Phase Equilibria in SBR/Polybutadiene Elastomer Blends: Application of Flory–Huggins Theory

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SYNOPSIS

Blends of anionically-polymerized polybutadiene (BR) and styrene–butadiene copolymer (SBR) must be treated as mixtures of terpolymers and tetrapolymers, due to the presence of three different BR isomers: cis-1,4, trans-1,4, and vinyl-1,2. Moreover, in the absence of specific interactions or chemical reactions that strongly influence miscibility, structural characteristics of the component polymers, such as BR isomer content, SBR styrene content, monomer sequence distribution, molecular weight, and molecular weight distribution, are expected to have an increased role in determining the blend miscibility characteristics. Small angle neutron scattering (SANS) studies of SBR/BR blends have resulted in the computation of the monomer–monomer segmental interaction energetics via a Flory–Huggins treatment. This allows quantitative prediction of miscibility behavior as a function of polymer structure. We have used the Flory–Huggins chi parameters, describing the styrene/cis-1,4, styrene/trans-1,4, and cis-1,4/trans-1,4 segmental interactions, to identify certain blend combinations expected to exhibit phase transitions in an experimentally accessible temperature range. The appropriate polymers were synthesized, solution blended, and the blends analyzed via optical microscopy and thermal analysis. Our results show that the blend behavior, observed experimentally, is consistent with the calculated cloud point curves. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Determination of the Flory–Huggins χ-interaction parameter of blends of mixed microstructure dienes has been the focus of a considerable amount of research. Blends of styrene-butadiene copolymer (SBR) and polybutadiene (BR) have been staples of the rubber industry for many years, and numerous studies[1-24] have been undertaken to determine the miscibility characteristics of these two polymers. Because of the presence of three BR microstructures, these blends cannot be treated simply as those of a copolymer and homopolymer. Although polymerized from the same 1,3-butadiene monomer, cis-1,4, trans-1,4, and the vinyl-1,2 microstructures are vastly different and, consequently, an SBR/BR blend is essentially that of a tetrapolymer and a ter-

polymer. However, only in the past few years have attempts been made to account for the multiple BR microstructures in terms of the Flory–Huggins segmental interaction parameters. This effort has been carried out via the utilization of small-angle neutron scattering (SANS), by which means one can determine the effective interaction parameter (χ_{Eff}), which is the weighted average of the monomer–monomer interactions. Through studies of blends of protonated and deuterated polymers and subsequent numerical analysis, individual interaction parameters have been calculated. Using this approach, Sakurai et al.[25] have published χ parameters for the segmental interactions between SBR and BR microstructural units.

In our study, these χ values were used to identify SBR/BR blend combinations that would exhibit phase transitions in experimentally accessible temperature ranges, and synthesis of polymers with the desired microstructures was then carried out. The objective was to develop a blend system that would

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pass through a phase transition under conventional curing conditions. In this way, one can study and control phase structure in the biphasic region and explore the potential impact on physical properties. Knowledge of the influence of polymer structure on SBR/BR blend miscibility and, in turn, the effect of miscibility behavior on cured rubber properties, has become increasingly important with the development of anionic polymerizations and the ability to precisely control and quantify the molecular weight, molecular weight distribution, and microstructural content of these polymers.[26,27] Thus, an unlimited number of SBRs and BRs are possible, and because of this, there exists an added processing variable in that the micro- and macrostructure of the polymers can be altered to yield the desired miscibility behavior of the blend. This, in turn, can be exploited to impact favorably the dynamic mechanical properties of the cured rubber blend for improved tire performance,[28] provided the phase separation, or conversely the phase dissolution kinetics and crosslinking kinetics, are such that the desired morphology is locked-in during the curing process.[29]

Utilization of the reported segmental X-parameters[25] offers a means to design appropriate blend systems, since the critical temperature and the spinodal curves can be estimated via the Flory–Huggins theory. This concept is confirmed in this investigation, in which we used thermal analysis of solution cast blends to demonstrate the ability of the X-parameters of Sakurai et al.[25] to predict the miscibility of SBR/BR blends containing polymers with microstructural content outside the range of those studied in the SANS experiments.

