pected T_g's is not as disturbing as it might be; it has been noted several times[14,15] that DSC data sometimes reveal only one of two expected T_g's in block copolymer samples since the other transition may be broadened so much that it is not observed on the DSC trace. The possible second transition seen in mix 23 is at too low a temperature to be associated with the types of styrene phases considered here. If our S–DMS diblock copolymer/PS mixtures can exist either with a mixed styrene phase or with S microphases and separate PS phases, depending on temperature, then our data can be rationalized. There appears to be no way, at present, of predicting the morphology of other block copolymer/homopolymer mixtures. The S–I/PS, the S–I/PI, and the S–B–S/PB mixtures observed by others using different methods may well have a different room-temperature morphology than our samples. Furthermore, the cooling history of these other samples is not known to us.

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Properties of Block Copolymers and Homopolymer Blends Comprised of 1,2-Polybutadiene and 1,4-Polybutadiene

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ABSTRACT: Four diblock copolymers, each comprised of a 1,2-polybutadiene block (99% 1,2) and a 1,4-polybutadiene block (36% cis, 51% trans, 13% 1,2), were examined along with several blends of the corresponding homopolymers. Dynamic mechanical tests, differential scanning calorimetry, and transmission electron microscopy were used to determine the homogeneous or heterogeneous character of each material. The overall trends of the present results combined with extensive data obtained previously on another set of double-diene materials are explained in a unified fashion with a type of phase diagram in which three separate regions can be identified—(i) a high molecular weight region in which block copolymers and the corresponding polymer blends are heterogeneous materials, (ii) a low molecular weight region in which blocks and blends are homogeneous materials, and (iii) an intermediate region, spanning a range of at least a factor of 5 in molecular weight, in which a block copolymer is homogeneous but its corresponding blend is heterogeneous. It is in this third interesting and largely unexplored region in which most of the polymers of the present study lie.

Introduction

Diblock copolymers and two-component polymer blends in which both constituents are rubbery at room temperature offer certain advantages in a research program aimed at establishing connections between molecular structure, morphology, and physical properties of multicomponent polymer systems. The rubbery nature of the constituents helps to minimize various nonequilibrium effects, which can influence the behavior of glassy/rubbery and glassy/glassy systems. In addition, if the rubbery constituents are based on diene monomers, chain microstructure can be used to vary molecular architecture while leaving chemical composition unchanged. The diblock copolymers[1] and homopolymer blends of 1,2-polybutadiene (1,2B) and 1,4-polybutadiene (1,4B) described in this paper represent one example of this type of two-component polydiene system.

Previous work[2–6] in this laboratory showed that diblock copolymers of 1,4-polybutadiene (45% cis, 45% trans, 10% 1,2) and *cis*-1,4-polyisoprene (1,4I) are homogeneous materials in the range of 250 000 molecular weight. On the other hand, the corresponding homopolymer blends of *cis*-1,4-polyisoprene and 1,4-polybutadiene are heterogeneous in essentially all proportions;[2,5] binary and ternary blends of a 1,4I/1,4B diblock with one or both of the corresponding homopolymers may be homogeneous or heterogeneous, depending upon the composition of the blend and the relative segment lengths of the copolymer.[2,4,5] In the previous work, the two components 1,4I and 1,4B differed both in microstructure and in chemical composition. Examination of homopolymer blends of 1,4I with polybutadienes of various microstructures[6] indicated that both of these variables affect the structure and properties of the materials. On the basis of these observations it appeared that copolymers and blends of 1,4-polybutadiene and 1,2-polybutadiene would be suitable for examining the role of chain microstructure alone and would lead to useful comparisons with the 1,4I/1,4B system studied earlier.

Experimental Section

Materials. The block copolymers and homopolymers used in this study were synthesized by Dr. Adel F. Halasa of the Firestone Tire and Rubber Co. A novel feature of this set of polymers is the unusually high vinyl content (99%) of the atactic

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Table I
Characterization of Polymers

	mol wt[b] × 10^{-5}			wt fraction	
sample code[a]	1,2B block[c]	1,4B block[d]	impurity[e,f]	impurity[f]	1,2 block[g]
90/0	0.85 (±0.09)	0	1.87	0.03	1.00
30/50	0.32 (±0.04)	0.52 (±0.07)	1.86	0.06	0.38 ± 0.05
30/100	0.31 (±0.06)	1.02 (±0.12)	3.01	0.08	0.23 ± 0.05
30/150	0.28 (±0.03)	1.37 (±0.16)	4.08	0.14	0.17 ± 0.02
30/200	0.26 (±0.08)	1.76 (±0.19)	5.00	0.15	0.13 ± 0.04
0/100	0	0.97 (±0.10)	2.20	0.12	0

