poly(styrene-*co*-methacrylic acid) and by others for hydrogen bonded blends.[6,8] The change from one region to another occurred at a "break" point that was estimated by noting the deviation from the straight line connecting the low-temperature data. The break point at 80–90 °C coincided with the $T_g$ of the blend, 83 °C.

**PHMP/PMMA Semi-IPNs.** Typical spectroscopic data for the semi-IPNs are shown in Figures 3 and 4. At the cross-linking temperature of 180 °C, dissociation of hydrogen bonding was extensive, and only a small fraction of the original hydrogen bonding was recovered in the semi-IPN upon cooling. Meanwhile, the semi-IPN cross-linked at a lower temperature of 70 °C retained a larger amount of hydrogen bonding. The variation of $(C{=}O)_b/(OH)$ with temperature can be seen more clearly in Figure 5. The network cross-linked by DIOXO had the same amount of bonded carbonyl groups at 180 °C as the blend. Upon cooling, a change in the slope of the curve was manifest at about 122–130 °C, about the same temperature as the $T_g$ of the network, namely, 122 °C. Due

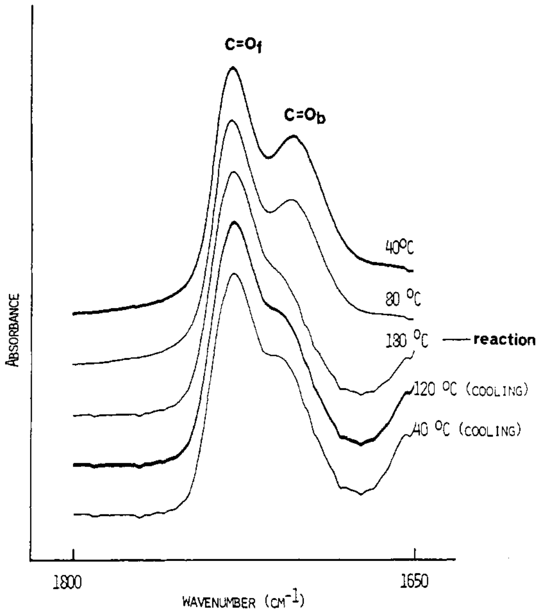

**Figure 4.** Carbonyl band in PHMP(HMTA)/PMMA semi-IPN (80/20 by weight) at various temperatures. Cross-linking was carried out at 180 °C.

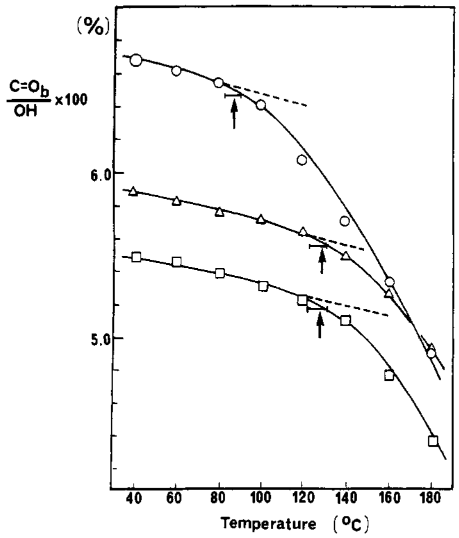

**Figure 5.** Variations of the extent of hydrogen bonding with temperature for (○) PHMP/PMMA blend (80/20 by weight), (△) PHMP(DIOXO)/PMMA semi-IPN (80/20 by weight), (□) PHMP(HMTA)/PMMA semi-IPN (80/20 by weight). Arrows indicate the break point.

**Table I**
**Cloud Point Temperatures of PHMP/Copolymer Blends[a]**

| COP | cloud point temp, °C | COP | cloud point temp, °C |
|---|---|---|---|
| 90 | >210 (dec)[b] | 36 | 176 |
| 80 | >210 | 34 | 170 |
| 70 | >210 | 32 | 162 |
| 60 | >210 | 30 | 155 |
| 50 | >210 | 20 | turbid at 25 °C |
| 40 | 191 | 10 | turbid at 25 °C |
| 38 | 185 | | |

[a] All blends contain 80% by weight of PHMP. [b] Decomposition.