EXPERIMENTAL

Blend Design

The X values of Sakurai et al.[25] are the most useful literature values, since SBR/BR blends were not considered simply as blends of a copolymer and a homopolymer. Instead, the different microstructures of polybutadiene were taken into account and this polymer was treated as a random copolymer, consisting of 1,4 and 1,2 linkages. Thus, the SBR/BR blend system was modelled as a mixture of a terpolymer and a copolymer. Therefore, three separate parameters are required to describe the energetics:

$$X_{VS} \Rightarrow 1,2\text{-BR}/\text{Styrene} \quad (\text{i.e., vinyl}/\text{styrene})$$

$$X_{BS} \Rightarrow 1,4\text{-BR}/\text{Styrene}$$

$$X_{VB} \Rightarrow 1,2\text{-BR}/1,4\text{-BR} \quad (\text{i.e., vinyl}/1,4\text{-BR})$$

For a random copolymer, X_{blend} then becomes the weighted average of the three interactions:

$$
\begin{aligned}
X_{blend} = {} & y\phi_S X_{VS} \\
& + (1-y)\phi_S X_{BS} \\
& + [y(1-x)(1-\phi_S) + \\
& \quad x(1-y)(1-\phi_S)] X_{VB} \\
& - x\phi_S(1-\phi_S) X_{VS} \\
& - \phi_S(1-x)(1-\phi_S) X_{BS} \\
& - [y(1-y) + \\
& \quad x(1-x)(1-\phi_S)^2 X_{VB}]
\end{aligned}
\left. \begin{array}{l} \\ \\ \\ \\ \\ \end{array} \right\}
\begin{array}{l} \text{Repulsion of} \\ \text{chemically} \\ \text{linked} \\ \text{monomer units} \end{array}
$$

which is simplified to:

$$X_{blend} = k\phi_S X_{VS} + (\phi_S - k)\phi_S X_{BS}$$
$$- k(\phi_S - k)X_{VB} \quad (1)$$

where $k = y - x(1 - \phi_S)$, ϕ_S = volume fraction of styrene in SBR, x = volume fraction of BR in SBR which is 1,2-linked, and y = volume fraction of BR in BR which is 1,2-linked.

Sakurai et al.[25] investigated blends of a deuterated low-vinyl (12%) BR, and of protonated BRs, with vinyl contents ranging from 20% to 85%, with SBRs having BR microstructures at 61% and 46% vinyl, and styrene contents at 15% and 20%. The results of this study determined that all three of the segmental interaction parameters are positive:

$$X_{VS} = 56.5 \times 10^{-3} + 5.62/T$$

$$X_{BS} = 8.43 \times 10^{-3} + 10.2/T$$

$$X_{VB} = 2.69 \times 10^{-3} + 1.87/T$$

These equations indicate that the vinyl/styrene "repulsion" is the greatest, followed by the 1,4-BR/ styrene and, last, the interaction between the two BR microstructures. Surprisingly, these results indicate via eq. (1) that an SBR with high vinyl and high styrene content may be miscible with low vinyl BRs, due to the repulsion between the vinyl and styrene units on the same SBR chain. In other words, as shown by eq. (1), X_{blend} is negative when k is negative, because X_{VS} is large and positive relative to X_{BS} and X_{VB}.

To identify blend combinations that would exhibit phase transitions in an experimentally accessible temperature range, a computer program was written to predict UCST phase behavior as a func-
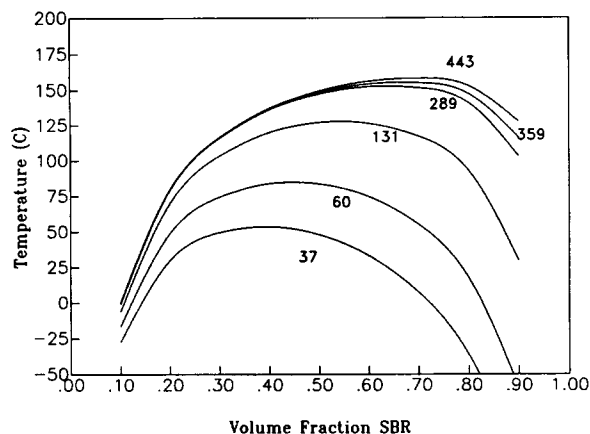
Figure 1 Phase diagrams, calculated from eq. (3), for blends of SBR42 (119,000 M_n, 30% styrene, 41% vinyl)/ BR (8% vinyl) as a function of BR molecular weight (M_n = 37,000 to 443,000).

tion of polymer microstructure, molecular weight, and blend composition for various combinations of the SBRs and BRs. In this manner, the χ-parameters, determined from polymers with one range of microstructures, could be extrapolated to estimate critical temperatures of blends with any microstructural content. Spinodal decomposition temperatures, T_S, were derived in the usual way, utilizing the Flory–Huggins expression:

$$\frac{\delta^2 \Delta G_m}{\delta \phi^2} = 0 = \frac{1}{N_{SBR}\phi_{SBR}}$$

$$+ \frac{1}{N_{BR}(1 - \phi_{SBR})} - 2\chi_{blend} \quad (2)$$

where ΔG_m = free energy of mixing per unit volume, ϕ_{SBR} = volume fraction SBR, and N_i = number average degree of polymerization of SBR, BR.

