Miscible Polyisoprene/Polybutadiene Blends: Relationship Between Average Statistical Segment Length and Vinyl Content

Michael R. Ambler

Ambler Consulting Services, 4016 Devonshire Circle, Stow, Ohio 44224

ABSTRACT: Average statistical segment lengths for a series of miscible protonated polyisoprene/deuterated polybutadiene (HPI/DPB) blends with considerable range in vinyl contents and blend ratios are used to determine average statistical segment lengths of the two polydienes in those blends. These blends exhibit a minimum in the plot of blend average statistical segment length versus blend total vinyl content because in blends the average statistical segment length of DPB decreases as both DPB vinyl content and HPI vinyl content increases and the average statistical segment length of HPI increases as both HPI vinyl content and DPB vinyl content increases. In a blend, both polydienes are more flexible than they are as isolated homopolymers. The increased flexibility of both polydienes when miscibly blended is due to immiscibility on a molecular scale, manifesting itself as an increase of free volume and allowing increased segmental mobility and depressed T_g. There is a matrix effect on the flexibility of each polydiene in a miscible blend. The vinyl content of each polydiene influences the average statistical segment length of the other polydiene. In miscible HPI/DPB blends (as well as polydiene homopolymers), the average statistical segment length of each polydiene chain can be viewed not as an inherent physical property describing the chain's flexibility, rather its flexibility is influenced by the vinyl content of the polydiene chains with which it is entangled. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2029–2042, 2008

Key words: miscibility; blends; polybutadiene; polyisoprene; average statistical segment length

INTRODUCTION

The average square statistical segment length, $\overline{b^2}$, of a mixture of polymer chains, such as a miscible protonated polyisoprene/deuterated polybutadiene (HPI/DPB) blend, is a measure of the average flexibilities of the different polymers in the mixture. A polymer chain's flexibility is a result of the amount of hindrance of its chain backbone bonds to freely rotate. Considering a chain to be a series of freely connected, rigid links, each link able to rotate to a different direction than the projections of the directions of its neighboring links, the length of each rigid link defines the average statistical segment length of the chain. For a freely rotating chain, the rigid link could be as short as one backbone bond, but for most flexible polymer chains with restricted mobility, the rigid link is several backbone bonds that coordinate as one rotating unit. As this link lengthens, the flexibility of the chain decreases and the chain is more rigid.

A previous[1] publication reported, for 24 miscible blends of HPI and DPB over a wide range of vinyl contents and blend ratios, that a plot of average statistical segment length of the blend, b, versus total vinyl content of the blend exhibited a minimum rather than a monotonic relationship. Those authors offered no explanation for the observed minimum other than to speculate that one or both of the polydienes must be more flexible in a blend than expected, resulting in a smaller b value. This hypothesis could not be properly tested since the compositions of the blends were not provided. A more recent publication reported[2] four miscible polydiene blends with opposite isotopic labeling. These 50/50 DPI/HPB blends used one DPI with low vinyl content, 7% −3,4, and four HPB's with 38–78% vinyl contents. Those data were felt by that author to not be in agreement with the observed minimum. Other than those two references, a search of the literature did not find any published b data for HPI/DPB or DPI/HPB blends that could be used to test the observation of the minimum.

In the original[1] publication, the assumptions were made, as many authors had done previously, that the two average statistical segment lengths of HPI and DPB homopolymers did not change when these two polydienes were miscibly blended, i.e., $_{\mathrm{hp}}b_I \cong b_I$ and $_{\mathrm{hp}}b_B \cong b_B$, and the polydienes were similar enough to assume that they were the same average statistical segment length when miscibly blended, i.e., $b_I \cong b_B$. For this work, a derivation was used

Correspondence to: M. R. Ambler (mhagolf@juno.com).

TABLE I
Microstructure of Polydienes

	Total w(-1,4)	Total w(-1,2 + -3,4) v(HPI)
Protonated polyisoprene (HPI)		
HPI-7	0.93	0.07
HPI-21	0.77	0.23
HPI-44	0.48	0.52
	Total w(-1,4)	Total w(-1,2) v(DPB)
Deuterated polybutadiene (DPB)		
DPB-9	0.91	0.09
DPB-26	0.74	0.26
DPB-39	0.61	0.39
DPB-70	0.30	0.70

that did not require these assumptions, since it was the intent to determine the average statistical segment lengths of HPIs and DPBs of varying vinyl contents when miscibly blended. By comparing these values, b_I and b_B, to the corresponding values of these polydienes as homopolymers, $_{hp}b_I$ and $_{hp}b_B$, the reported[1] minimum in blend b when plotted as a function of blend total vinyl content was interpreted.

EXPERIMENTAL

The microstructures of the polydienes used are reprinted[1] in Table I. For polyisoprene, the -3,4 iso-

mer is in much higher concentration than the -1,2 isomer, and vinyl content is considered as the sum of -3,4 and -1,2 isomer contents. These blends consist of two families of polydienes, protonated polyisoprene and deuterated polybutadiene, with vinyl contents, v(HPI) and v(DPB), varying from 7 to 70%. From the polydienes of Table I, 24 blends of different polyisoprenes and polybutadienes with 32/68, 52/48, and 72/28 (vol/vol, HPI/DPB) blend ratios had been prepared. For both polydienes there was a wide range of vinyl contents, wider than any previous data-set in the literature with reported b values. It is apparent that the authors had attempted to study miscible HPI/DPB blends as a function of blend composition, which is a function of two variables: the volume fractions of the two polydienes in the blend as well as their vinyl contents. It is the wide range in vinyl content and volume fraction that makes this study possible.

Although not listed in the original[1] publication, the volume fractions and average square statistical segment lengths for the 24 blends are listed in Table II[3]. The experimental error seems consistent with earlier estimates.[4] Since the authors had noted that there was no change in average statistical segment length over the range of temperature of the SANS experiments, the values listed represent the average over the experimental temperature range of 25–100°C (the

