Homogeneous and Heterogeneous Blends of Polybutadiene, Polyisoprene, and Corresponding Diblock Copolymers

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ABSTRACT: The miscibility of homogeneous diblock copolymers of 1,4-polybutadiene and *cis*-1,4-polyisoprene with either or both of the corresponding linear homopolymers was found to depend upon the relative lengths of the block segments and upon the coordinates of the binary or ternary mixture on the appropriate triangular composition diagram. Evidence from a variety of experiments was used to draw overall conclusions regarding the location of the diblock in these blends and its influence on physical properties. Experimental methods employed were transmission electron microscopy on suitably stained specimens, thermomechanical analysis at a heating rate of 5 °C/min, and dynamic mechanical testing at 3.5 Hz over a temperature range from −130 to 40 °C.

In previous publications we have reported on the structure and properties of three diblock copolymers of 1,4-polybutadiene and *cis*-1,4-polyisoprene[2,3] and on selected blends of these copolymers with the corresponding polybutadiene and polyisoprene homopolymers. The three diblock copolymers had identical diene microstructures (45% cis-1,4, 45% trans-1,4, 10% vinylpolybutadiene, and greater than 92% *cis*-1,4-polyisoprene) and were nearly identical in overall molecular weight (ca. 260 000). The three diblocks differed in relative lengths of the block segments of polybutadiene and polyisoprene; the values of the B/I ratio (molar) were 2/1, 1/1, and 1/2 for the three copolymers.

The results of these previous studies indicated that the three diblocks were essentially homogeneous materials whereas blends of the two corresponding homopolymers (identical in diene structure and with molecular weights in the same range as the individual block lengths in the copolymers) were clearly heterogeneous.[3] A complete study was also made of the blends of various compositions in the ternary system using the two homopolymers and one of the diblocks (1/1 mole ratio B/I and polybutadiene/polyisoprene molecular weights of 110 000/140 000).[4,5] It was concluded that this homogeneous block copolymer was soluble in either of the two homopolymers and that large amounts (>80%) of this diblock would homogenize a blend of the two incompatible homopolymers.[5,6] Preliminary results suggested, however, that when the block lengths were unequal, this mutual solubility of the homogeneous diblock and either of the two homopolymers would not always be observed; instead it was suggested that the solubility regime would be skewed to favor compositions rich in the material which comprised the longer segment of the selected diblock.[2,5,6] In the present paper we report on our experimental studies of binary and ternary blends composed of the two diene homopolymers discussed above and either of the diblock copolymers (2/1 and 1/2) containing unequal block lengths. The results presented here, coupled with earlier findings, lead to a general perspective on the structures and the range of viscoelastic response achievable using a ternary system of a homogeneous block copolymer and the two corresponding homopolymers.

Experimental Section

Details of the molecular characterization of the diblock copolymers and homopolymers are provided elsewhere.[3,5,6] Of particular interest in this paper are two of the diblocks with sample codes 2144 and 2148, 2/1 and 1/2 for the molar ratio B/I, and which have polybutadiene/polyisoprene block molecular weights of 160 000/104 000 and 78 000/192 000, respectively. The polybutadiene (BR) and polyisoprene (IR) homopolymers had molecular weights of 120 000 and 133 000, respectively.

Blends of various compositions (wt % diblock/wt % BR/wt % IR) were obtained using a slow solvent-evaporation casting technique described in detail elsewhere.[5,6] Benzene was the solvent used in the preparation of all the samples discussed here. A few samples cast from other solvents were examined;[6] the results obtained on such samples were essentially identical to those described below.

Transmission electron micrographs were obtained using a Phillips 200 microscope; adequate phase contrast was obtained[5] using the staining method of Smith and Andries.[7] Dynamic mechanical properties of the blends were determined in forced oscillation on a Rheovibron DDV-II-C viscoelastometer using appropriate tensile grip modifications[8] and loss tangent correction factors.[9] Thermal analysis was carried out on a DuPont 900 thermomechanical analyzer at a heating rate of 5 °C/min. Complete details of the procedures employed in the various experiments are reported elsewhere.[3,5,6]

Results and Discussion

Figure 1 is a montage of log tan δ vs. temperature curves obtained at a frequency of 3.5 Hz for 16 sample compositions. The location of each plot on the overall triangular diagram represents the composition of each sample according to the weight percentage of each of the three components. As expected each of the homopolymers exhibited only one damping peak located near the appropriate glass transition temperature (−82 °C for polybutadiene and −49 °C for polyisoprene). The polyisoprene-rich diblock copolymer (1/2), as reported previously,[3] also showed only one damping peak, located at −58 °C. The remainder of the blends exhibited either one or two loss peaks depending upon the composition, but all peaks were located within the limits of temperature defined by the behavior of the two homopolymers. The corresponding log E' vs. temperature curves are presented elsewhere.[6]