Solving for T_S yields the following equation:

$$T_S = \frac{-6.45\,k\phi_S + 10.2\,\phi_S^2 + 1.87\,k^2}{\{0.5[(1/N_{SBR}\phi_{SBR}) + (1/N_{BR}(1 - \phi_{SBR}))] + -0.00843\,\phi_S^2 - 0.04538\,k\phi_S - 0.00269\,k^2\}}$$

(3)

As noted above, based on computer analysis of eqs. (2) and (3), opportunities to observe phase transitions are predicted to occur for a blend of a high-styrene, high-vinyl SBR, and a low-vinyl BR. In addition, blends of such polymers can have markedly composition-dependent glass transition temperatures, which may offer the ability to tailor dynamic mechanical properties, provided that at least some partial miscibility occurs. Figure 1 illustrates the effect of BR molecular weight on calculated phase diagrams for such a series of SBR(42)/BR blends. As expected for a system with a UCST, increasing the molecular weight of the BR increases the UCST and shifts the critical composition toward the higher molecular weight polymer.

Materials

Anionic solution polymerization offers the flexibility and control of the polymer structure required for this study, and was utilized to produce elastomers with a variety of microstructures and molecular weight characteristics. Polymerizations were carried

Table I Characteristics of Polymers Used for this Study

Polymer (Code)	Polymerization Conditions Temp. (°C)	Modifier Ratio	Microstructure Vinyl	Cis-1,4	Trans-1,4	Styrene	Molecular Weight M_n (× 1000)	MWD
Batch BRs								
91-17	65	0	8	42	50	—	289.9	1.22
91-18	50	0	8	39	53	—	37.3	1.04
90-84	50	0	8	39	53	—	131.1	1.16
91-23	50	0	8	43	49	—	443.5	1.13
PBD63	50	0	8	43	49	—	359.0	1.10
91-08	50	0	8	39	53	—	60.2	1.04
Batch SBR								
SBR42	50	3.0	41	11	18	30	118.5	1.08

out in the following manner: First, solvent–monomer premixes were prepared batchwise which consisted of 20% monomer and 80% hexane solvent by weight. In order to remove impurities, such as water, that could deactivate the initiator, premixes were passed through drying columns that were packed with molecular sieves and silica gel. The total residence time in the drying columns was approximately one h, and all premixes were tested for impurity level and found to have less than 2 ppm water equivalent impurity. A low premix impurity level is requisite for anionic polymerizations, due to the sensitivity of the initiator and consequent impact on polymer molecular weight.

Polymerizations were carried out batchwise in temperature-controlled reacting vessels with either a one or five gallon volume. Reactors were filled with the premix, and then the modifier, N,N,N',N'-Tetramethylethylenediamine (TMEDA), and the initiator, n-Butyllithium (n-BuLi), were added. Isothermal temperature control was provided by an integrated glycol cooling/heating system. Following the kinetic polymerization models, established previously at The Goodyear Tire & Rubber Company,[26,27] the reactor temperature and TMEDA level were set to achieve the desired microstructure, and the appropriate amount of n-BuLi was added to achieve the desired molecular weight.

After polymerizations were completed, reactions were terminated by the addition of ethanol, and an antioxidant and UV-stabilizer were added to increase the "shelf-life" of the polymers. Polymers were subsequently dried in a heated vacuum oven to remove residual solvent. After the polymers were dried, they were characterized for molecular weight and molecular weight distribution by GPC; and complete characterization of BR and SBR microstructures was carried out by FTIR and NMR techniques. Characteristics of the polymers used for this study are shown in Table I.