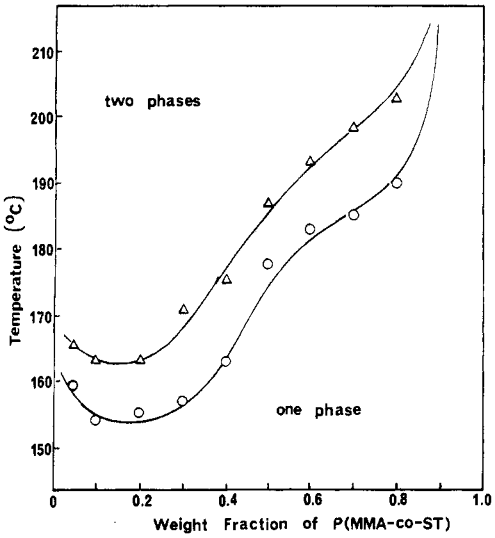

**Figure 6.** Measured cloud point curves for (○) PHMP/COP30 blend and (□) PHMP/COP32 blend.

to the intervention of glass transition, the reestablishment of the remaining hydrogen bonds was not achieved below this temperature. Therefore the concentration of bonded carbonyl at 40 °C was smaller than that in the blend that had a lower $T_g$. The HMTA cross-linked semi-IPN behaved differently in that the concentration of bonded carbonyl after reaction at 180 °C was smaller than the value for the blend or the DIOXO cross-linked network. Apparently, cross-linking decreased chain mobility so that the dynamic equilibrium between the interacting groups could not be maintained. (We were unable to ascertain whether there was a similar effect for cross-linking reaction at 70 °C because the amount of dioxolane was present in large quantities and the spectra resolution was not satisfactory.) Upon cooling, the decrease in bonded carbonyl group concentration paralleled the trend observed for the DIOXO network, with a change in slope again occurring near the $T_g$ of the semi-IPN. Our results are similar in many respects to those described in ref 9 in which a full discussion of the contributing factors has been given for semi-IPNs consisting of phenolic resins and ethylene–vinyl acetate copolymers.

**PHMP/Copolymers.** The miscibility of PHMP with copolymers of methyl methacrylate and styrene depended systematically on copolymer composition as shown in Table I. When the MMA content of the copolymer was 50% or higher, miscibility was maintained to at leasdt 210 °C, above which decomposition occurred. For copolymers containing 20% or less MMA units, the blends were turbid at room temperature. Blends (80/20) prepared from copolymers ranging from 40 to 30% MMA were miscible at ambient conditions but underwent phase separation at elevated temperatures. The cloud point was 155 °C for the COP30 blend, but the temperature increased to 191 °C for the COP40 blend. The cloud point curves for COP30 and COP32 blends over the entire composition range are given in Figure 6. Photomicrographs of one of the COP32 blends are shown in Figure 7. Dual phases showing a high degree of interconnectivity was evident at 180 °C. Phase connectivity as a morphological feature was predicted by Cahn's theory of spinodal decomposition[22] and was observed in other systems.[23,24]

As the density of interacting groups decreased in the copolymers, the number of bonded carbonyl groups also decreased, as could be seen in Figure 8. Again, hydrogen bonds dissociated more quickly once the temperature exceeded the $T_g$ of the blend. When temperatures were further raised to the cloud points identified by arrows in Figure 8, we found that the $(\mathrm{C{=}O})_b/(\mathrm{OH})$ ratios had approximately the same value of 2.5% for all six copolymer blends. This correlation implies that a critical value of hydrogen bonding interaction is needed to maintain a