An important feature in Figure 1 is the fact that all binary blends of the copolymer (1/2) with IR exhibited a single loss peak. Both the position and shape of the loss peak of each one of the blends on the right edge of the triangle change systematically with composition. On the other hand, binary blends of this copolymer with BR exhibit two distinct damping peaks, suggesting that this diblock copolymer forms a separate phase in this case.

Figure 2 summarizes the location of the various transitions (peak in log tan δ) along the temperature scale for the 16 samples of Figure 1 and for five additional blends taken along the isopleth (i.e., the line of constant composition, 71 wt % polyisoprene). The temperatures indicated in Figure 2 exhibit a systematic trend with overall blend composition. For example, if we examine the data obtained along the isopleth, the observed shifts in the location of the higher temperature loss peak suggest that

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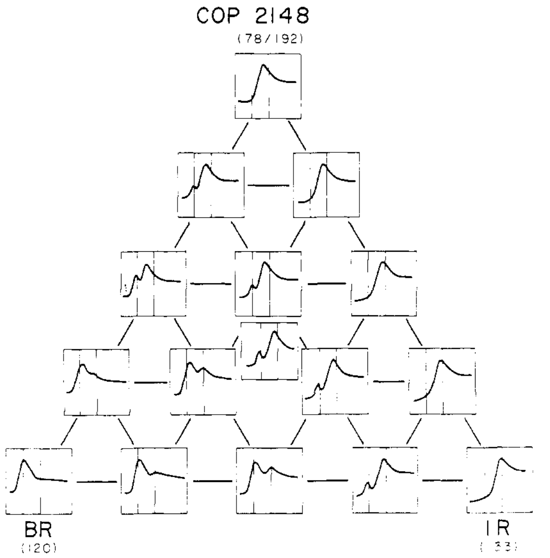

Figure 1. Tan δ vs. temperature curves at 3.5 Hz for 16 ternary blends of copolymer 2148 (1/2), BR and IR. The two vertical lines indicate the location of the two homopolymer peak maxima. The numbers in parentheses represent the respective molecular weights in thousands.

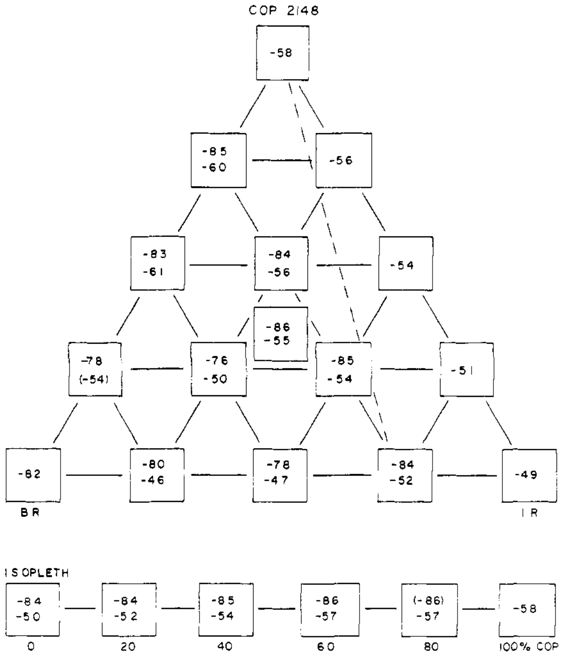

Figure 2. Tan δ (3.5 Hz) peak location in deg C for various blends. The dashed line in the triangle indicates the position of the isopleth. Numbers in parentheses indicate that the loss peak was not clearly defined.