Blend Preparation

Combinations of polymers, expected to show transitions in experimentally accessible temperature
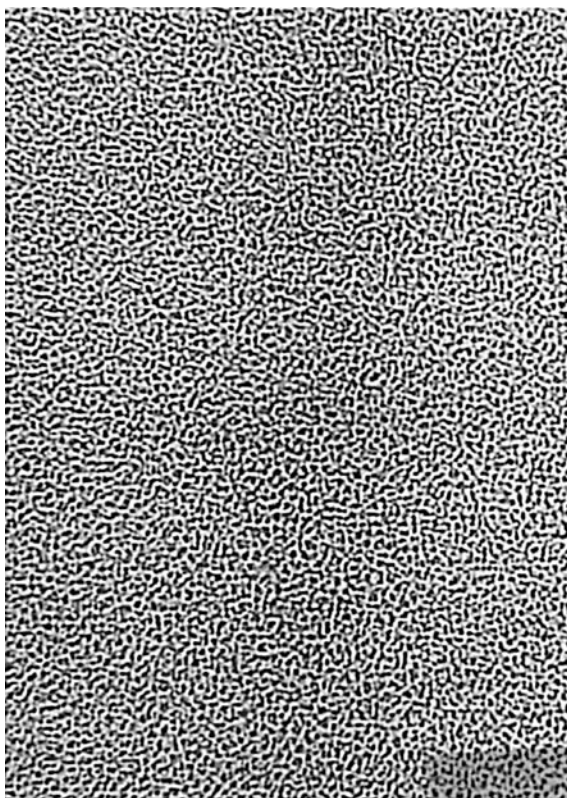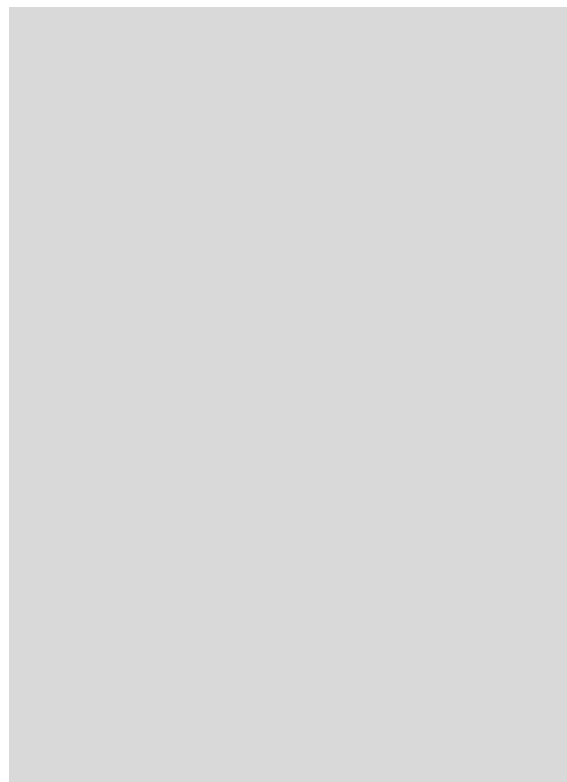
a)   b)

Figure 2   60/40 SBR42/BR (91-08) blend 250×micrographs: (a) not annealed and (b) annealed at 175°C.

ranges, were solution-blended in toluene (8% polymer by weight) with the following SBR/BR weight ratios: 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10. Solutions were placed on a shaker overnight to ensure complete dissolution. These polymer-toluene solutions were then filtered through a 0.45 micron microfilter to remove any

contaminants and were poured into a pan for evaporation. Also, slides for microscopy and light scattering were prepared by solvent casting. The cast solutions were allowed to dry slowly under a Petri dish in a hood for 48 h. This was followed by 24 h in a vacuum oven at 40°C to ensure complete evaporation of the toluene solvent.
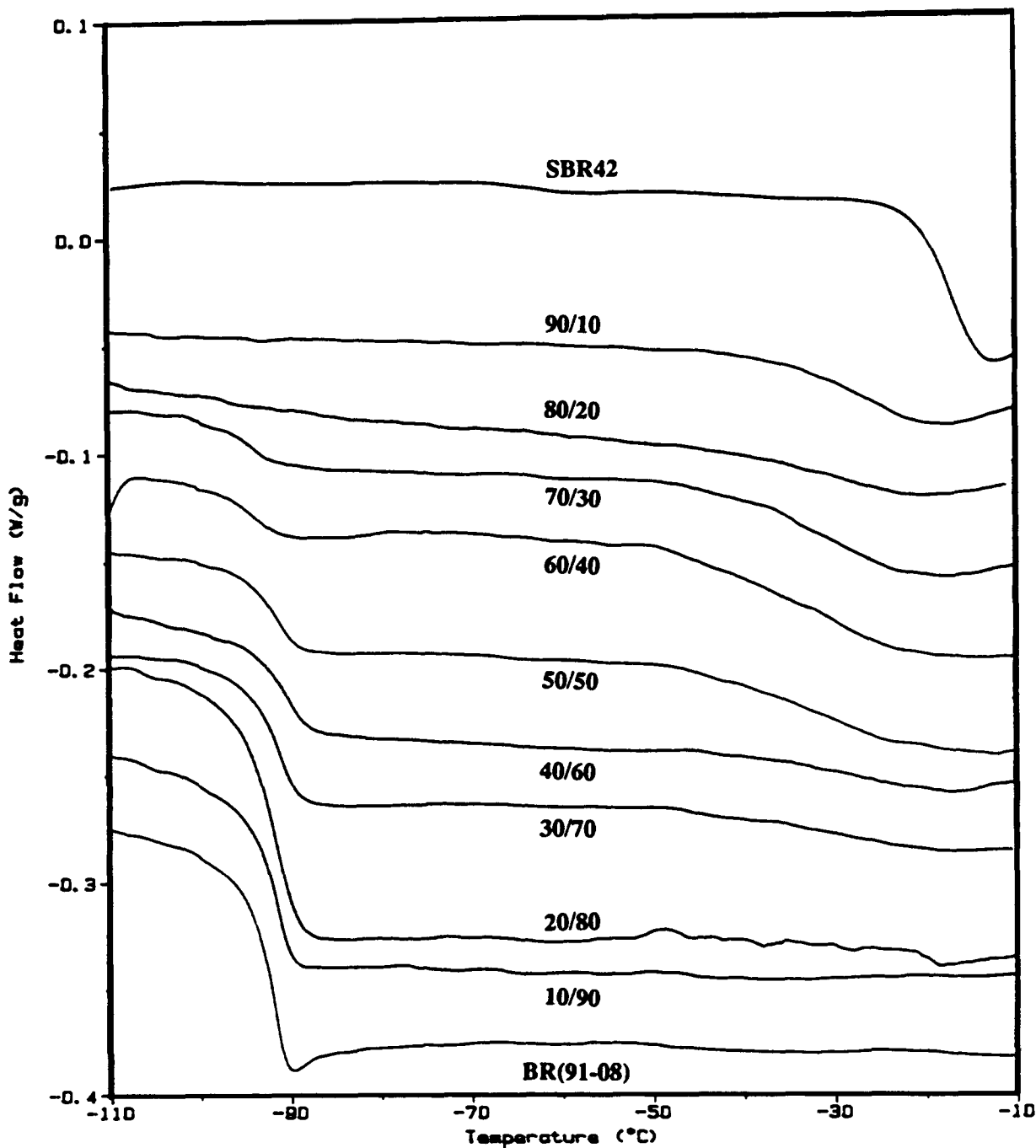