TABLE II
Blend Properties

Blend	HPI	Volume fraction, Φ_I	DPB	Volume fraction, Φ_B	$\overline{b^2}(\text{Å}^2)$
7-3268-9	HPI-7	0.32	DPB-9	0.68	72.3 ± 5.2
7-5248-9	HPI-7	0.52	DPB-9	0.48	101.2 ± 6.1
7-7228-9	HPI-7	0.72	DPB-9	0.28	139.0 ± 17.0
7-3268-26	HPI-7	0.32	DPB-26	0.68	60.1 ± 3.1
7-5248-26	HPI-7	0.52	DPB-26	0.48	64.2 ± 4.9
7-7228-26	HPI-7	0.72	DPB-26	0.28	92.9 ± 1.9
21-3268-9	HPI-21	0.32	DPB-9	0.68	48.4 ± 1.4
21-5248-9	HPI-21	0.52	DPB-9	0.48	51.4 ± 1.4
21-7228-9	HPI-21	0.72	DPB-9	0.28	54.0 ± 1.5
21-3268-26	HPI-21	0.32	DPB-26	0.68	50.6 ± 1.4
21-5248-26	HPI-21	0.52	DPB-26	0.48	44.0 ± 1.3
21-7228-26	HPI-21	0.72	DPB-26	0.28	51.6 ± 2.9
21-5248-39	HPI-21	0.52	DPB-39	0.48	49 7 ± 1.4
21-7228-39	HPI-21	0.72	DPB-39	0.28	46.9 ± 1.4
7-3268-70	HPI-7	0.32	DPB-70	0.68	52.0 ± 2.9
7-5248-70	HPI-7	0.52	DPB-70	0.48	47.6 ± 1.4
21-3268-70	HPI-21	0.32	DPB-70	0.68	55.5 ± 3.0
21-5248-70	HPI-21	0.52	DPB-70	0.48	55.5 ± 3.0
21-7228-70	HPI-21	0.72	DPB-70	0.28	45.4 ± 1.4
44-3268-39	HPI-44	0.32	DPB-39	0.68	90.1 ± 5.8
44-5248-39	HPI-44	0.52	DPB-39	0.48	74.3 ± 1.7
44-3268-70	HPI-44	0.32	DPB-70	0.68	98.2 ± 4.0
44-5248-70	HPI-44	0.52	DPB-70	0.48	78.0 ± 3.6
44-7228-70	HPI-44	0.72	DPB-70	0.28	95.5 ± 2.0

median temperature of 63°C was assumed in all calculations). For each of the nine HPI/DPB blend systems there was two or three blend ratios prepared, allowing for the first time an evaluation of the composition dependency of b through a systematic analysis of $\overline{b^2}$, the average square statistical segment length of the blend, and χ, the effective polymer–polymer interaction parameter of the blend, as determined by Small-Angle-Neutron-Scattering (SANS), as a function of volume fraction of protonated polyisoprene, v(HPI), one of two polydienes in the miscible binary blend.

The result of the curve-fitting of the SANS data, the average square statistical segment length of the blend, $\overline{b^2}$, had been used to calculate the average statistical segment length of the blend, b, using the identity

$$b \equiv (\overline{b^2})^{1/2}. \qquad (1)$$

The terminology for $\overline{b^2}$ and b, "average square statistical segment length" and "average statistical segment length," used in prior literature and continued here should be more precisely referred to as "mean-square statistical segment length" and "root-mean-square statistical segment length," respectively. The fitting parameter that emerges from the SANS experiment is the mean-square statistical segment length of the miscible binary blend, $\overline{b^2}$ (in units of dimension-squared), and represents the mean of all the squares of the discrete values of the statistical segment lengths in the blend for the individual members of the blend, which in this case is a mixture of two discrete populations, each population having one value of root-mean-square statistical segment length, b_I or b_B, since the two polymers used are monodisperse in molecular weight and homogeneous in composition. What is usually calculated from this fitting parameter is the root-mean-square statistical segment length of the blend, b, or more precisely, $(\overline{b^2})^{1/2}$ (in units of dimension). To calculate b, the square-root of $\overline{b^2}$ must be taken using eq. (1), hence, the nature of the averaging process must be kept in mind. This averaging process applies not only to the blend but also to the polymers used in the blend, i.e., b, b_I and b_B root-mean-square length parameters must all be considered as based on their respective mean-square length parameters, $\overline{b^2}$, b_I^2 and b_B^2.

RESULTS AND DISCUSSION

Model for calculating b_I and b_B from $\overline{b^2}$

The value of the average square statistical segment length of each blend was calculated[1] from the experimental SANS profile for each blend, $S(q)$ versus q, using the total structure factor represented as the equality

$$[\kappa_N/S(q)] = \{1/[\Phi_I N_I v_I S_D(U_I)]\}$$
$$+ \{1/[\Phi_B N_B v_B S_D(U_B)]\} - [2\chi/v_0], \quad (2)$$

with the variables and constants the same as previously defined[1]: $S(q)$ the experimental scattering intensity at q; protonated polyisoprene (HPI) and deuterated polybutadiene (DPB); N_i the degree of polymerization; q the scattering length [$q = (4\pi/\lambda)\sin\theta$] with λ the wavelength of the incident beam in Angstroms and 2θ the scattering angle in radians; v_0, v_I and v_B the molar volumes of the reference unit cell [$v_0 = (v_I v_B)^{1/2}$] and of HPI and DPB segments (of all vinyl contents), respectively, with v_I = 74.6, v_B = 60.4, v_0 = 67.1 (25°C, mol cm^3) and v_I = 76.3, v_B = 62.1, v_0 = 68.8 (63°C, mol cm^3); Φ_I and Φ_B the volume fractions of HPI and DPB in the blend, respectively, with [$\Phi_I + \Phi_B$ = 1.0]; the Debye scattering function (single Gaussian chain structure factor) $S_D(U_i)$,

$$S_D(U_i) = (2/U_i^2)[\exp(-U_i) - 1 + U_i], \qquad (3)$$

with

$$U_i = q^2 R_{gi}^2 = q^2(N_i b_i^2/6); \qquad (4)$$

and the contrast factor,

$$\kappa_N = N_A[(a_I/v_I) - (a_B/v_B)]^2, \qquad (5)$$

with N_A Avogadro's number and a_i the scattering length per mole of monomer. (The Appendix is a short analysis indicating that no error was introduced to the χ and $\overline{b^2}$ results[1] by using a form of the molar volume of the reference unit cell, v_0, that was independent of concentration, instead of the concentration-dependent form, which should have been used in that study.) Equation (2) contains three unknown parameters, χ, b_I^2 and b_B^2. To reduce to two unknowns for the fitting routine of the experimental data, b_I^2 and b_B^2 were equated. Since it is known[1] that the homopolymers of HPI and HPB have sufficiently similar values, i.e., $_{hp}b_I \cong {}_{hp}b_B$, it was assumed that the similarity of average statistical segment length for HPI and HPB (or DPB) also applies when these polydienes are miscibly blended, i.e., $b_I \cong b_B$ or $b_I^2 \cong b_B^2$. This may not be the case, but it is usually an assumption that has to be made to reduce unknowns to two for the fitting routine. Best-fit values of χ and $\overline{b^2}$ were calculated[1] by applying eq. (2) to the data, assuming $b_I^2 \cong b_B^2 \cong \overline{b^2}$, and listed[3] in Table II.