[a] The first entry represents the nominal value of the molecular weight (in thousands) of the 1,2B sequence; the second entry provides similar information for the 1,4B block. [b] Values of molecular weight and error estimates based on a variety of characterization methods (see text and ref 10). [c] 99% 1,2-polybutadiene microstructure.[8,9] [d] 36% cis 1,4, 51% trans 1,4, 13% 1,2-polybutadiene microstructure. [e] Always approximately 2× diblock molecular weight, suggesting coupling during termination. [f] Value determined by HPSEC. [g] Does not include the 13% vinyl content of the 1,4B block.

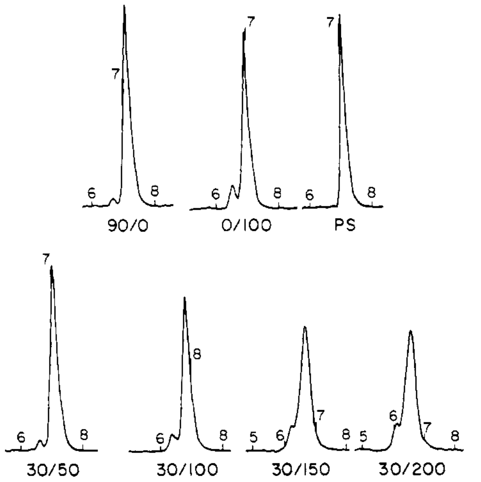

Figure 1. Refractive index increment vs. elution volume (mL) from HPSEC experiments on the four diblock copolymers of 1,2B and 1,4B and on the corresponding homopolymers. For sample codes, see Table I. Also shown is the trace for a polystyrene standard (M_n = 100 000; M_w/M_n = 1.06).

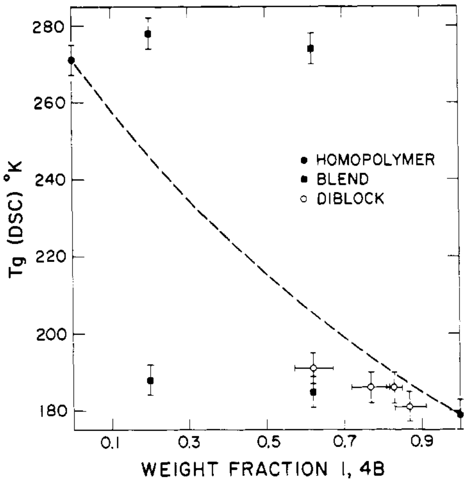

Figure 2. Composition dependence of the glass transition temperatures as determined by DSC measurements.

1,2-polybutadiene sequences; this microstructure is obtained via butyllithium-initiated anionic polymerization of 1,3-butadiene monomer in hexane in the presence of a polar modifier, bis(piperidino)ethane (DPE) as reported in detail by Halasa and coworkers.[1,7,8] The 1,4-polybutadiene microstructure of the present set of polymers is 36% cis, 51% trans, and 13% 1,2, comparable to the 1,4B materials studied previously. Detailed microstructural analyses were carried out at Firestone[8,9] using infrared and ^{13}C NMR techniques. Molecular weights were determined by a variety of methods at Firestone (GPC, yield plus stoichiometry, and first-block (1,4B) sampling plus copolymer IR analysis) and by high-performance size exclusion chromatography (HPSEC) in this laboratory[10] using a set of DuPont Zorbax PSM Bimodal-s columns. Figure 1 shows HPSEC traces for all six polybutadiene samples and for one of the ten polystyrene standards used to calibrate the instrument. All samples contain a small amount of a high molecular weight impurity (approximately twice the molecular weight of the main peak), which probably arises from a coupling reaction at the end of the "living" synthesis. The diblock samples are essentially free of unwanted 1,4B homopolymer. Table I summarizes the results of the characterization experiments.

