Effect of Sequence Distribution on Miscibility in Polymer Blends

Introduction. For decades polymers have been blended to yield materials with properties that are superior to those of the parent polymers. Early work, both experimental and theoretical, dealt with blending homopolymers and determining how the chemical nature of the two homopolymers affected miscibility.[1] During the last decade, attention has shifted to investigating copolymer blends. Several theories have been developed to explain how the chemical composition of the copolymers affects miscibility.[2-5] With copolymers, however, chemical composition does not uniquely describe the material. Two copolymers with the same composition of A and B units can be very different materials depending on how the A and B units are linked together, i.e., depending on their sequence distribution. Since polymer blends in which one component is a copolymer have many technological applications, it is important to understand when sequence distribution might cause phase separation to occur.

Balazs and co-workers have extended the Flory-Huggins theory on miscibility of copolymers to include sequence distribution effects in copolymer blends[6] and in ternary blends[7] containing one copolymer and the two corresponding homopolymers. The first assumption made in these theories is that the χ parameter for mixing A and B units is influenced by the nearest neighbors that are chemically linked to the A and B units. Thus the χ parameter for the copolymer was defined in terms of the triad distribution of A and B monomers in the copolymer. Unique energies were assigned to two triad interactions, AAA-BBB and ABA-BAB. All other triad interactions were assigned an average energy (χ_{AB}). Each energy was then multiplied by the probability of its occurrence, and all the energies were added to give χ for the mixture. This χ was used to calculate the free energy of mixing for the system using the Flory-Huggins equation. Results from these theories predict that even small differences in sequence distribution can have large effects on the blend miscibility.

To date, very little experimental work exists on the effects of sequence distribution on miscibility in ternary blends. Rigby and Roe[8] used cloud-point measurements to study blends of styrene-butadiene block or random copolymers mixed with low molecular weight styrene and butadiene homopolymers. Riess et al.[9] have examined the ternary phase diagrams for the styrene and methyl methacrylate homopolymers mixed with a random or block copolymer of the same monomers. In this case, miscibility was evaluated totally in terms of optical clarity, an unreliable method.

Both of these studies dealt with large sequence distribution differences, between the block and a random copolymer. Thus they are poor tests of the present theory. Our goal is to evaluate the effects of smaller sequence distribution differences. This can be accomplished in the styrene-methyl methacrylate system. It is one of a very few polymer systems in which it is possible to synthesize well-defined strictly alternating copolymers. In addition, the random copolymer has been shown to be alternating in character.[10] Only 10% of the triads are homotriads. Therefore a comparison of the alternating and random copolymer will allow us to study small differences in sequence distribution. This system has the added advantage that blends of the two homopolymers have been well characterized and the χ parameter has been measured.[11] This paper will report on the initial experimental evaluation of the ternary phase diagrams for the mixtures of block random, or alternating copolymer with the two homopolymers.

Materials and Methods. Polymers: Synthesis and Fractionation. Random Copolymer of Styrene and Methyl Methacrylate. Benzene, styrene, and methyl methacrylate were purified by passing them through a column of activated basic alumina. A reaction vessel was charged with 50 mL of methyl methacrylate, 45 mL of styrene, and 130 mL of benzene. Oxygen was removed from this mixture by a freeze/pump/thaw cycle, and the vessel was back-filled with argon. After heating to 60 °C, 0.119 g of benzoyl peroxide in 1 mL of benzene was added to the mixture. The reaction was stopped around 5% conversion by precipitating the polymer into methanol. To obtain a narrow molecular weight sample, the polymer was fractionated in a mixture of toluene and cyclohexane at 0 °C.

Alternating Copolymer of Styrene and Methyl Methacrylate. Toluene was distilled from living polystyrene. The inhibitor was removed from both monomers with KOH. After the mixture was stirred over CaH_2 for a least 1 day, the monomers were distilled under vacuum before use. In accordance with the method of Hirai et al.,[12] 0.9 M $Et_3Al_2Cl_3$ in toluene was added to the reaction flask in a drybox. Methyl methacrylate was then added to the flask to obtain a methyl methacrylate to Al ratio of 1.7:1. This mixture was cooled on ice for 30 min. The styrene was then added, and polymerization proceeded for 1 h. The polymer was precipitated into HCl-methanol, redissolved in toluene, and precipitated into methanol three times. Fractionation was accomplished with cold toluene-cyclohexane mixtures.

Polystyrene and Poly(methyl methacrylate). Narrow molecular weight fractions were purchased from Polymer Laboratories.

Characterization. NMR. ^1H and ^{13}C solution NMR were acquired in hexachlorobutadiene on a JEOL GX-500 NMR. These spectra were used to calculate copolymer composition. Comparison with literature proved that the alternating copolymer was strictly alternating[13] and that the random copolymer had the same triad distribution as reported by Bovey.[10] NMR also proved that the copolymers and the homopolymers were atactic. This allows us to study only sequence distribution affects.