The original[1] work calculated one fitting parameter for the average statistical segment length of the blend, b, as listed here in Table II. For this study, a second calculation was made for values of b_I and b_B. The original[1] results were based on SANS data of small enough q that the derivation of Shibayama et al.,[4] could be used to interpret $\overline{b^2}$ as a function of b_I^2 and b_B^2. In this limiting case, with $U_i < 1$, eq. (2) can be rewritten as

$$[\kappa_N/S(q)] = \{1/[\Phi_I N_I \nu_I] + 1/[\Phi_B N_B \nu_B] - [2\chi/\nu_0]\}$$
$$+ q^2\Big\{[1/(18\Phi_I\Phi_B)][\overline{b^2}/\nu_0]\Big\}, \quad (6)$$

with the average square statistical segment length of the blend, $\overline{b^2}$ defined in terms of the average square statistical segment lengths of the blend polydienes, b_I^2 for HPI and b_B^2 for DPB,

$$(\overline{b^2}/\nu_0) = \Phi_I\Phi_B[(b_I^2/\nu_I\Phi_I) + (b_B^2/\nu_B\Phi_B)], \quad (7)$$

which reduces to

$$(\overline{b^2}/\nu_0) = (\Phi_B b_I^2/\nu_I) + (\Phi_I b_B^2/\nu_B). \quad (8)$$

In the original[1] publication, SANS data were taken for $[0.004 < q < 0.07]$. The requirement for $U_i < 1$ comes from the fact that in the expression for the Debye scattering function, eq. (3), the bracketed term containing the exponential factor comes from the series expansion $[\exp(x) = 1 + x + x^2/2! + x^3/3! + \dots]$, and only values of $x < 1$ will converge.[5] Given the polydiene physical properties, the requirement that $U_i < 1$ means that experimental data must be taken for $q < 0.007$, assuming that all $b_i < 12$ Å. To determine χ and $\overline{b^2}$, the Ornstein-Zernicke form[4] of eq. (6) can be applied to the experimental data for $q < 0.007$ when $[\kappa_N/S(q)]$ is plotted versus q^2, (χ/ν_0) being determined from the y-intercept and $(\overline{b^2}/\nu_0)$ determined from the initial slope.

Rearranging eq. (8) and expressing blend volume fraction in terms of HPI,[6]

$$\overline{b^2} = (\nu_0/\nu_I)b_I^2 + \Phi_I\Big\{[(\nu_0/\nu_B)b_B^2] - [(\nu_0/\nu_I)b_I^2]\Big\}. \quad (9)$$

Using eq. (9) to interpret $\overline{b^2}$ does not require the assumption that $b_I^2 \cong b_B^2$. Rather, eq. (9) allows independent analyses for b_I^2 and b_B^2 from the experimental $\overline{b^2}$ result if appropriate data are available. For any given blend system, with results for the average square statistical segment lengths of multiple and sufficiently different blend ratios, eq. (9) can be applied to calculate the average square statistical segment lengths of the two polydienes in the blend, b_I^2 and b_B^2. Equation (9) describes a straight-line relationship when volume fraction is plotted versus the blend's average square statistical segment length. The slope is $\{[(\nu_0/\nu_B)b_B^2] - [(\nu_0/\nu_I)b_I^2]\}$; at $\Phi_I = 0$, the y-intercept is $[(\nu_0/\nu_I)b_I^2]$; at $\Phi_I = 1$ ($\Phi_B = 0$), the y-intercept is $[(\nu_0/\nu_B)b_B^2]$. The functional form of eq. (9), which is the composition dependency of the average square statistical segment length, allows b_I^2 values of each polydiene in the blend to be determined from the two y-intercepts. Thus, even though the
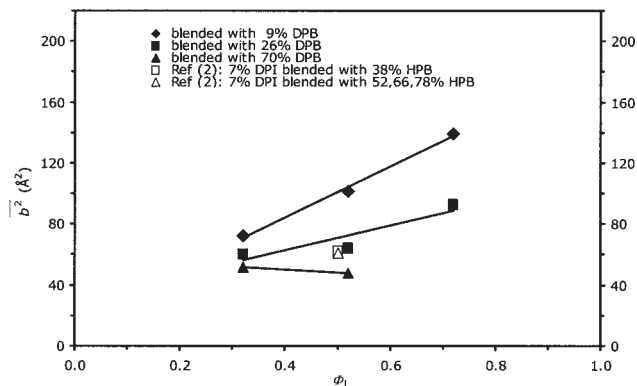

Figure 1 Example of concentration dependence of $\overline{b^2}$: 7% vinyl HPI blended with DPB of 9–70% vinyl.

original[1] authors invoked the assumption $b_I \cong b_B \cong b$ to interpret the experimental data, the double-extrapolation of $\overline{b^2}$ versus Φ_I plots using eq. (9) based on the Shibayama et al.,[4] derivation allows accurate determinations of b_I^2 and b_B^2.

Table II is grouped into nine binary blend systems consisting of one HPI and one DPB, and within each blend system, two or three blend ratios, expressed as HPI volume fraction, Φ_I. Equation (9) was applied to the data in Table II by plotting $\overline{b^2}$ versus HPI volume fraction, as illustrated in Figure 1. There is little data in the literature that can be used to verify the accuracy of eq. (9) when applied to the data in Table II. Four blends were found[2] that had polydiene compositions similar to three blend systems, HPI-7 blended with DPB-9, -26, and -70, i.e., 7-xxxx-9, 7-xxxx-26 and 7-xxxx-70. Using that author's results of b_{HPB} for the four HPBs and his assumed b_{DPI} for DPI, four $\overline{b^2}$ values for the four blends were back-calculated using eq. (7). These results are included in Figure 1. Good agreement between the data of this work and that author's results[2] is seen for his data-points corresponding to 38–52% HPB, with reasonable agreement for the 66–78% data-points.

Equation (9) appears to be an appropriate way to describe the concentration dependence of the HPI/DPB blend systems in Table II. Linear dependence of $\overline{b^2}$ on Φ_I is demonstrated, as well as good quantitative agreement with previously published DPI/HPB blends. Equation (9) can be applied to understand whether either of the polydienes HPI and DPB, which as homopolymers have average square statistical segment lengths $_{hp}b_I^2$ and $_{hp}b_B^2$, undergo changes in their average square statistical segment lengths b_I^2 and b_B^2 when miscibly blended, the changes presumably occurring because of the influence of one polydiene on the other in the miscible blend. This influence in turn results from the local environment each polydiene exists in, as expressed by the blend ratio. Equation (9) can only be applied as a concentration