Experimental Methods. Uniform films of about 1-mm thickness were prepared by spin casting[5,11] filtered solutions of 5 wt % polymer in cyclohexane. The spin caster was blanketed with dry nitrogen, and all specimens were stored in the dark under vacuum prior to use. HPSEC analyses at various points in the experimental program indicated that our handling procedures were successful in eliminating any significant degradation of the polybutadiene chains. As in previous studies it was necessary to cross-link some of the samples for ease in handling in certain mechanical and microscopy experiments; this was accomplished by using a 3-MeV electron beam and various doses ranging from 2 to 30 Mrd. Mechanical tests were carried out on a nitrogen-blanketed Rheovibron DDV-II-C viscoelastomer at temperatures between −100 and +20 °C at a fixed frequency of 3.5 Hz; appropriate apparatus correction factors[6,12] and tensile gripping methods[13] were applied. Thermal analysis was carried out between −125 and +30 °C on a Perkin-Elmer DSC-II at a heating rate of about 20 °C/min. Electron micrographs were obtained on a Philips EM200 microscope; thin sections of previously hardened samples were obtained with an LKB Ultratome III microtome fitted with freshly made glass knives. The necessary hardening was accomplished by exposing previously cross-linked specimens to a 120 °C mixture of sulfur, rubber accelerator (*N-tert*-butyl-2-benzothiazolyl)sulfenamide; R. T. Vanderbilt Co.), and zinc stearate. This "ebonite method" was first reported by Smith and Andries[14] as a means of obtaining contrast in electron microscopy studies of various elastomer blends. As in previous studies in our laboratory[2,3,5] we found that this simple and reliable method resulted in adequate contrast for electron microscopy of the double-diene system under investigation.

Results

The determination of whether or not diblock copolymers and polymer blends are heterogeneous or homogeneous is best accomplished[15] by examining the results of several complementary experiments; the array of data presented in Figures 2–5 and the micrographs of Figures 6–8 have been obtained with this objective in mind. In Figure 2, the observed glass transition temperatures obtained by DSC measurements are plotted as a function of 1,4B weight fraction; the dashed curve is a plot of the Fox equation,[16] which has been used frequently to describe the composition dependence of the glass transition temperature of random copolymers and miscible polymer blends. The transition temperatures of the homopolymers are 271 and 179 K, respectively, for 1,2B and 1,4B. Both of the

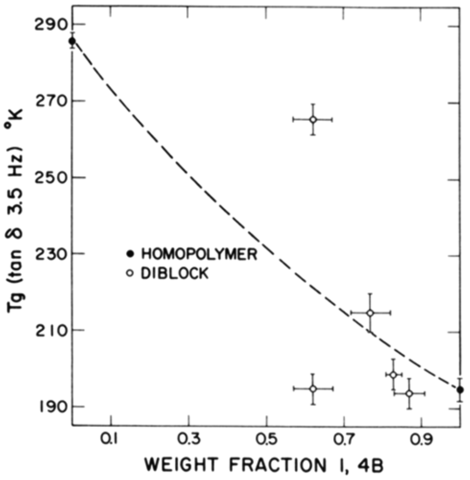

Figure 3. Loss tangent (3.5 Hz) maxima plotted as a function of composition. All samples were cross-linked with a 2-Mrd dose of electrons.

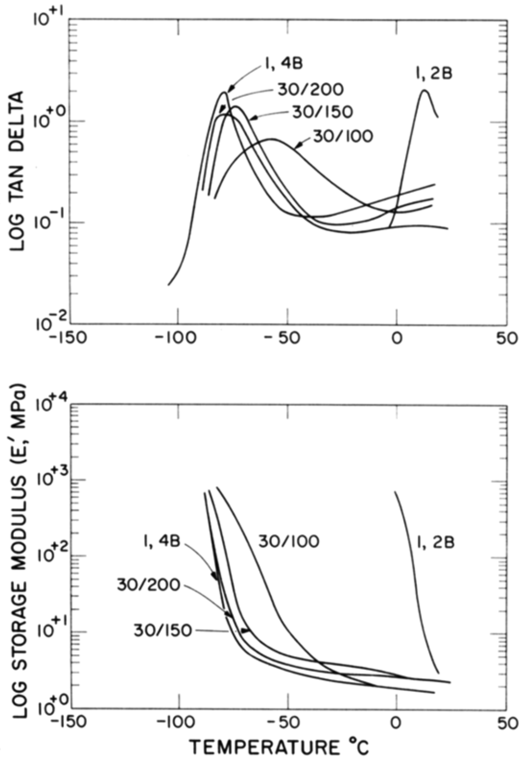

Figure 4. (Top) Loss tangent (3.5 Hz) plotted as a function of temperature for three of the diblock copolymers and the corresponding homopolymers. (Bottom) Storage modulus curves for the same samples.