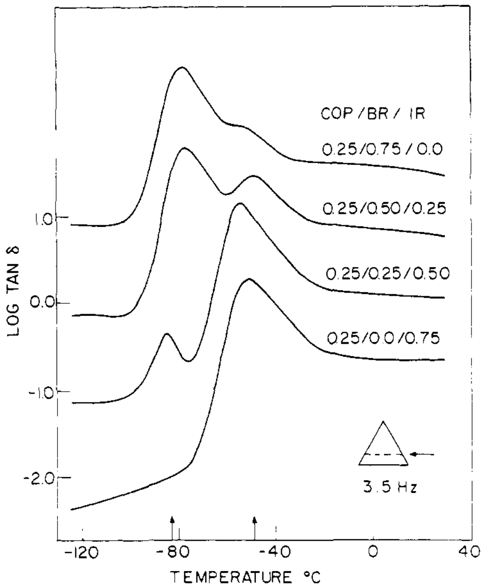

Figure 3. Tan δ vs. temperature curves at 3.5 Hz for four blends, each containing 25 wt % copolymer 2148 (1/2). The top three curves have been shifted upwards for clarity of presentation. The two vertical arrows indicate the locations of BR and IR homopolymer glass transitions.

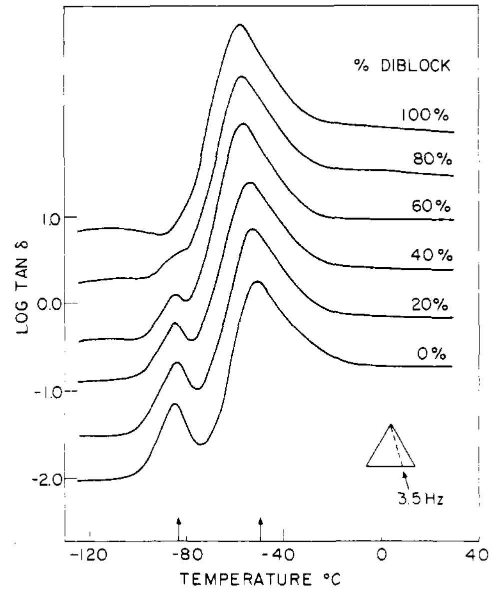

Figure 4. Tan δ vs. temperature curves at 3.5 Hz for several blends along the isopleth of Figure 1. The scale on the ordinate corresponds quantitatively to the bottom curve only.

the IR phase present in heterogeneous blends does not remain pure when diblock is present. The lower temperature (BR) peak remains essentially unshifted, indicating that the diblock is solubilized preferentially by the IR phase.

Loss tangent vs. temperature curves for blends containing 25 wt % of diblock are presented in Figure 3. The bottom curve, corresponding to a diblock–IR blend, exhibits a single peak while the top curve which corresponds to a diblock–BR curve exhibits two transitions, the second one being distinguishable as a shoulder on the lower temperature peak. The two intermediate curves can be broken down into two peaks each. For the three top curves, the location of the peak due to the BR phase does not change much with composition indicating that this phase remains relatively pure, again suggesting that the diblock tends to go to the IR phase.

Interesting changes in the loss tangent curve are also observed when the amount of diblock in the blend is varied while maintaining the overall composition constant, i.e., along the isopleth. Figure 4 is a series of loss tangent curves which slow the effect of gradually replacing IR and BR molecules by an equivalent number of diblock molecules. Note that while the low-temperature (BR) peak remains essentially at the same location, the IR peak gradually drifts to lower temperatures as diblock is added. The BR transition is distinguishable even in an 80 wt % diblock blend, when polybutadiene accounts for only about 8 wt % of the total sample.

An independent determination of the glass transition temperature(s) of each blend was made by thermal analysis (TMA). The results for the ternary system discussed above

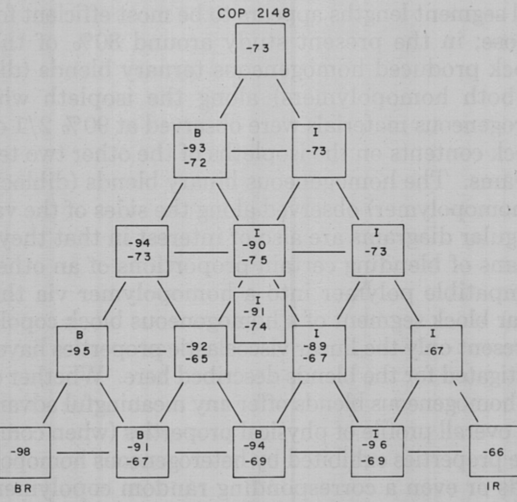

Figure 5. Glass transition temperature in deg C for blends of diblock copolymer 2148 (1/2), BR and IR. The letter in each box indicates the continuous phase, determined as described in the text.