Figure 3 The effect of blend composition on SBR42/BR (91-08) DSC thermograms; heating rate = 10°C/min.

Blend Analysis

Optical microscopy and differential scanning calorimetry (DSC) were used to evaluate the accuracy of the predicted UCSTs. Optical micrographs of solution cast blends were prepared using a Leitz Laborlux 11 Pol S Optical Microscope. Figure 2 illustrates the change in blend morphology that takes place as the sample is heated above its UCST. Originally, the as-cast film had a course, two-phase morphology, with a phase dimension ranging from 5 to 10 microns. After annealing at 175°C for 30 min,
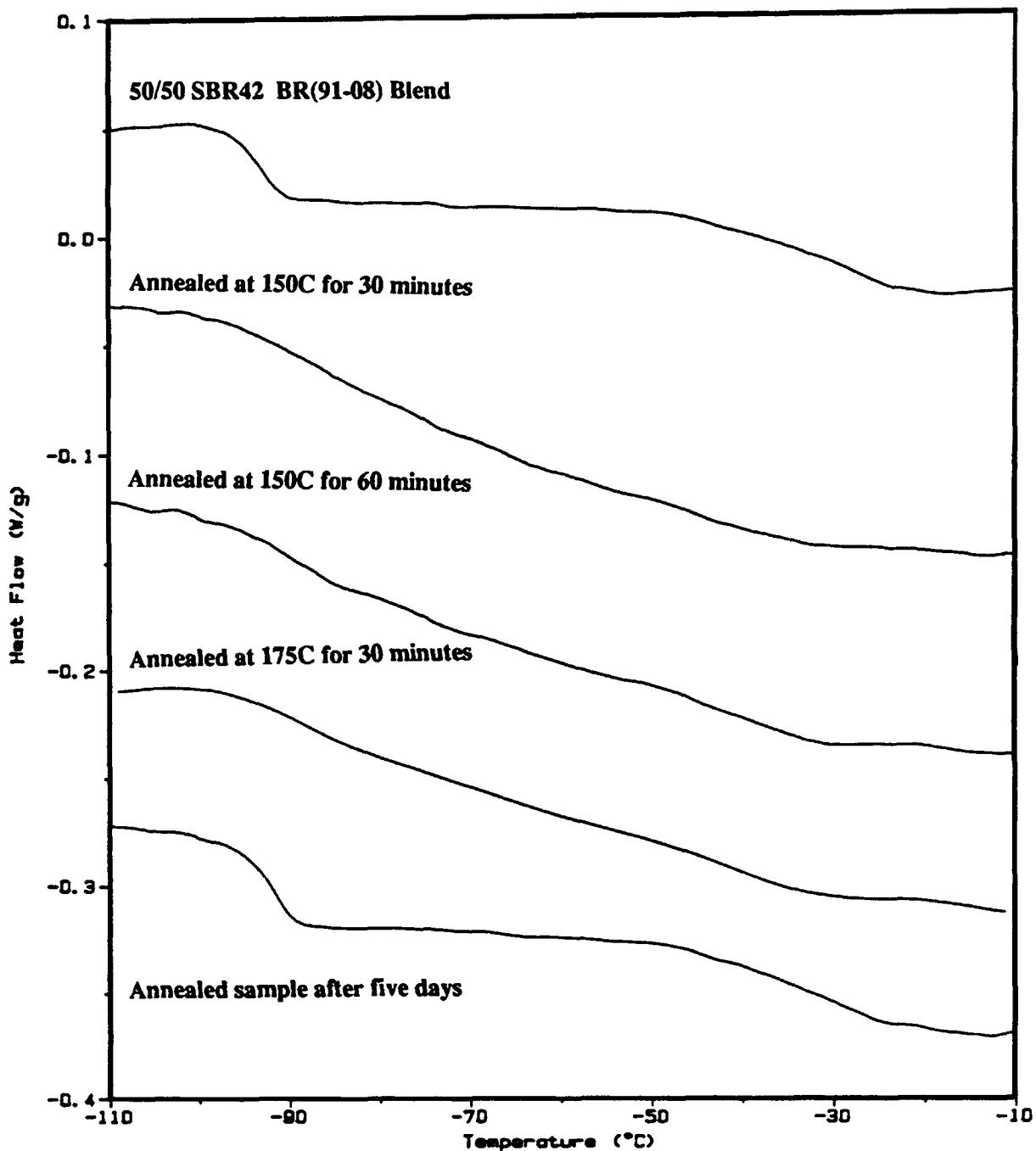
Figure 4   The effect of annealing 50/50 SBR42/BR (91-08) blends at various temperatures; bottom trace is that of a previously annealed sample that was allowed to stand at room temperature for five days; heating rate = 10°C/min.