GPC. Size-exclusion chromatography was performed on a Waters 150 GPC with bimodal Zorbax columns. Polymer molecular weights and compositions are listed in Table I. Note that the copolymers have high molecular weights. This is because the polymerization of the alternating copolymer gives only high molecular weight material. The molecular weights of the block and random copolymer were selected to match the molecular weight of the alternating copolymer. Low molecular weight (30K) homopolymers were used to facilitate mixing.

DSC. Glass transition temperatures were measured on a Perkin-Elmer DSC-4 at a heating rate of 10 °C/min.

Blend Preparation. Films were cast from dilute (<1%) solutions of the polymers in tetrahydrofuran. THF was chosen as the solvent because it is a good solvent for both polystyrene and poly(methyl methacrylate). Evaporation of the solvent occurred slowly over an 8-h period. The films were air dried overnight and then annealed under a N_2 flow at temperatures between 140 and 160 °C for 1 week.

Results and Discussion. The ternary phase diagram for a mixture of polystyrene, poly(methyl methacrylate),

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Table I[a]

polymer	% MMA	MW	PD
poly(methyl methacrylate)	100	30K	1.10
polystyrene	0	22K	1.03
poly(St-*b*-MMA)	46	283K	1.08
random copolymer	48	286K	1.49
alternating copolymer	50	279K	1.41

[a] Fractionated in cold toluene–cyclohexane (R & A).

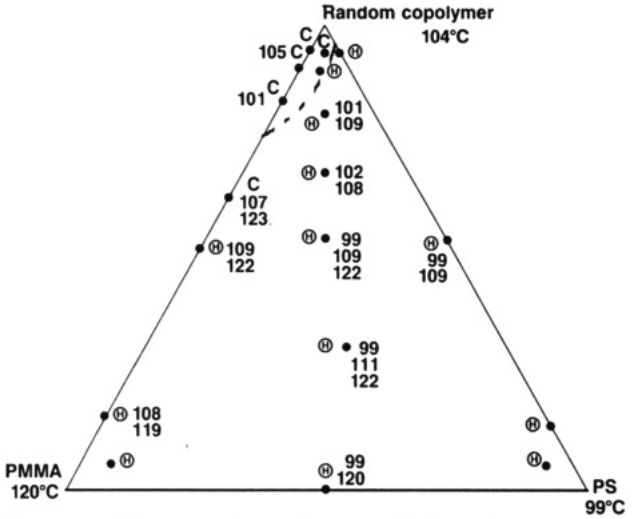

Figure 1. Ternary phase diagram of the polymer system consisting of a random copolymer of styrene and methyl methacrylate, polystyrene and poly(methyl methacrylate). The numbers indicate the observed glass transition temperatures. C means that the film was clear. H means the film was hazy.

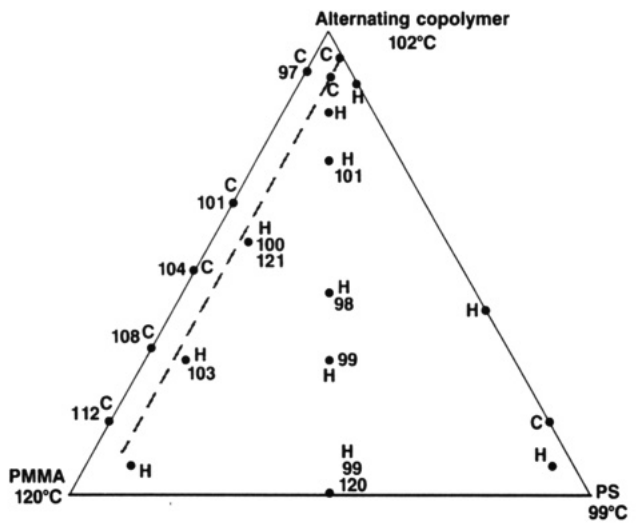

Figure 2. Ternary phase diagram of the polymer system consisting of an alternating copolymer of styrene and methyl methacrylate, polystyrene and poly(methyl methacrylate).

and the random copolymer of styrene and methyl methacrylate is shown in Figure 1. Our results are similar to those of Riess[9] (Figure 2). Optically clear films were obtained for mixtures containing high concentrations of copolymer with poly(methyl methacrylate). DSC indicates that these films have only one T_g. At higher PMMA loadings, two glass transition temperatures are evident. Some of the three-component blends have three distinct T_g's, indicating complete phase separation. These data demonstrate that there is very little thermodynamic compatibility in this system.