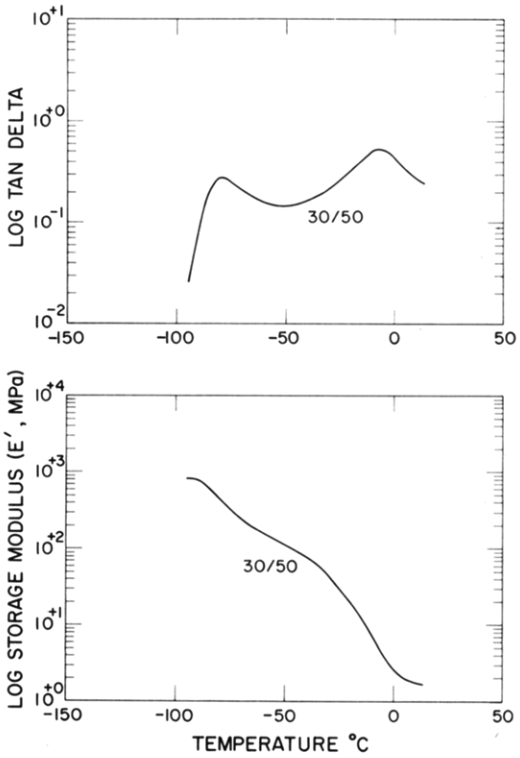

Figure 5. Loss tangent and storage modulus vs. temperature for diblock copolymer sample 30/50.

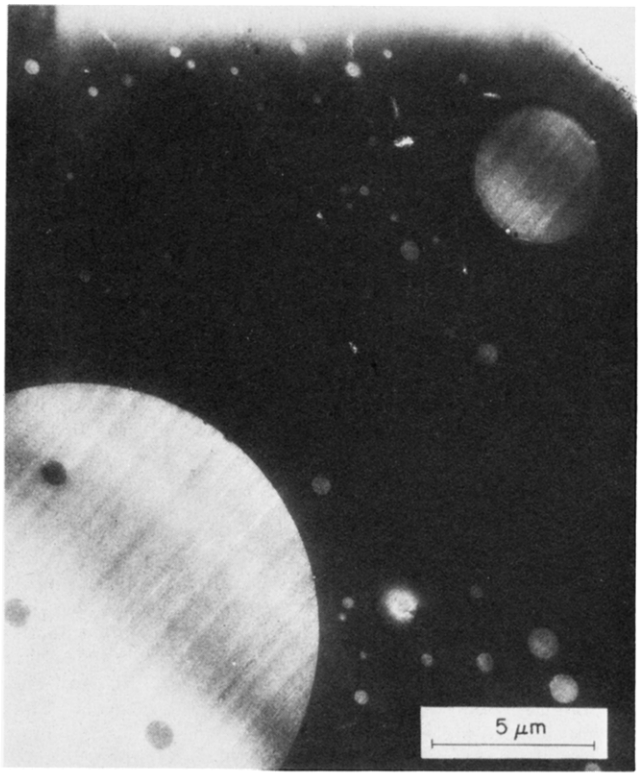

Figure 6. Transmission electron micrograph of a blend of 1,2B and 1,4B (38 wt % 1,2B). The blend was cross-linked with a 30-Mrd dose of electrons, stained,[14] and sectioned prior to observation in the microscope.

homopolymer blends exhibited two distinct glass transitions located at temperatures close to the homopolymer T_g values. In these DSC experiments, only one clear transition could be observed for each of the four diblock copolymers.

A slightly different picture is obtained from the dynamic mechanical measurements. Figure 3 is a plot of the location of the maxima in the viscoelastic loss tangent, tan δ, for the four block copolymers and the corresponding homopolymers. Compared to the DSC data, all transitions appear at higher temperatures in the dynamic mechanical experiments, a phenomenon that has been observed and discussed in previous studies on similar materials.[5] More significant, however, is the fact that two distinct transitions are obtained in the viscoelastic experiments for one of the diblocks (30/50) whereas only one transition could be seen in the DSC experiments. The increased resolving power of low-frequency dynamic mechanical measurements over DSC experiments for materials of this type has also been reported previously.[2,5,6,17]

That the 30/50 diblock is substantially different in mechanical behavior from the other materials listed in