the blend became miscible, with no evidence of phase structure. This indicates that the annealing temperature was above the UCST, and the time was sufficient to allow the phase change fully to take place.

DSC annealing experiments are useful as a means of determining approximately the phase transition temperatures of elastomer blends. If two polymers are immiscible, the DSC thermogram will exhibit two distinct T_gs at values similar to those of the parent polymers. Conversely, a miscible blend has a single T_g intermediate between the two, and various degrees of miscibility are illustrated by the width of the T_g transition. This type of analysis is applicable only for polymers that have T_gs of sufficiently different temperatures, due to the difficulty in resolving individual transitions on the DSC trace. By annealing the SBR/BR blends at various temperatures, followed by quenching, and subsequent thermal analysis, it is possible to identify the approximate cloud point curve for a particular blend. In other words, if a blend exhibits two T_gs before annealing and only a single T_g after annealing, the blend passed through a phase transition during the annealing process. This technique was used to assess the accuracy of the phase diagrams calculated from the X parameters of Sakurai et al.[25]

A Du Pont Instruments 912 DSC was used to determine DSC thermograms and to anneal the samples. After annealing, the samples were quickly removed and placed on the metal working surface to cool quickly to room temperature while the heating element cooled. This room temperature quench was sufficient to lock in the annealed structures and showed no differences when compared to samples that were quenched in liquid nitrogen. After the heating element cooled to below room temperature, the pans were placed in the usual manner and further cooling proceded via liquid nitrogen addition.

RESULTS AND DISCUSSION

Results are illustrated in Figure 3 for a series of SBR(42)/BR(91-08) blends. The traces in the top and bottom rows are those of the homopolymers, which indicate the T_g of the SBR is $\sim$ $-20°$C while that of the BR is $\sim$ $-95°$C. Two distinct peaks are observable for SBR/BR blend compositions of 30/70, 40/60, 50/50, 60/40, and 70/30, indicating various degrees of immiscibility.

The effect of annealing this blend combination is illustrated in Figure 4. Here, the top trace is that of the 50/50 blend, which indicates two T_gs. After

annealing at 150°C, the two distinct T_gs have disappeared and only a single broad T_g remains. The thermograms for samples annealed at 150°C, for 30 and 60 min, are nearly identical, indicating that 30 min is sufficient time for phase dissolution to occur. Also, the samples annealed at 150°C have a nearly identical thermogram as that of the 175°C sample, therefore, a temperature of 150°C is sufficient for the system to become miscible. The bottom trace is that of a previously annealed, quenched, and analyzed sample, which was allowed to stand at room temperature for five days. This illustrates the reversibility of the process, in that the thermogram is essentially identical to the initial, unannealed blend trace at the top.

Although this is an indirect method, it does allow estimation of the spinodal phase boundary. More accurate determination of the phase transition temperatures and the phase separation kinetics will be carried out later, using laser light scattering. For now, this thermal analysis provides a means of determining approximate phase diagrams, and is therefore sufficient for the design of chemical pinning[30] experiments to lock in different morphologies. This will be the focus of future work.

Similar analyses were carried out for many of the different blend combinations. After completion of the annealing experiments, a phase diagram (Fig. 5) was constructed to compare DSC data vs. the theoretical curve. For this blend, with a 60,000 Mn BR, the predicted phase boundaries are in good agreement with the DSC results.