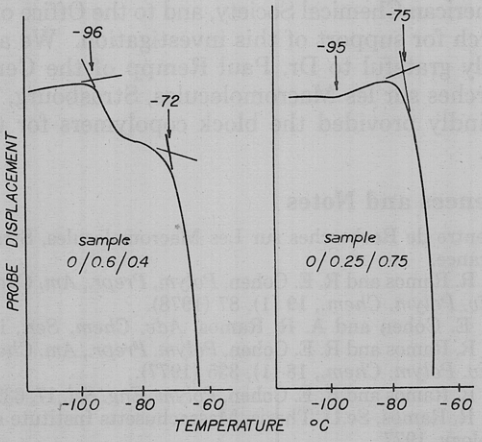

Figure 6. Schematic of TMA method for determining phase continuity. The curve on the left corresponds to a BR continuous blend, while the one on the right corresponds to an IR continuous blend.

are shown in Figure 5. Where possible, a letter B or I is included to indicate whether polybutadiene or polyisoprene appeared to be the continuous phase. The information on the phase relationship was obtained from the TMA recordings using the following criterion (see Figure 6): A blend for which the BR phase is continuous softens (probe penetration downward) at the BR glass transition, while at this same temperature for a blend for which the BR phase is dispersed only a sudden increase in the thermal expansion coefficient is observed (probe displacement upward). Interpretations of phase relationships in this way correlated well with information obtained from transmission electron micrographs of the same samples, to be discussed below.

As a check of the internal consistency of the data reported here, we note that the trend of the glass transition values shown in Figure 5 obtained by thermomechanical analysis (static test) agrees well with that seen for the values obtained on the Rheovibron (dynamic test). The single exception is blend 0.25/0.75/0.0 which showed only one transition in the TMA, but presented a hint of a second transition in the dynamic measurements. For such cases the added information from electron microscopy was helpful in determining whether or not two distinct phases were present in the material.

A montage of electron micrographs, corresponding to the 16 blends selected in the triangular composition diagram,

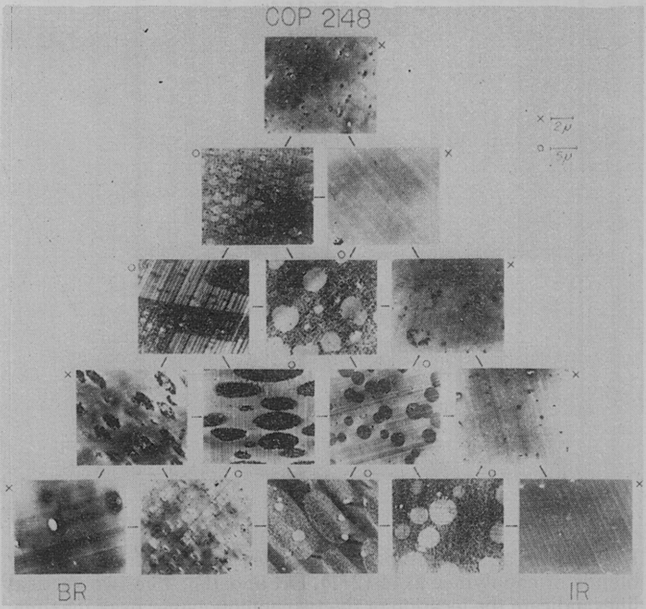

Figure 7. Transmission electron micrographs of various ternary blends of copolymer 2148 (1/2), BR and IR. Magnifications as indicated.

is shown in Figure 7. In the work of Kawai[10] on polystyrene–polyisoprene systems, the emulsifying effect of a heterogeneous diblock was unambiguously demonstrated by the gradual changes in the two-phase morphology as the amount of diblock was varied. Such behavior is not evident in the present case, as seen in Figure 7. The identification of the IR and the BR phases in the micrographs was complicated by the tendency of the IR phase to vary considerably in texture and tone. For example, in the micrographs corresponding to blends 0/0.50/0.50 and 0/0.25/0.75 the IR phase (dispersed phase in the former case and continuous phase in the latter as deduced from TMA and dynamic mechanical measurements) has a rough texture and is somewhat darker in color than the BR phase. On the other hand, in blend 0/0.75/0.25, the dispersed IR phase appears smooth, and lighter than the continuous BR phase. In general, identification of the IR phase as the one with a rough texture *or* lighter in color led to results in good agreement with TMA and dynamic measurements.

The evidence contained in the set of micrographs in Figure 7 supports the earlier hypothesis that binary blends of the isoprene-rich copolymer (1/2) and IR are homogeneous. The micrographs also show in a definitive way that the blends along the other two edges of the triangular diagram are heterogeneous.