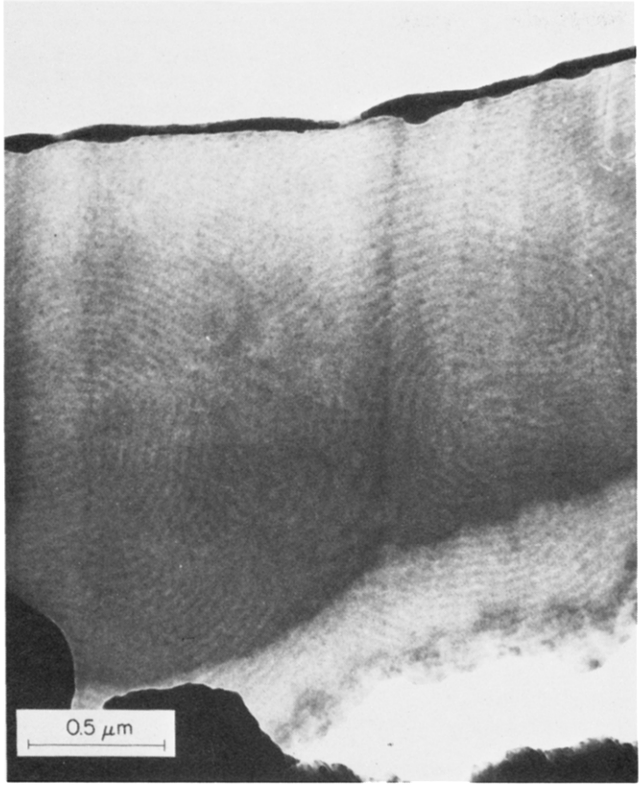

Figure 7. Transmission electron micrograph of diblock 30/50. Specimen preparation procedures identical with those of Figure 6.

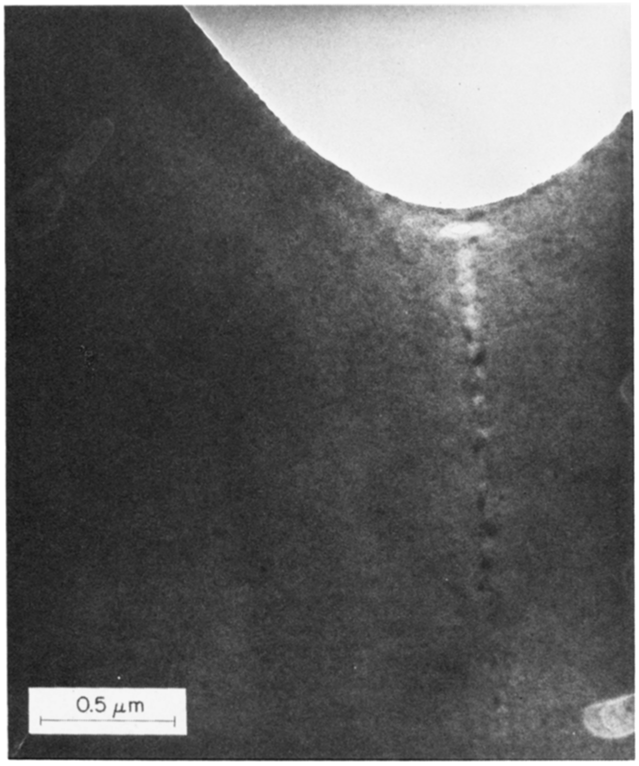

Figure 8. Transmission electron micrograph of the 1,2B homopolymer, prepared under conditions identical with those of Figure 6. Samples 1,4B, 30/100, 30/150, and 30/200 all showed micrographs that were similar to this figure.

Table I is brought out more convincingly in Figures 4 and 5, in which the entire set of storage modulus (E') and loss tangent ($\tan \delta$) data is presented. In Figure 4 it is clear that only a single inflection is observed in the storage modulus–temperature curves for the two homopolymers and for copolymers 30/100, 30/150, and 30/200. There is a systematic shift of the curves toward that of the 1,4B homopolymer as the percentage of 1,4B in the copolymer increases. A similar trend is observed in the loss tangent curves shown in Figure 4. Figure 5 shows the corresponding plots for copolymer 30/50. Two distinct transitions are observed in both the storage modulus and the loss tangent curves.

When viewing the electron micrographs presented in Figures 6–8, one should keep in mind that selective staining in a double-diene system is a much more difficult task than for the more familiar case of a polystyrene/polydiene system. It is quite clear, however, that the selected staining method[5,14] is successful in exposing the two-phase structure of homopolymer blends of 1,2B and 1,4B (Figure 6). Here large regions of 1,2B are imbedded in the 1,4B continuous phase and some occluded 1,4B appears within the 1,2B domains. Similar morphologies were observed earlier for solvent-cast homopolymer blends of 1,4B and *cis*-1,4-polyisoprene.[2,3,5] Figure 7 is a high-magnification micrograph of the morphology observed for the 30/50 diblock; a pattern of curved lamellae is just barely observable in the figure. Figure 8 is included here to show that the structure seen in Figure 7 is not artificially introduced by the staining method. Figure 8 is a micrograph of the 1,2B homopolymer that had been stained and sectioned in a manner identical with that for samples of Figures 6 and 7. When handled in this way, both of the homopolymers and diblock copolymers 30/100, 30/150, and 30/200 showed a total absence of structure similar to that of Figure 8.