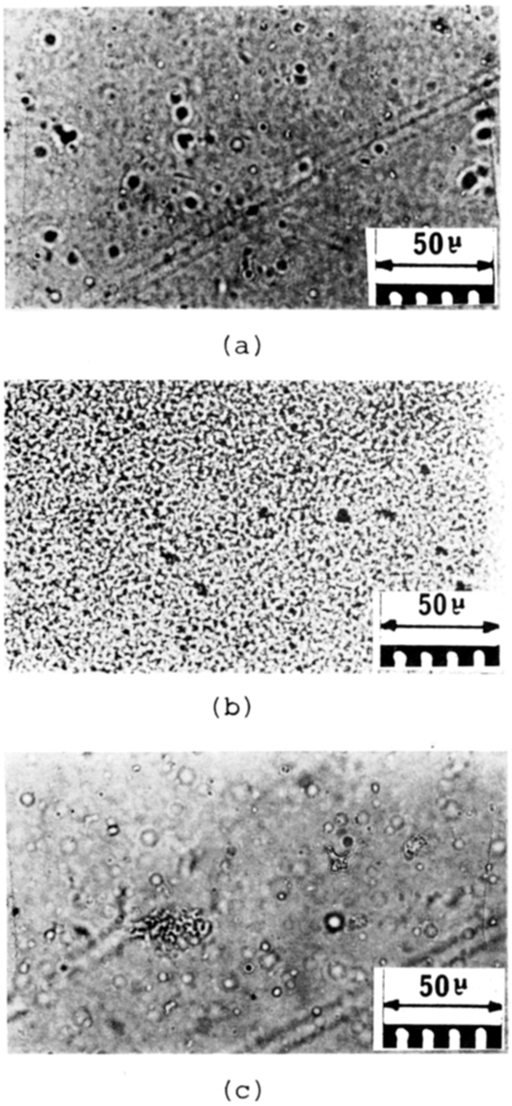

**Figure 7.** Photomicrographs of PHMP/COP32 blend (80/20 by weight): (a) at 80 °C, 10 min, (b) at 180 °C, 10 min, and (c) at 80 °C, 10 min after exposing sample (b) to the vapor of $CH_2Cl_2$/THF (90/10 by volume) and drying it at room temperature.

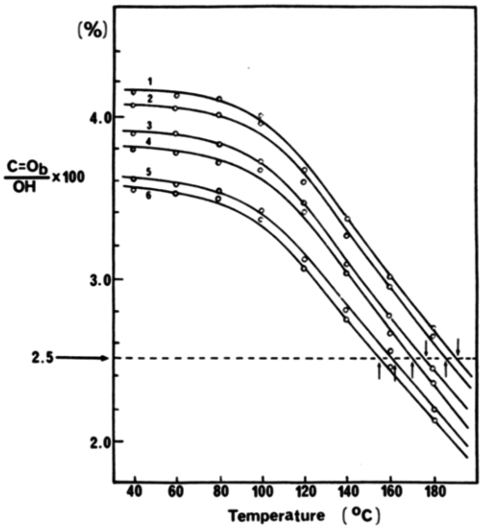

**Figure 8.** Variations of the extent of hydrogen bonding with temperature for (1) PHMP/COP40, (2) PHMP/COP38, (3) PHMP/COP36, (4) PHMP/COP34, (5) PHMP/COP32, and (6) PHMP/COP30. All samples have the same composition of PHMP/COP (80/20 by weight).

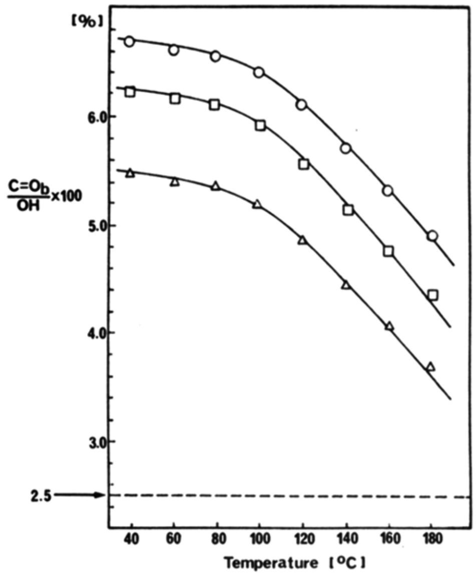

**Figure 9.** Variations of the extent of hydrogen bonding with temperature for (○) PHMP/PMMA, (□) PHMP/COP80, and (△) PHMP/COP60. All samples have the same composition of PHMP/COP (80/20 by weight).