dependence of b_I^2 and b_B^2 if it can be assumed that all values of both b_I^2 and b_B^2 are respectively, the same in all blend ratios applied to eq. (9). If each blend system of Table II can be interpreted as having the same respective values of b_I^2 and b_B^2 at all blend ratios, then a plot of $\overline{b^2}$ versus Φ_I will exhibit a good fit to a linear line. The question is whether that assumption is valid for these HPI/DPB blend systems. There are two ways to satisfy the condition that the b_I^2 and b_B^2 results are the same in all blend ratios: either they are not changing over the range of blend ratios employed, or they change and the values obtained represent average values over the range of blend ratios. Two previous studies demonstrated that the former assumption of constant b_I^2 and b_B^2 applied to certain polydiene blends. Watanabe et al.,[7] reported the dielectic relaxation spectrum of miscible blends of two low concentrations of polyisoprene in polybutadiene. For the two blend ratios, the reduced relaxation spectrum for polyisoprene was identical, and since the spectrum intensity is proportional to mean-square-end-to-end distance, this indicates to this author that the average statistical segment length for polyisoprene was also constant for both blend ratios. Sakurai et al.,[8] reported the SANS analysis of DPB/HPB miscible blends, and showed that blend correlation length was independent of the concentration of DPB when the concentration is close to zero, by derivation of an equation demonstrating independence as well as an empirical proof by plotting calculated b_{DPB} against c_{DPB}, arguing that the good fit to a linear line justified the assumption of constancy of b_{DPB}. Even though this prior evidence[7,8] supports the assumption that miscible HPI/DPB blends could have constant values of b_I^2 and b_B^2, there is no direct evidence to allow or disallow this assumption to be applied to the blend systems of this study. Instead, the less-restrictive latter assumption will be applied to this work, namely, that the values of b_I^2 and b_B^2, obtained from applying eq. (9) to the experimental data, are assumed to represent average values of the two parameters over the range of blend ratios. The graphical technique involving extrapolation of the least-squares line to y-intercepts will be the method used to solve eq. (9) and establish error estimates for b_I^2 and b_B^2. Assuming that the solution to eq. (9), b_I^2 and b_B^2, represents average values implies that these parameters are not necessarily constant but rather could change with blend ratio, but the changes that occur in this case likely will not be a large percentage change of that parameter, since the experimental blend ratios employed in the calculation are sufficiently far from being a dilute state of either polydiene in the other that their concentrations are not changing much as a percentage of average concentration. In other words, these average values of b_I^2 and b_B^2 can be assumed to

be reasonable approximations of constant values, especially since all blend systems had the same range of blend ratios and would be expected to have the same degree of "reasonableness."

b_I and b_B results

Equation (9) was applied to the six blend systems in Table II that had SANS results for three blend ratios. In addition to determining b_I and b_B, precision of the results was determined since the precision of the experimental data-points was known. Analyses of the three blend systems with only two data-points was not included because their analysis for error was less statistically significant because of the fact that only two data-points were being used to describe the linear relationship represented by eq. (9). Linear least-squares relationships were established and extrapolated to $\Phi_I = 1$ (corresponding to b_B^2) and to $\Phi_I = 0$ (corresponding to b_I^2), as illustrated by the solid line in Figure 2. Good fits were found for all six blend systems, justifying the assumption of constancy of b_I and b_B as blend ratio changed. From the y-intercept values, the average square statistical segment lengths, b_I^2 and b_B^2, were calculated from eq. (9). Final results for b_B and b_I for all six blend systems were then calculated from eq. (1) and are listed in Table III. Figure 3 shows the relationships[1] between average statistical segment length and vinyl content for the homopolymers of HPI and HPB. From Figure 3, values for the average statistical segment lengths for the protonated homopolymer versions of both polydienes in each blend system are interpolated and listed in Table III.

Comparing the value of average statistical segment length for each polydiene in a blend system to what it is as a homopolymer, the results in Table III suggest that both polydienes exhibit increased flexibility in miscible blends, but that conclusion can only be
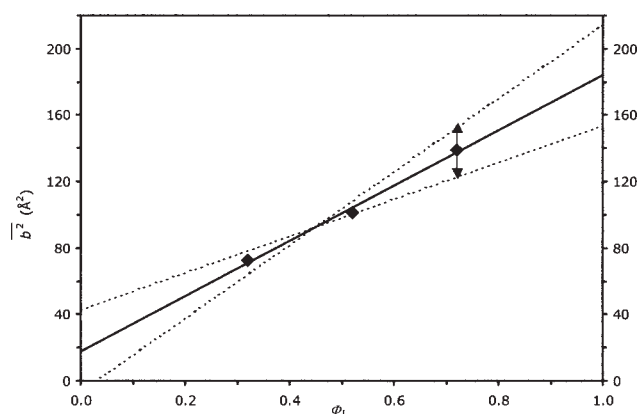

Figure 2 Example of error estimation for a blend system with three data-points: 7% vinyl HPI blended with 9% vinyl DPB.

Blend system	HPI	DPB	Experimental			Interpolated	
			Slope, $d\overline{b^2}/d\Phi_I$	b_I (Å)	b_B (Å)	$_{hp}b_I$ (Å)	$_{hp}b_B$ (Å)
7-xxxx-9	HPI-7	DPB-9	166.8	4.4 ± 2.5	12.9 ± 1.0	9.2	9.4
7-xxxx-26	HPI-7	DPB-26	82.0	5.8 ± 0.7	10.0 ± 0.2	9.2	10.2
21-xxxx-9	HPI-21	DPB-9	14.0	7.0 ± 0.3	7.2 ± 0.2	9.4	9.4
21-xxxx-26	HPI-21	DPB-26	2.5	7.3 ± 0.3	6.7 ± 0.4	9.4	10.2
21-xxxx-70	HPI-21	DPB-70	−25.3	8.5 ± 0.4	6.0 ± 0.4	9.4	11.7
44-xxxx-70	HPI-44	DPB-70	−6.8	10.2 ± 0.5	8.9 ± 0.3	10.2	11.7

made in light of an error analysis of the precision of the $\overline{b^2}$ data, the error in the extrapolated b_I^2 and b_B^2 results, and calculated error in the calculated b_I and b_B results. This analysis is needed because the data have reasonably small but finite precision; the linear least-squares fits using eq. (9) have some error whenever the data-points do not fall perfectly on the least-squares line; and extrapolations were large compared to the range of Φ_I. Figure 2 includes an example of the error analysis of the $\overline{b^2}$ versus Φ_I plot. For this blend system, the data-point corresponding to the highest Φ_I has a relatively large precision in $\overline{b^2}$, indicated by the vertical positive- and negative-error bars; the data-points of the lower two Φ_I have precision in $\overline{b^2}$ within the size of their data-point symbols. (The reader is referred to the ± values listed in Table II for the three blends of this blend system.) First, the linear least-squares relationship was extrapolated to $\Phi_I = 1$ (corresponding to b_B^2) and to $\Phi_I = 0$ (corresponding to b_I^2), the solid line, and values of b_I^2 and b_B^2 were calculated from eq. (9). Next, the positive-error in $\overline{b^2}$ of the highest Φ_I data-point was added to its mean $\overline{b^2}$ value, the negative-error of the lowest Φ_I data-point was subtracted from its value, and no change was made to the middle Φ_I data-point. A new linear least-squares fit using these "adjusted" data-points was extrapolated, shown as the more-vertical dotted line, and values of b_I^2 and b_B^2 were calculated for this line from eq. (9). Then, the process was reversed: the negative-error in $\overline{b^2}$ of the highest Φ_I data-point was subtracted from its mean $\overline{b^2}$ value, the positive-error of the lowest Φ_I data-point was added to its value, and no change was made to the middle Φ_I data-point. A new linear least-squares fit using the "adjusted" data-points was extrapolated, shown as the less-vertical dotted line, and values of b_I^2 and b_B^2 were calculated for this line from eq. (9). Last, by adding or subtracting the b_I^2 and b_B^2 values corresponding to the two dotted lines to those of the solid line, positive- and negative-errors were established for b_I^2 and b_B^2. Total errors in b_I and b_B were calculated from these results and listed in Table III as the ± values. Also listed in Table III are the slopes, $d\overline{b^2}/d\Phi_I$, of the solid lines.