Discussion

Consideration of the body of experimental evidence presented in the previous sections leads to the following conclusions regarding the room-temperature behavior of the 1,2-polybutadiene/1,4-polybutadiene system:

1. Blends of homopolymers of 1,4B and 1,2B ($M \approx 100\,000$) are heterogeneous materials.

2. Diblock copolymers comprised of 1,4B and 1,2B are either homogeneous or heterogeneous, depending on the overall molecular weight of the copolymer and the relative lengths of the 1,4B and 1,2B segments. Specifically (a) the lowest molecular weight diblock ($M = 80\,000$), having the highest proportion of 1,2B (sample 30/50), is a heterogeneous material similar to conventional microphase-separated block copolymers and (b) the higher molecular weight samples ($M > 130\,000$), containing a lower proportion of 1,2B (samples 30/100, 30/150, and 30/200), are all homogeneous diblock copolymers.

These conclusions are somewhat different from those drawn from the extensive data obtained previously[2,3,5] on the 1,4I/1,4B system; in that case all the diblocks studied ($M \cong 250\,000$) were homogeneous materials while all homopolymer blends of 1,4I and 1,4B ($M \sim 100\,000$) were heterogeneous. Both investigations taken together raise some important questions regarding rubbery/rubbery diblock copolymers and the corresponding homopolymer blends. First, is it reasonable that the single junction between long sequences in a diblock copolymer can exert sufficient influence on the thermodynamics of phase separation to change an otherwise incompatible heterogeneous two-component system into a homogeneous one? Second, can the trend seen in the 1,2B/1,4B diblocks—tending toward homogeneous behavior as molecular weight increases and relative block length ($M_{1,2}/M_{1,4}$) decreases—be explained in a self-consistent manner? Finally, can any such explanation be based on thermodynamic considerations alone, without resorting to kinetic arguments[18] to

Table II
Quantitative Considerations of Selected Polymer Pairs

(a) Solubility Parameters, δ, $(\mathrm{cal/cm^3})^{1/2}$

polymer	range of δ in lit.[23,24]	value selected for detn of α[23,24]
polystyrene (PS)	8.6-9.7	9.12
1,4-polybutadiene	8.35-8.60	8.38
1,2-polybutadiene	8.10	8.10
cis-1,4-polyisoprene	7.9-8.35	8.22

(b) Interaction Parameter, α, m^{-3}

polymer pair, AB	$10^3 T^{-1} \times (\delta_A - \delta_B)^2$ [a]	α	$M_{\mathrm{crit}}^{\mathrm{diblock}}$ [b]	$M_{\mathrm{crit}}^{\mathrm{blend}}$ [c]
PS/1,4B	1.5	1111 [d]	14 300	2 700
1,2B/1,4B	0.26	193	76 800	13 800
1,4I/1,4B	0.081	60.0	247 000	42 000
1,4I/1,2B	0.048	16.3	930 000	76 200

[a] For the polystyrene-containing pair, the glass transition temperature of PS ($T = 373$ K) was used; for all other pairs $T = 298$ K. [b] Obtained by using Helfand's program to search for the molecular weight at which the free energy of mixing, ΔG, equals zero for the case of a diblock copolymer in which $M_A + M_B$ and the weight fraction is 0.5. [c] Obtained by searching for the molecular weight at which $\delta^2 G/\delta V_A^2 = 0$ (spinodal) using the Flory-Huggins expression[22b,26] for a 50:50 AB polymer blend. Here M is the number-average molecular weight for the two-component system, which allows for the possibility that the two monodisperse homopolymers in the blend may not be of identical molecular weight. [d] This value of α is used by Helfand[20] for PS/1,4B and is based on the experiments of Rounds.[25] All other values of α were obtained by scaling to this PS/1,4B value.

describe the heterogeneous-to-homogeneous transitions in these materials?