single phase in each of these blends. In support of this interpretation was the observation that phase separation did not take place at 180 °C in COP60 and COP80 blends for which the $(C{=}O)_b/(OH)$ ratios exceeded the 2.5% value (Figure 9). The importance of the enthalpic contribution to the free energy of mixing is demonstrated fully by these results. However, we did not observe a discontinuous decrease in the fraction of bonded carbonyl at the cloud point (see curves 3–6 in Figure 8) and the reason was not understood.

The thermal reversibility of the phase-separation phenomenon, though a minor issue in the present context, deserves some comment. The morphological features seen at 180 °C (Figure 7a) did not revert to a single phase when the specimen was cooled to below the cloud point of 162 °C. On the other hand, if phase separation was allowed to take place at only ~5 °C above the cloud point, the dual-phase structure reverted to a single phase when the film was annealed at temperatures several degrees below the cloud point. The reversibility of the phase-separation process depended on the coarseness of the dual-phase structure, cooling rate, and annealing conditions.[25,26] Recently Cowie and Saeki[27] studied the effect of solvent on both upper and lower cloud points. The solvent was thought to reduce the diffusional barrier toward segmental motion. We adopted the same approach and exposed the phase-separated sample, at room temperature, to the vapor of the same solvent mixture that had been used as the cast solvent for the blend. Upon exposure to the solvent vapor, the film regained transparency, as shown in Figure 7c. Transparency remained after the imbibed vapor was removed by drying in a vacuum oven.

**Semi-IPN-Containing Copolymers.** The extent of hydrogen bonding in copolymer semi-IPNs depended on the MMA content of the copolymer, as in the case of blends. As the MMA concentration in the copolymer decreased, hydrogen bonding interaction decreased correspondingly in the semi-IPN. These data are shown in Figures 10 and 11.

A significant difference was observed in the phase behaviors of COP40 semi-IPN synthesized under different conditions. When the network was formed at 180 °C, the $(C{=}O)_b/(OH)$ ratio was smaller than the critical value of 2.5% and the heterogeneous nature of the material was

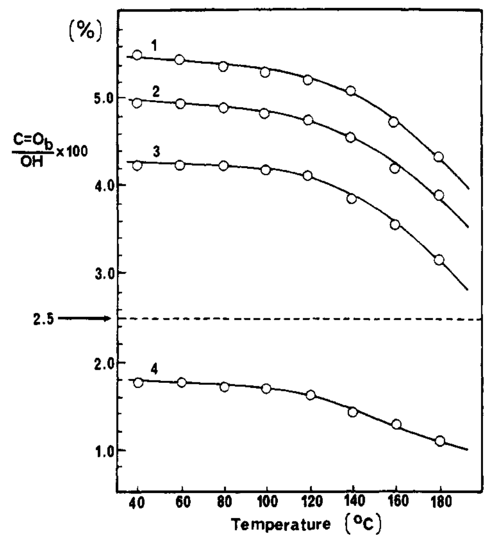

**Figure 10.** Variations of the extent of hydrogen bonding with temperature for (1) PHMP(HMTA)/PMMA semi-IPN, (2) PHMP(HMTA)/COP80 semi-IPN, (3) PHMP(HMTA)/COP60 semi-IPN, and (4) PHMP(HMTA)/COP40 semi-IPN. All samples have same composition of PHMP/COP (80/20 by weight).