Three conclusions can be drawn from the results in Table III. (1) Even though the average statistical segment lengths for homopolymers of HPI and DPB are approximately the same, in miscible blends the average statistical segment lengths for HPI and DPB are not the same. (2) With three exceptions, both b_i values are less than their corresponding $_{hp}b_i$ values, indicating that both polydienes are more flexible in miscible blends than they are as homopolymers. Two of the three exceptions, b_B when HPI-7 is blended with either DPB-9 or DPB-26, are probably due to these blends approaching the boundary condition of immiscibility for blends of low vinyl polydienes.[9] The other exception, b_I when HPI-44 is blended with DPB-70, is probably explained by the observation in the original publication[1] that the -3,4 isoprene isomer is the only isomer with positive effective interaction parameters, χ_{ij}, indicating that it is strongly immiscible with the -1,4 butadiene isomers and only weakly miscible with the -1,4 isoprene isomers. (3) In blends with polydienes of comparable composition, HPI and DPB change in average statistical segment length in different ways. The results of Table III are plotted in Figure 4 to better illustrate these contrasting dependencies. For HPI, at 7% vinyl content, b_I increases at a relatively
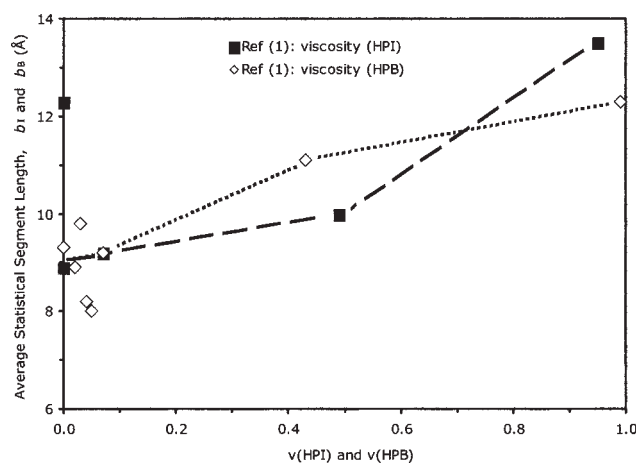

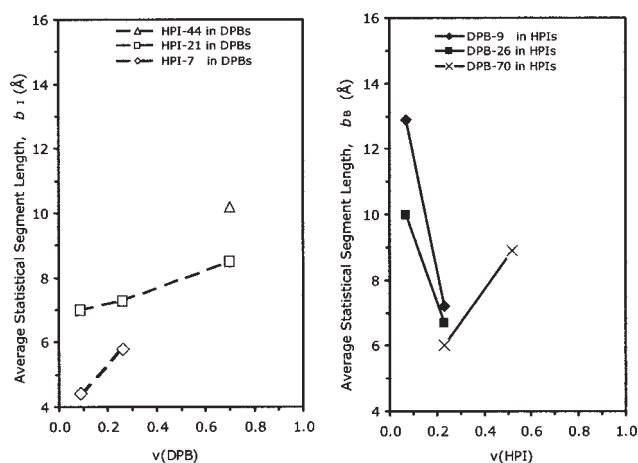**Figure 3** b versus vinyl content: HPI and HPB homopolymers.

Figure 4 Change in average statistical segment length of one polydiene as the vinyl content of the other polydiene changes. Left: HPI in DPB; Right: DPB in HPI.

high rate as the vinyl content of DPB increases; and at 21% vinyl content, the rate of increase lessens. For DPB, at 9% vinyl content, b_B decreases at a relatively high rate as the vinyl content of HPI increases; at 26% vinyl content, the rate of decrease lessens; and at 70% vinyl content, b_B increases as the vinyl content of HPI increases but at an even lower rate.

The results in Table III can be used to compare the listed values for the polydienes in blend systems, b_I and b_B, to their homopolymers, $_{hp}b_I$ and $_{hp}b_B$. The estimate of positive-error in b_I and b_B (except for b_B in 7-xxxx-9 and 7-xxxx-26, and b_I in 44-xxxx-70, the three exceptions mentioned earlier) never allows the b_I and b_B values to be greater than the homopolymer values, indicating that both polydienes exhibit increased flexibility in miscible blends. The accuracy of the b_I and b_B results was determined as follows. Equation (8) was used to calculate values of $\overline{b^2}$ for the 18 blends in Table II that comprise the six blend systems in Table III. As a percentage of the experimental value, the average absolute difference for the 18 blends was 5.1%. This level of accuracy in calculated $\overline{b^2}$ is comparable to the precision of the experimental $\overline{b^2}$ values listed in Table II, 4.5% (of the experimental value). This fact combined with the precision of the b_I and b_B results demonstrate that HPI and DPB exhibit increased flexibility in blends compared to their flexibility as homopolymers.

Minimum in the plot of b versus total vinyl content

In Figure 5, the data of Table II are plotted along with homopolymer data for HPI and HPB from the original[1] publication, along with spline-fits of the relationships for $_{hp}b_I$ and $_{hp}b_B$ originally shown in

Figure 3. Total vinyl content (TVC) of the sample is the same variable used originally,[1]

$$TVC = (\Phi_I)[v(HPI)] + (\Phi_B)[v(DPB)]. \qquad (10)$$

The best-fit polynomial line of the data of all of the original blends is parabolic with a broad minimum at 30-40% TVC. Also shown in Figure 5 are the data[2] for DPI/HPB blends that were perceived to not be in agreement with the HPI/DPB data of Table II, using ($\Phi_I = \Phi_B = 0.5$) in eq. (10). Since the data-points fall in the region of the plateau of the minimum, they cannot be an adequate test of whether the minimum is real. Considering the scatter in the data of this work, these four data-points appear to be consistent with the data of this work. The slight bias suggested between the data from the two sources could be due to the opposite isotopic labeling (DPI and HPB instead of HPI and DPB).

This nonmonotonic dependency of average statistical segment length on composition has not been reported in the literature for any miscible blend system. The only reported[4] miscible blend system with an extensive range of composition is deuterated polystyrene/hydrogenated poly(vinyl methyl ether), PSD/PVME. Over the composition range of 30–80% PSD, there was no change in b. For HPI/DPB, it was speculated[1] that the minimum was due to "one or both of the polymer chains must be more flexible in the chain backbone to result in a smaller b value." That speculation is consistent with the result of this work, that both polydienes when miscibly blended have lower average statistical segment lengths relative to their respective homopolymer values. But that doesn't explain why the SANS-based b data for blends exhibit a minimum.