The surprising results of this study are evident in Figure 2, the ternary phase diagram of the polystyrene, poly(methyl methacrylate), and alternating styrene–methyl

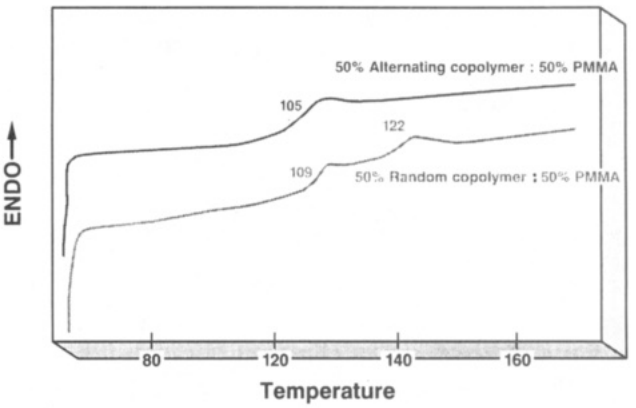

Figure 3. DSC scan of two polymer blends. The top scan is of a 50:50 mixture of PMMA and the alternating copolymer. The bottom scan is of a 50:50 mixture of PMMA and the random copolymer.

methacrylate copolymer. Focus on the binary axis of the alternating copolymer mixed with poly(methyl methacrylate). Films cast with any composition of the alternating copolymer with PMMA were optically clear and had only one T_g which increased toward the T_g of PMMA as the percent PMMA increased. In Figure 3, DSC traces of a 50:50 mixture of PMMA and the alternating copolymer and PMMA and the random copolymer are shown. This proves that DSC would be able to differentiate the T_g's of PMMA and the alternating copolymer if the blend were phase separated, since the T_g of the alternating copolymer is very close to that of the random copolymer.

Films with all three polymer components (polystyrene, alternating copolymer, and PMMA) were optically hazy but have only one T_g. At this time we cannot say whether these blends are thermodynamically miscible. The T_g of the compatible PMMA–alternating copolymer mixture is too close to the T_g of polystyrene (99 °C) for DSC to separate them. For this reason a line has been drawn to separate the alternating–PMMA axis from the interior points in Figure 2. Once the polystyrene in these ternary blends is stained with RuO_4, TEM should tell us if the polystyrene has separated. Enthalpy relaxation experiments might also be useful in determining the phase structure of these blends.[14] But, whether the interior points are miscible or immiscible, the alternating diagram is still distinctly different from the random diagram along the binary axis. Only one T_g is evident in all mixtures of alternating copolymer and PMMA.

It should be noted that studies have shown that only 10% of the methyl methacrylate units are in MMM triads in the random copolymer.[10] Most have one or two styrene neighbors. Likewise, only 10% of the styrene units are in SSS triads. The random copolymer is, therefore, very alternating in character. Yet, the ternary phase diagrams for the alternating and random copolymers are very different. While theory has predicted that this may occur, this is the first time that such a small change in sequence distribution has been shown to have a large effect on miscibility in ternary blends.

A possible explanation for these differences lies in the χ parameters. If the χ parameters are expressed in terms of triad sequences, only one χ parameter is necessary to describe the PMMA–alternating copolymer interaction, $\chi_{MMM\text{-}MSM}$. The random copolymer–PMMA axis is, however, described by three χ parameters. They are $\chi_{MMM\text{-}MSM}$, $\chi_{MMM\text{-}MSS}$, and $\chi_{MMM\text{-}SSS}$. It is known from previous work[11] that $\chi_{MMM\text{-}SSS}$ is positive and would therefore favor phase separation. In the second part of

this study, the χ parameters for the systems will be measured and an attempt will be made to fit this data to theory.

References and Notes

(1) *Polymer–Polymer Miscibility*; Olabisi, O., Robeson, L., Shaw, M., Eds.; Academic Press: New York, 1979.
(2) Scott, R. L. *J. Polym. Sci.* **1952**, *9*, 423.
(3) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(4) Kambour, R. P.; Bender, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(5) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(6) Balazs, A. C.; Sanchez, I. C.; Epstein, I. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1985**, *18*, 2188.
(7) Balazs, A. C.; DeMeuse, M. T. *Macromolecules* **1989**, *22*, 4260.
(8) Roe, R.; Rigby, D. *Advances in Polymer Science 82*; Springer-Verlag: New York, 1987; p 94.
(9) Riess, V. G.; Kohler, J.; Tounut, C.; Banderet, A. *Macromol. Chem.* **1967**, *101*, 58.
(10) Bovey, F. A. *J. Polym. Sci.* **1962**, *62*, 197.
(11) Russell, T. P.; Hjelm, R. P.; Seeger, P. A. *Macromolecules* **1990**, *23*, 890.
(12) Hirai, H.; Tanabe, T.; Koinuma, H. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 843.
(13) Heffner, S. A.; Bovey, F. A.; Verge, L. A.; Mirau, P. A.; Tonelli, A. E. *Macromolecules* **1986**, *19*, 1628.
(14) Bosma, M.; ten Brinke, G.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.

Mary E. Galvin

AT&T Bell Laboratories, 600 Mountain Avenue Murray Hill, New Jersey 07974

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Registry No. (St)(MMA) (copolymer), 25034-86-0; (St)-(MMA) (alternating copolymer), 108266-99-5; PS (homopolymer), 9003-53-6; PMMA (homopolymer), 9011-14-7.