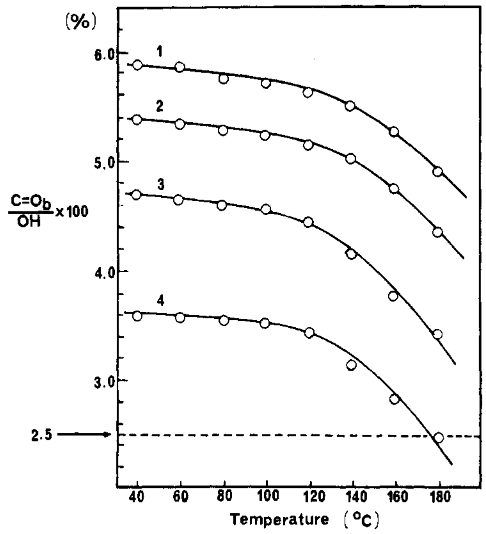

**Figure 11.** Variations of the extent of hydrogen bonding with temperature for (1) PHMP(DIOXO)/PMMA semi-IPN, (2) PHMP(DIOXO)/COP80 semi-IPN, (3) PHMP(DIOXO)/COP60 semi-IPN, and (4) PHMP(DIOXO)/COP40 semi-IPN. All samples have same composition of PHMP/COP (80/20 by weight).

readily seen by microscopy. But the network prepared at 70 °C retained a much larger amount of hydrogen bonding and maintained the characteristics of a single-phase material at 180 °C. Additional evidence of heterogeneity in the former material was provided by $T_g$ and dynamic mechanical property measurements. The HMTA cross-linked network showed two $T_g$'s, 100 and 135 °C. The former value was the same as that of COP40 while the latter was close to the $T_g$ of the PHMP/HMTA, 124 °C. In contrast, the DIOXO cross-linked network had a single $T_g$ at 125 °C. The loss tangent data in the range 70–110 °C supported the $T_g$ measurements (Figure 12). However, the mechanical spectra also suggest the possible presence of some degree of heterogeneity in two of the DIOXO cross-linked networks.

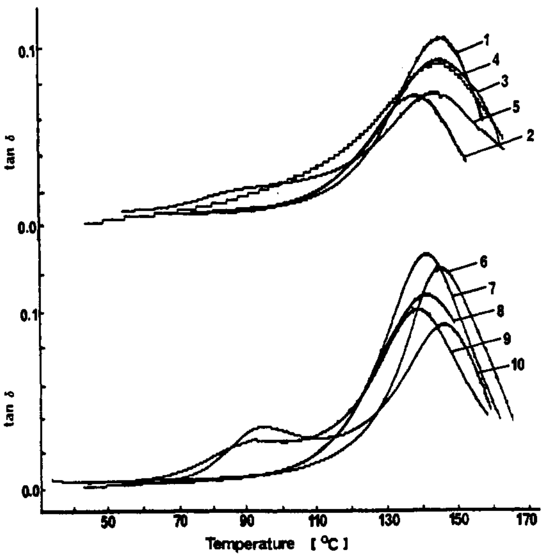

**Figure 12.** Mechanical spectra of (1) PHMP(DIOXO-cured), (2) PHMP(DIOXO)/PMMA semi-IPN, (3) PHMP(DIOXO)/COP80 semi-IPN, (4) PHMP(DIOXO)/COP60 semi-IPN, (5) PHMP-(DIOXO)/COP40 semi-IPN, (6) PHMP(HMTA-cured), (7) PHMP(HMTA)/PMMA semi-IPN, (8) PHMP(HMTA)/COP80 semi-IPN, (9) PHMP(HMTA)/COP60 semi-IPN, and (10) PHMP(HMTA)/COP40 semi-IPN. All samples have same composition of PHMP/COP (80/20 by weight).

In conclusion, we have demonstrated that it is possible to control the morphology of interpenetrating networks by manipulating the extent of hydrogen bonding. Work is in progress to apply the principles established here for the design of a rubber-reinforced network by using appropriate combinations of PHMP and rubbery acrylic polymers.

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**Registry No.** PHMP, 9003-35-4; (HMTA)(phenol)(formaldehyde) (copolymer), 37337-65-8; (DIOXO)(phenol)(formaldehyde) (copolymer), 119771-09-4; PMMA, 9011-14-7; (styrene)(methyl methacrylate) (copolymer), 25034-86-0.