Several investigations were made of the data of Table II in an attempt to understand why the minimum
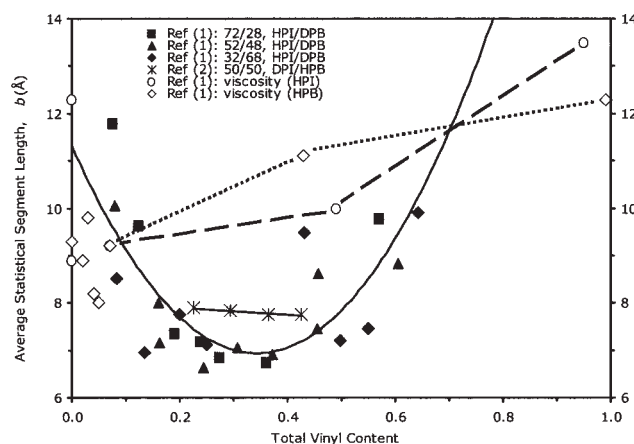

Figure 5 b versus total vinyl content: PI/PB blends and homopolymers.
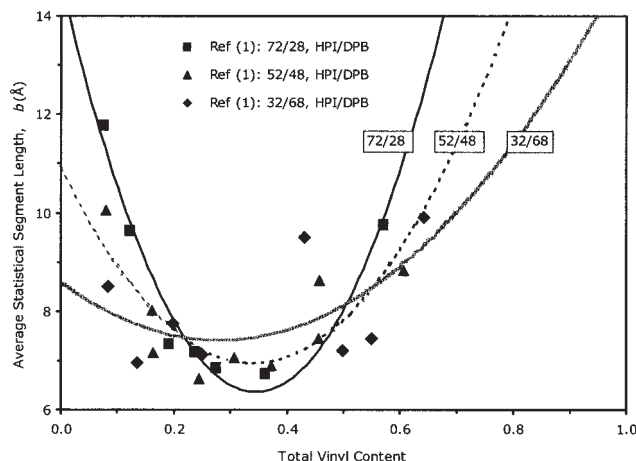
Figure 6 b versus total vinyl content: 72/28, 52/48, 32/68; HPI/DPB blends.

occurred. In Figure 6, the data of Table II are plotted, differentiating three different HPI/DPB blend ratios. The best-fit polynomial lines for three different HPI/DPB blend ratios are all also parabolic with a broad minimum at 30–40% TVC, similar in shape to the parabolic relationship originally[1] published. There is a progressive shift of the characteristics of the relationships with HPI/DPB blend ratio. Table II groups the nine blend systems by vinyl content of the polydienes used in the blend. When the polydienes are both low in vinyl content (top three groups), as HPI content increases, $\overline{b^2}$ increases. When one of the polydienes is high in vinyl content (groups 4–7), as HPI content increases, $\overline{b^2}$ does not change. When both polydienes have high vinyl contents (bottom two groups), as HPI content increases, $\overline{b^2}$ decreases. There is an interaction between HPI and DPB that is affecting their flexibilities, and the interaction changes depending on the vinyl contents of the two polydienes.

This interaction was investigated further as a possible cause of the observed[1] minimum in the plot of b versus TVC. Two parameters were defined to help describe how the composition of the blend influences the flexibility of the blend. The first parameter ratios the flexibility of a polydiene in a blend to its flexibility as a homopolymer, defined as the Flexibility Ratio (FR) between the average statistical segment lengths of a polydiene in a blend and as a homopolymer,

$$(FR)_i = [b_i /_{hp} b_i]. \qquad (11)$$

When FR < 1, the polydiene is more flexible in a blend than it is as a homopolymer. The second parameter describes the relative contributions of the flexibilities of the two polydienes to the flexibility of the blend. The relative contributions of b_I^2 and b_B^2 to

the observed $\overline{b^2}$ are described from a rearranged eq. (9),

$$\overline{b^2} = b_I^2[(v_0/v_I) - (v_0/v_I)\Phi_I] + b_B^2[(v_0/v_B)\Phi_I]. \qquad (12)$$

Dividing by $\overline{b^2}$, eq. (12) reduces to

$$1 = [b_I^2/\overline{b^2}][(v_0/v_I) - (v_0/v_I)\Phi_I] + [b_B^2/\overline{b^2}][(v_0/v_B)\Phi_I], \qquad (13)$$

which simplifies to

$$1 = [14 - I] + [14 - B], \qquad (14)$$

with

$$[14 - I] = [b_I^2/\overline{b^2}][(v_0/v_I) - (v_0/v_I)\Phi_I] \qquad (15)$$

being the relative contribution of the flexibility of HPI to the blend flexibility and

$$[14 - B] = [b_B^2/\overline{b^2}][(v_0/v_B)\Phi_I] \qquad (16)$$

being the relative contribution of the flexibility of DPB to the blend flexibility. Equation (14) has the form of a normalized equation with respect to $\overline{b^2}$ and provides the relative contributions to the observed $\overline{b^2}$ from the b_I^2 and b_B^2 terms. Recalling eq. (9), which relates how the flexibilities of the two polydienes contribute to the flexibility of the blend, this parameter identifies whether the flexibility of one or the other polydiene is dominating the flexibility of the blend.

In Table IV, these parameters are listed for the 18 blends of the six blend systems in Table III. The blends are arranged in the order of increasing [14-I] and corresponding decrease in [14-B]. Arranged this way, the blends are ranked in order of blend flexibility being influenced by the flexibility of DPB the most (96%, blend 7-7228-9) to the least (22%, blend 21-3268-70). Several conclusions can be drawn from these results. (1) Generally, as the contribution of the flexibility of HPI to the blend flexibility increases from 0.04 to 0.78, TVC is increasing from 0.08 to 0.64. (2) In Figure 7, where FR is plotted versus TVC for HPI and DPB, for most of the blends, the polydienes have flexibilities in blends greater than they are as homopolymers (FR < 1). For the two polydienes, FR changes with TVC but in different directions. Starting at low TVC, as TVC increases, HPI flexibility relative to homopolymer decreases and then levels off to no change at a flexibility approaching that of homopolymer, whereas relative flexibility increases for DPB, then remains constant at a large relative flexibility increase, then decreases to values approaching that of homopolymer.[3] Figure 8 is similar to Figure 5 except only the 18 blends in Table II