The answers to all of these questions may be sought within the framework of the various thermodynamic theories for microphase separation in block copolymers.[19-22a] All of the aforementioned theories suggest that the critical molecular weight, M_{crit}, for phase separation in block copolymers is higher than for the case of the corresponding homopolymer blend. Leibler[21] makes the explicit prediction that a value of 5.25 is to be expected for the ratio $M_{\mathrm{crit}}^{\mathrm{diblock}}/M_{\mathrm{crit}}^{\mathrm{blend}}$ for a hypothetical symmetric diblock copolymer of equal block lengths. Thus it is expected that there is a regime of molecular weight in which it is thermodynamically stable for a homopolymer blend to be heterogeneous while the corresponding diblock is homogeneous, and this is one of the essential qualitative features observed in our experiments. It would be particularly satisfying to take this qualitative explanation one step further and obtain quantitative agreement between theory and our entire set of current and past experimental findings. The theory of Helfand lends itself readily to quantitative comparison with experiment owing to the fact that a Fortran listing of the theory has been published.[20]

We have used Helfand's program in the following manner to explain the results of our experiments. We first ran Helfand's program through several sensitivity tests and determined that, of the various input data needed,[20] only the temperature-dependent interaction parameter, α, had a significant effect on the numerical value of $M_{\mathrm{crit}}^{\mathrm{diblock}}$ for a given AB pair. We also determined that, except for the repeat unit molecular weights of the A and B blocks, none of the input parameters exerted a significant influence on the shape of the composition-dependent boundary between homogeneous and heterogeneous materials. We estimated unknown values of α for our polymer pairs (1,4I/1,4B and 1,2B/1,4B) by assuming that α is proportional to the quantity $T^{-1}(\delta_A - \delta_B)^2$, where δ_A and δ_B are the solubility parameters[23,24] for the polymers in question. The δ values for PS, 1,2B, and 1,4B are based on Small's group additivity values. The PI δ value given in Table II was selected such that the experimental data of Ramos[2] on diblocks and blends of PI and 1,4-B were consistent with the predicted phase transitions of the Helfand and Flory-Huggins theories. Table II summarizes this method of estimating α.

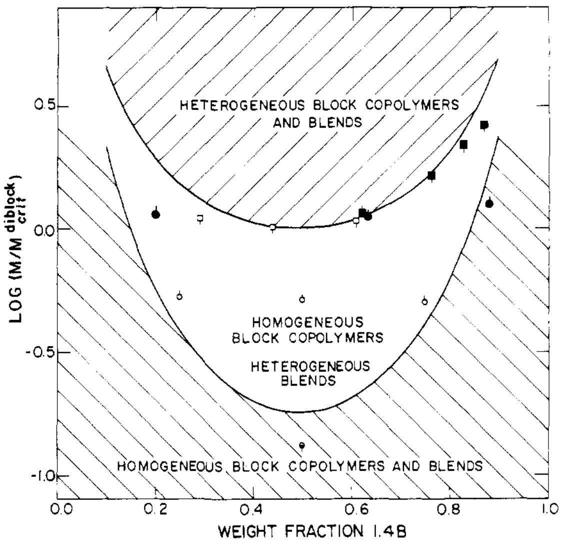

Figure 9. Phase diagram showing the three distinct regions discussed in the text. Data points identified as follows: square points, diblock copolymers; circles, polymer blends; pip up, heterogeneous material; pip down, homogeneous material; solid points, 1,2B/1,4B; open points, 1,4I/1,4B; half-open point, 1,4I/1,2B (for this point, the abscissa represents the weight fraction of 1,2B).

Having estimated the needed input parameters, it was then possible to use Helfand's program to estimate the molecular weight at the transition from homogeneous to heterogeneous behavior for a diblock of specified chemical composition and segment molecular weight ratio. This was accomplished via an iterative search for the value of M at which the free energy of mixing, ΔG, equals zero.[20] For the case of blends, the appropriate Flory-Huggins expression[22b,26] was used to calculate a spinodal curve which defines the boundary between homogeneous and heterogeneous blends. Figure 9 is a plot of these boundaries which applied to either the case of 1,2B/1,4B or of 1,4I/1,4B. (The parabolic shapes of the curves differ only slightly for these two cases; this general geometric form would change significantly only if the ratio of repeat unit molecular weights differed substantially from unity.) Table II lists the values of $M_{\mathrm{crit}}^{\mathrm{diblock}}$ needed to redimensionalize the ordinate in Figure 9. Also shown in Figure 9 are 14 data points representing the four diblocks and three blends of the 1,2B/1,4B system studied here, the three diblocks and the three blends of 1,4I/1,4B studied previously, and a single blend of 1,2B and 1,4I that has been found to be homogeneous in an ongoing parallel study in this laboratory.[27]