Figure 8 is a summary of the dynamic mechanical behavior of a similar ternary system, this one incorporating the polybutadiene-rich diblock (2/1) into the appropriate blends. An incomplete version of this figure has been presented previously.[5] The data of Figure 8 indicate that the behavior of this system is opposite to that discussed above, i.e., this particular diblock is soluble in the polybutadiene homopolymer but not in the polyisoprene, as expected.

All of the results taken together lead to the schematic summary shown in Figure 9 where the cross-hatched areas represent regions in which essentially homogeneous blends have been found. This general picture may well hold for a variety of systems in which the diblock copolymer is homogeneous and blends of the corresponding homopolymers are heterogeneous. The polystyrene/poly(α-methylstyrene) system studied by Shen and co-workers[13–15]

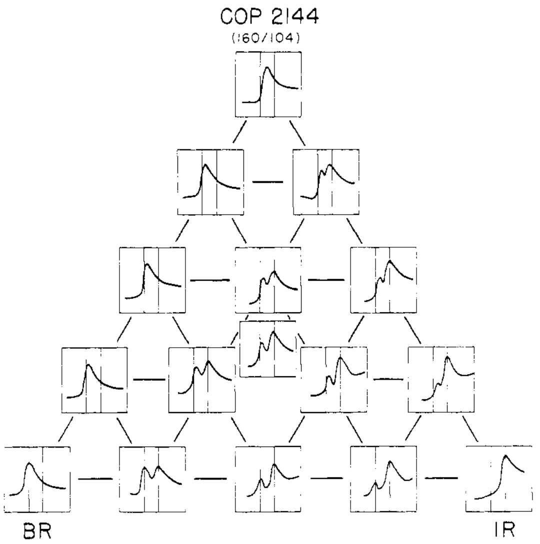

Figure 8. Tan δ vs. temperature curves at 3.5 Hz for 16 ternary blends of copolymer 2144 (2/1), BR and IR. The two vertical lines indicate the location of the two homopolymer peak maxima. The numbers in parentheses represent the respective molecular weights in thousands.

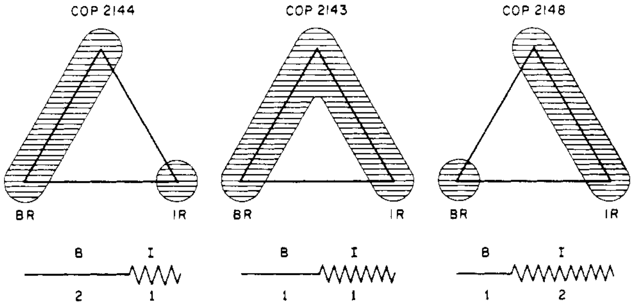

Figure 9. Schematic summary of the behavior of the entire array of samples tested. Essentially homogeneous materials appear in the cross-hatched areas of the three composition diagrams.

could be used to test the generalization of Figure 9. The implications of Figure 9 are decidedly different from the emulsifying effects of heterogeneous diblock copolymers reported by Kawai[10-12] and by Reiss,[16-19] in which the fineness of the phase-separated morphology was controlled by the amount of diblock present. The homogeneous diblocks used in the present study appear to have a homogenizing effect in large quantities; in small quantities they are solubilized by the homopolymer which corresponds to the longer segment of the diblock. In the case in which the block lengths were identical, it was concluded earlier[5] that the diblock was soluble in either of the two corresponding homopolymers.

From the practical point of view, the results of this study suggest methods for producing essentially homogeneous blends of otherwise immiscible polymers. The diblock with equal segment lengths appears to be most efficient for this purpose; in the present study around 80% of the 1/1 diblock produced homogeneous ternary blends (diblock and both homopolymers) along the isopleth whereas heterogeneous materials were observed at 90% 2/1 or 1/2 diblock contents on the isopleths of the other two ternary diagrams. The homogeneous binary blends (diblock and one homopolymer) observed along the sides of the various triangular diagrams are also of interest in that they offer a means of blending certain proportions of an otherwise incompatible polymer into a homopolymer via the dissimilar block segment of a homogeneous block copolymer. At present only the linear viscoelastic properties have been investigated for the blends described here. Whether or not such homogeneous blends offer any meaningful advantages in an overall profile of physical properties (when compared to the properties exhibited by heterogeneous homopolymer blends or even a corresponding random copolymer) is a matter yet to be determined.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Office of Naval Research for support of this investigation. We are particularly grateful to Dr. Paul Rempp of the Centre de Recherches sur les Macromolecules, Strasbourg, France who kindly provided the block copolymers for this research.

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