TABLE IV
Deviation in Average Statistical Segment Length: In Blends Versus as Homopolymers

| | Blends | | Polydienes | | | | Flexibility Ratio | | Equation (14) | | Equation (17b) calculated |
| | | | In Blend | | Homopolymer | | | | | | |
Blend	Total vinyl content	b, Å	b_I, Å	b_B, Å	$_{hp}b_I$, Å	$_{hp}b_B$, Å	HPI	DPB	[14-I]	[14-B]	$d\overline{b^2}/dTVC$
7-7228-9	0.076	11.8	4.4	12.9	9.2	9.4	0.478	1.372	0.035	0.965	−1368
7-5248-9	0.080	10.1	4.4	12.9	9.2	9.4	0.478	1.372	0.080	0.920	−1284
7-7228-26	0.123	9.6	5.8	10.0	9.2	10.2	0.630	0.980	0.096	0.904	−832
7-3268-9	0.084	8.5	4.4	12.9	9.2	9.4	0.478	1.372	0.167	0.833	−1159
7-5248-26	0.161	8.0	5.8	10.0	9.2	10.2	0.630	0.980	0.201	0.799	−613
21-7228-9	0.191	7.3	7.0	7.2	9.4	9.4	0.745	0.766	0.230	0.770	−429
21-7228-26	0.238	7.2	7.3	6.7	9.4	10.2	0.777	0.657	0.272	0.728	−287
44-7228-70	0.570	9.8	10.2	8.9	10.2	11.7	1.000	0.761	0.293	0.707	385
7-3268-26	0.199	7.8	5.8	10.0	9.2	10.2	0.630	0.980	0.367	0.633	−389
21-7228-70	0.362	6.7	8.5	6.0	9.4	11.7	0.904	0.513	0.388	0.612	6
21-5248-9	0.163	7.2	7.0	7.2	9.4	9.4	0.745	0.766	0.414	0.586	−342
21-5248-26	0.244	6.6	7.3	6.7	9.4	10.2	0.777	0.657	0.470	0.530	−161
44-5248-70	0.606	8.8	10.2	8.9	10.2	11.7	1.000	0.761	0.496	0.504	350
21-5248-70	0.456	7.4	8.5	6.0	9.4	11.7	0.904	0.513	0.600	0.400	148
21-3268-9	0.135	7.0	7.0	7.2	9.4	9.4	0.745	0.766	0.620	0.380	−205
21-3268-26	0.250	7.1	7.3	6.7	9.4	10.2	0.777	0.657	0.672	0.328	−42
44-3268-70	0.642	9.9	10.2	8.9	10.2	11.7	1.000	0.761	0.694	0.306	274
21-3268-70	0.550	7.4	8.5	6.0	9.4	11.7	0.904	0.513	0.776	0.224	183

corresponding to the six blend systems in Table III are plotted and the blends are differentiated by the dominance of the flexibility of one or the other polydiene on the blend's flexibility. This differentiation is arbitrarily defined as follows: for any blend in Table IV that has a [14-I] or [14-B] term greater than 0.67 (twice the contribution to blend flexibility by one polydiene compared to the contribution by the other polydiene), its flexibility is controlled mainly by the flexibility of either HPI or DPB, respectively. Using this differentiation, the data-points to the left of the minimum (low TVCs; the top eight blends in Table IV) are blends whose major contributor to the experimental b is DPB, all but one (circled) of the data-points to the right of the minimum (high TVCs; the bottom three blends in Table IV) are blends whose

major contributor to the experimental b is HPI, and the data-points that describe the plateau of the minimum (medium TVCs; the middle seven blends in Table IV) are those blends where neither polydiene dominates the blend flexibility.

Generally, when data describe a minimum, two different dependencies exist, one having a positive slope and the other a negative slope. Close to the minimum, the two dependencies contribute appreciably to the data, and far from the minimum at the extremes of the data, one or the other dependency dominates the data. In this case, for the blends at the extremes in TVC, b_I or b_B for one or the other polydiene controls b. The results in Table IV and Figure 6 indicate that there is a complex interaction between
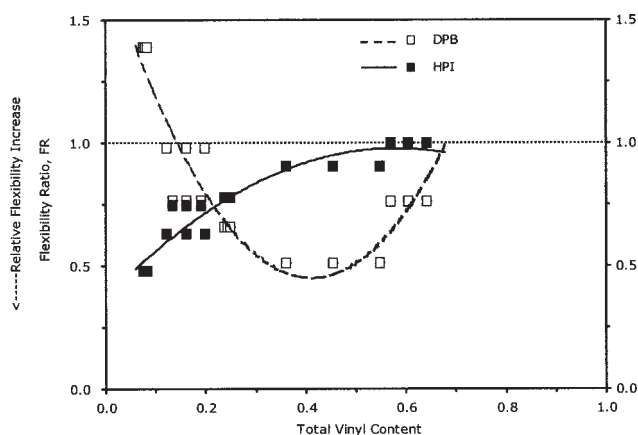

Figure 7 Change in flexibility with total vinyl content: polydienes in blends.
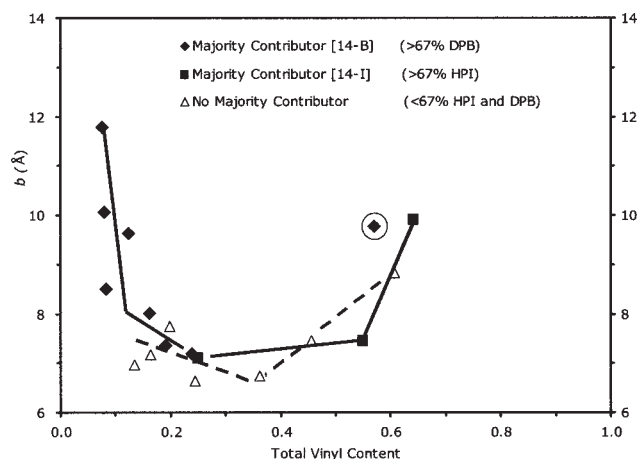

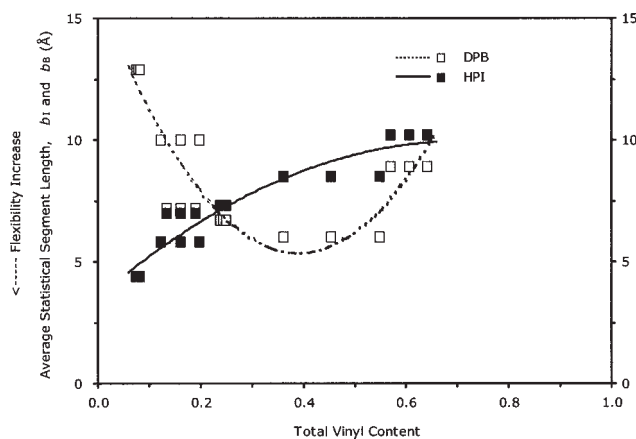**Figure 8** b versus total vinyl content: blends segregated by majority contributor to flexibility.