To carry out successfully the curing reactions on different morphologies, it is necessary to identify a
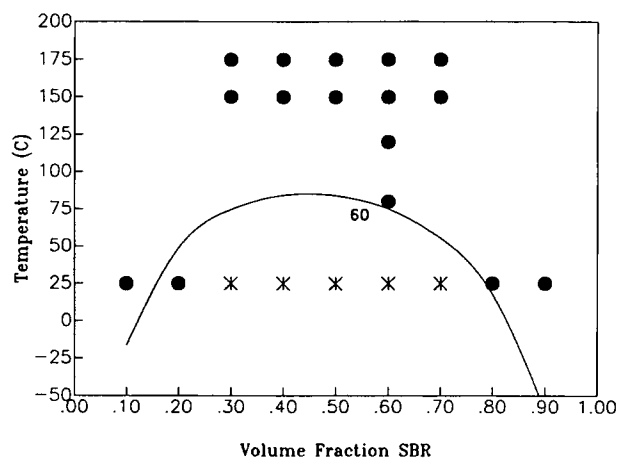
Figure 5   Results of annealing SBR42/BR91-08 (60,000 M_n, 8% vinyl) blends vs. calculated phase diagram; ($*$) immiscible, and ($\bullet$) miscible, based on DSC analysis.
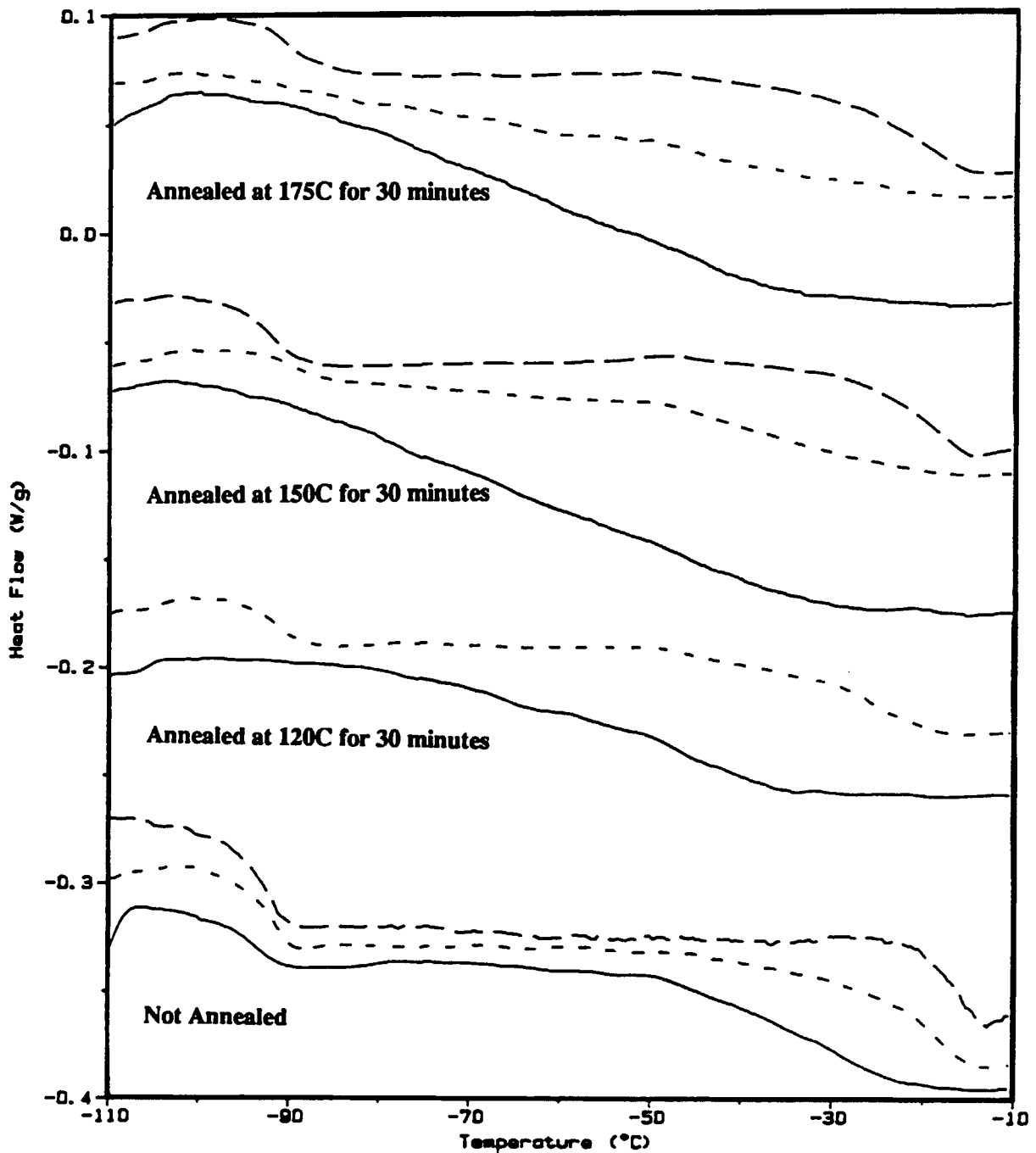
Figure 6 The effect of molecular weight of the polybutadiene blend component on 60/40 SBR42/BR cloud point, as determined by DSC annealing experiments; (—) BR (91-08) 60,000 M_n, (- - -) BR (90-84) 131,000 M_n, (– – –) BR (91-17) 290,000 M_n; heating rate = 10°C/min.