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# Investigation of the Microphase Separation Transition in Low Molecular Weight Diblock Copolymers

**John N. Owens,[†] Irena S. Gancarz,[‡] and Jeffrey T. Koberstein[*]**

*Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544*

**Thomas P. Russell**

*IBM Research Division, Almaden Research Center, 650 Harry Road,*
*San Jose, California 95120-6099.*

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ABSTRACT: The microphase separation transition in three diblock copolymer systems is studied by differential scanning calorimetry and small-angle X-ray scattering analyses. The experimental absolute scattered intensity profiles for a symmetric poly(styrene-*block*-isoprene) in the homogeneous state compare quantitatively to the theoretical predictions of Leibler. The scattering profiles for homogeneous poly(styrene-*block*-1,2-butadiene) and poly(styrene-*block*-butene) copolymers exhibit a mismatch in the critical scattering vector, $q^*$, compared to the theoretical prediction. These two diblock copolymers are asymmetric as a result of a dissimilarity in the statistical segment lengths of the two components. The theoretical scattering profiles may be brought in agreement with experiment by empirically adjusting the copolymer chain dimensions assumed in the calculation. These comparisons are used to evaluate the interaction parameters and their temperature dependence for the three copolymer systems. In all three systems, the observed conditions for the apparent spinodal are found to be in good agreement with the predictions of Leibler's theory.

## Introduction

The broad range of present and potential applications of block copolymers has led to numerous studies of their structure and properties.[1,2] The majority of previous work has focused on characterization of block copolymers in the strong segregation limit where microphase separation into well-ordered microdomain geometries is observed. More recently, there has been considerable interest in the thermodynamics of block copolymers in the weak segregation limit. Under these conditions, the materials undergo a microphase separation transition (MST) at which point the spatially ordered microdomains spontaneously disorder to form a so-called homogeneous phase.

The microphase separation transition has been treated by Leibler[3] in a theory based upon the consideration of concentration fluctuations within the homogeneous state. The theory utilizes the formalism of de Gennes' random phase approximation (RPA).[4] A mean-field approach that considers polymer/polymer interactions is used to calculate an order parameter for the system as the MST is approached by the homogeneous diblock copolymer. The theory predicts a first-order transition similar in many respects to a liquid-solid transition.

The theory of Leibler also provides a calculation of the small-angle X-ray (SAXS) and neutron-scattering (SANS) functions for homogeneous diblock copolymers. A strong dependence of the scattering curve on the Flory interaction parameter, $\chi$, is predicted, and the use of the theory to determine the $\chi$ parameter from experimental scattering is proposed. The calculation of scattering curves for homogeneous diblock copolymers has been extended to include the effects of polydispersity[5,6] and composition fluctuations.[7]

Small-angle scattering measurements on block copolymers in the disordered state have been reported in the literature for a variety of systems. Roe et al.[8] report qualitative agreement with Leibler's theory for SAXS data from a styrene–butadiene diblock copolymer. Qualitative agreement between Leibler theory and SAXS data has been found for styrene–isoprene[9] and styrene–butadiene[10] diblock copolymers and has subsequently been used to determine the $\chi$ parameter and its temperature dependence. SANS data for a set of 1,2-butadiene–1,4-butadiene diblock copolymers[11] covering a range of compositions and molecular weights were also found in agreement with the predictions of Leibler's theory.

In addition to determining the $\chi$ parameter for the 1,2-PB–1,4-PB system, Bates[12] reports a rheological transition in the diblock copolymers corresponding to the MST. A rheological transition corresponding to the MST has been reported by several other investigators.[13-17] At low frequencies, a transition in the dynamic viscosity is observed as the temperature of the system is increased through the MST region. At temperatures below the MST

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[*] To whom correspondence should be addressed: Department of Chemical Engineering and the Institute of Materials Science, U-136, University of Connecticut, Storrs, CT 06268.

[†] Present address: General Motors Research Laboratories, Warren, MI 48090-9055.

[‡] Present address: Technical University of Wroclaw, Wroclaw, Poland.