A detailed inspection of Figure 9 provides the desired quantitative explanation of our experimental results. First considering the 1,2B/1,4B diblocks, it is now clear that the 30/50 sample is expected to be just at the point of phase separation (i.e., on the upper curve) whereas a closely similar homopolymer blend is well above the lower curve and is therefore strongly phase separated. Furthermore, the observed homogeneity of the 30/100, 30/150, and 30/200 diblocks is now clarified owing to the fact that the data points for these samples lie on or below the upper curve in Figure 9, in the region of homogeneous block copolymer behavior. Significantly higher molecular weights would be required for the 30/200 and 30/150 diblocks to undergo microphase separation whereas the 30/100 sample is expected to be close to the regime of heterogeneous behavior. This may help to explain the unusually broad viscoelastic transition observed for sample 30/100 in Figure 3. Figure 9 also shows that diblock copolymers of 1,4I/1,4B are expected to be homogeneous in all proportions as long as the overall molecular weight of the diblock is less than about 250000, a condition that was satisfied in the earlier experimental work on these materials. Homopolymer blends of 1,4I and 1,4B were observed to be heterogeneous in this range of molecular weight, and the corresponding data points in Figure 9 do fall well above the lower boundary as required. We also note that the very low value of α (or the correspondingly high value of $M_{\rm crit}^{\rm blend}$) for the system 1,4I/1,2B in Table II explains why in earlier work[3] blends of high-vinyl polybutadiene and *cis*-1,4-polyisoprene were found to be homogeneous and why the datum point for the 1,4I/1,2B blend in Figure 9 falls below the lower curve.

The gap between the two curves in Figure 9, i.e., the region of homogeneous diblocks and heterogeneous blends for a specified AB system, while being noted earlier for certain glassy/glassy[28,29] and glassy/rubbery systems,[30] has not been heavily explored in either experimental or theoretical studies on binary and ternary blends of diblock and corresponding homopolymers. Based on the results of our earlier work on the 1,4I/1,4B system[2-5] it is possible to conclude that in this region of the "phase diagram", diblock copolymers act as homogenizing agents in a ternary mixture with the two incompatible homopolymers. On the other hand, above the upper curve in Figure 9 the well-documented emulsifying effect is observed when block copolymers are blended with the corresponding homopolymers.[31,32] Finally, it is interesting to note that our value for the ratio (Table II, Figure 9) $M_{\rm crit}^{\rm diblock}/M_{\rm crit}^{\rm blend}$ is about 5–6, obtained from calculations using the Helfand and Flory–Huggins theories as discussed above. This is in reasonable agreement with Leibler's prediction[21] of 5.25 and Meier's estimate[19] of 2.5–5.0 for the same quantity.

Summary

A set of experimental results has been reported for the particular binary system 1,2-polybutadiene/1,4-polybutadiene. Based on these results and those of an earlier study on closely similar materials, a unified explanation has been given for the behavior of rubbery/rubbery diblock copolymers and polymer blends. The explanation takes the form of a thermodynamic "phase diagram" that defines three regions that depend on molecular weight and composition. In the low molecular weight region, blends of A and B are homogeneous and the corresponding AB diblock copolymer is also homogeneous. At very high molecular weights both the blends and diblocks are heterogeneous materials. Between these regions there is a gap, which spans a range of at least a factor of 5 in molecular weight. It is in this largely unexplored region that much of the present experimental results fall. Boundaries between the various regions are readily calculated from existing theories provided that the appropriate AB interaction parameter can be estimated.

The success of the present analysis in describing the experimental findings on systems comprised of polydienes may arise in part from the fact that these are essentially nonpolar hydrocarbon molecules for which conventional Van Laar-type interaction parameters, based on the quantity $(\delta_A - \delta_B)^2$, are appropriate and for which an upper critical solution temperature (UCST) is observed. We have made relatively crude attempts,[3,33] based on rheological methods,[34] to determine the UCST values for the double-diene systems described here. The estimated UCST value of about 80 °C, the fact that the interaction parameter α varies inversely with temperature, and the tabulated estimates of $M_{\rm crit}$ provided in the present paper should serve as useful guidance in the selection of materials and operating conditions in other experimental programs (e.g., those based on scattering methods) aimed at locating homogeneous-to-heterogeneous boundaries such as those of Figure 9. These considerations may also be helpful in attempts to explore possible technological advantages of materials that lie in the relatively unexplored region in which a block copolymer is homogeneous but the corresponding polymer blend is heterogeneous.

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