blend combination with UCST between 130 to 150°C. Blends of the SBR, with the 60,000 Mn BR, had too low a UCST to be used in such experiments, consequently, a combination with a higher UCST was sought. A more useful combination was pro-

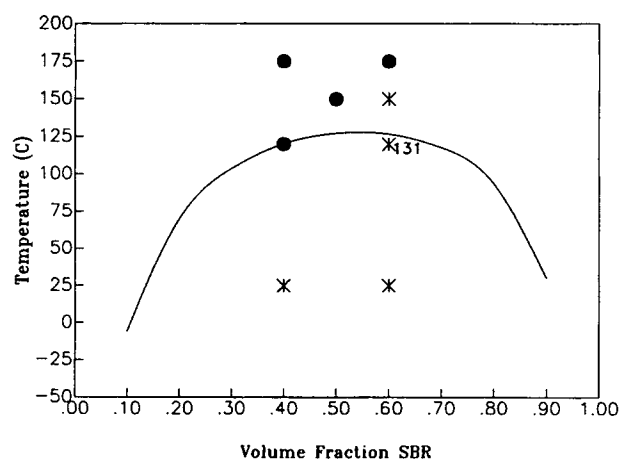duced by increasing the molecular weight of the BR blend component.

Figure 6 shows the DSC annealing results of 60/40 blends of SBR(42) with BRs of three different molecular weights at 120°C, 150°C, and 175°C. The
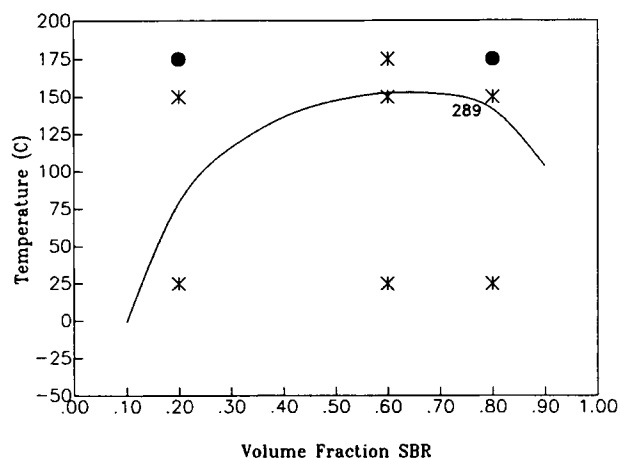
solid line shows the result, already discussed, with the 60,000 Mn BR, which has a relatively low UCST. The dotted and broken lines illustrate the changes that occur when higher molecular weight BRs (131,000 and 289,000 g/mol, respectively) are considered. Phase dissolution of the former blend occurs between 150 and 175°C, while for the highest Mn BR, no phase dissolution occurred, even when blends were annealed at 175°C. Figures 7 and 8 show that the phase diagrams for blends, with the higher molecular weight BRs, are also approximately consistent with theoretical predictions.

CONCLUSION

Bearing in mind that the study of Sakurai et al.[25] did not take into account potential effects, such as possible composition and molar mass dependence of χ, and the difference between *cis-* and *trans-*1,4 microstructures, our investigations indicate that the monomer-monomer χ-interaction-parameters, derived from the SANS experiments, are sufficiently accurate to design SBR/BR blend systems that will exhibit phase transitions at desired temperatures. Even though the SBRs used for the SANS experiments, had a limited range of microstructures, our results show that the χ values obtained can be used to target structures outside the range of those previously studies with reasonable success, despite the sensitivity of the calculations to small changes in microstructural content, and the inherent limitations of the Flory–Huggins treatment. The accuracy

Figure 8 Results of annealing SBR42/BR91-17 (289,000 M_n, 8% vinyl) blends vs. calculated phase diagram; (✳) immiscible and (○) miscible, based on DSC analysis.

is sufficient to design blends that will exhibit transitions in the range of conventional curing temperatures. Because the 60/40 blend of high-vinyl, high-styrene SBR(42) with the low-vinyl, 131,000 Mn BR (90–84) exhibits a UCST that is near conventional curing temperatures, this blend combination has been chosen as the best candidate for chemical pinning experiments,[30] and this will be the focus of future work.

Figure 7 Results of annealing SBR42/BR90-84 (131,000 M_n, 8% vinyl) blends vs. calculated phase diagram; (✳) immiscible and (○) miscible, based on DSC analysis.

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