Figure 9 Polydiene b_I and b_B versus total vinyl content.

blend ratio, polydiene type, and vinyl content that causes the minimum in Figure 5 that can be reproduced in Figure 8. In Figure 9, the relationships between the flexibilities of the two polydienes in a blend and blend total vinyl content are shown. The plots have the same shape as those in Figure 7 since homopolymer flexibilities are relatively constant. In Figure 10, the data of Figures 5 and 9 are combined to make it easier to understand the complex manner in which the two polydienes change in flexibility. Shown are three plots of average square statistical segment length as a function of total vinyl content. To make it easier to compare trends, the data points are left off and only the least-squares polynomial lines describing the parabolic relationships are shown. The solid line represents the average square statistical segment lengths of the 24 blends of Table II; the two dashed lines represent the average square statistical segment lengths of the two polydienes in the 18 blends in Table II corresponding to the six blend systems in Table III. To understand how the changes in b_I^2 and b_B^2 with TVC influence the blend's change in $\overline{b}^2$ with TVC, a qualitative interpretation is offered in terms of the change in flexibility represented by the curved lines (shown in Fig. 10) as well as the rate of change in flexibility represented by the magnitude of the slopes of the tangents (not shown in Fig. 10) of the curved lines.

The flexibility of blends of low TVC to the left of the minimum of the solid line is dominated by the flexibility of DPB but the domination decreases as TVC increases (column 11 of Table IV). In this region, as TVC increases, flexibility increases for DPB (downward curvature of the parabolic line) and decreases for HPI (upward curvature), and even though the relative contribution by DPB's flexibility to the flexibilities of the blends is decreasing and the relative contribution by HPI's flexibility is increasing (columns 10 and 11 of Table IV), the rate of flexibility increase (slopes of tangents) is greater for DPB

than the rate of flexibility decrease for HPI, and the net result is that the blends become more flexible with increasing TVC (downward curvature). This effect manifests itself as the negative slopes of any tangent to the parabolic solid line to the left of the minimum in Figure 10. For the blends in the region of the minimum, the flexibility of neither polydiene dominates the flexibilities of the blends (compare columns 10 and 11 of Table IV for the mid-range values of TVC), and as TVC increases, flexibility does not change much for both HPI and DPB (compare columns 2, 4, and 5 of Table IV for this mid-range group), resulting in little change in flexibility for the blends (little curvature in that parabola, approaching zero tangent slope). The flexibilities of blends of high TVC to the right of the minimum are dominated by the flexibility of HPI and the domination increases as TVC increases (column 10 of Table IV). In this region, as TVC increases, flexibility is relatively constant for HPI and decreases for DPB, as evidenced by the differences in curvature of their parabolas. Even with the relative contribution by HPI's flexibility to the flexibility of the blend increasing and the relative contribution by DPB's flexibility decreasing (columns 10 and 11 of Table IV), the higher rate of flexibility decrease for DPB (higher positive slopes of tangents) dominates the almost zero rate of flexibility decrease for HPI (much lower positive slopes of tangents), and the net result is that the blends become less flexible with increasing TVC (upward curvature). This effect manifests itself as the positive slopes of any tangent to the solid line to the right of the minimum in Figure 10.

This qualitative interpretation is supported by the following calculation. Recall that eq. (8) describes the flexibility of the blend as a function of the volume fractions of its two polydienes. An analogous equation can be written that describes the flexibility of
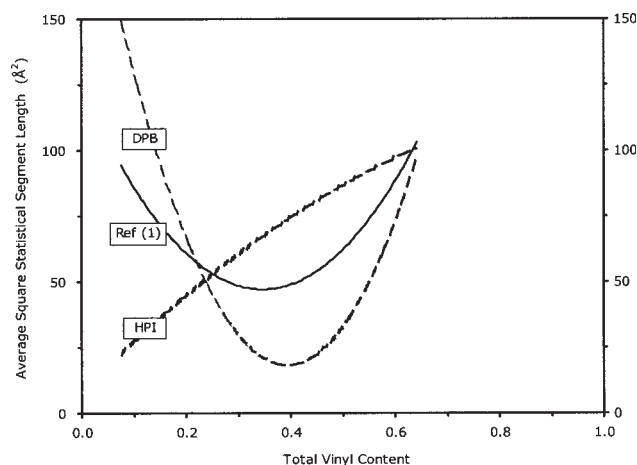

Figure 10 Change in flexibility with total vinyl content: blends and polydienes in blends.

the blend as a function of the relative contributions to blend flexibility from its two polydienes,

$$\overline{b^2} = (v_0/v_I)[14 - I](b_I^2) + (v_0/v_B)[14 - B](b_B^2). \quad (17a)$$

Using the data in Table IV, this equation predicts $\overline{b^2}$ to within an average 14% of the experimental values. By taking the first derivative of eq. (17a), the rate of change of $\overline{b^2}$ with TVC can be expressed as

$$(d\overline{b^2}/dTVC) = (v_0/v_I)\big\{[14 - I](db_I^2/dTVC)$$
$$+ (b_I^2)(d[14 - I]/dTVC)\big\} + (v_0/v_B)$$
$$\big\{[14 - B](db_B^2/dTVC) + (b_B^2)(d[14 - B]/dTVC)\big\}. \quad (17b)$$

For the blends in Table II and the polydienes in Table III, the relationships shown in Figure 10 are

$$\overline{b^2} = 640.33(TVC)^2 - 443.95(TVC) + 124.0300;$$
$$(TVC)_{min} = 0.347,$$
$$b_I^2 = -89.00(TVC)^2 + 202.02(TVC) + 7.7518;$$
$$(TVC)_{max} > 1.000,$$
$$b_B^2 = 1287.60(TVC)^2 - 1015.40(TVC) + 218.4500;$$
$$(TVC)_{min} = 0.394, \quad (18a)$$

and their rates of change are

$$(d\overline{b^2}/dTVC) = 1280.66(TVC) - 443.95,$$
$$(db_I^2/dTVC) = -178.00(TVC) + 202.02, \quad (18b)$$
$$(db_B^2/dTVC) = 2575.20(TVC) - 1015.40.$$

From Table IV, the monotonic relationships of [14-I] and [14-B] to TVC are

$$[14 - I] = 0.2237(\ln TVC) + 0.714,$$
$$[14 - B] = -0.2237(\ln TVC) + 0.286, \quad (19a)$$

and their rates of change are

$$(d[14 - I]/dTVC) = 0.2237/TVC,$$
$$(d[14 - B]/dTVC) = -0.2237/TVC. \quad (19b)$$

Equations (18b) and (19b) can be used in eq. (17b) to calculate values of $(d\overline{b^2}/dTVC)$ for each of the 18 blends; results are listed in Table IV. The eight blends to the left of the minimum with low TVC have negative values, indicating a decreasing $\overline{b^2}$ value with TVC, with the rate of decrease decreasing with TVC as the minimum is approached. The three blends to the right of the minimum with high TVC have positive values, indicating an increasing $\overline{b^2}$ value with TVC, with the suggestion that the rate of

increase is increasing with TVC as the data shifts farther from the minimum. For the seven blends defining the minimum, there is on average very little rate of change compared to the regions with greater positive and negative rates of change.

The flexibility of HPI and DPB in blends versus as homopolymers

This work has shown that both HPI and DPB are more flexible when miscibly blended than they are as homopolymers. There is prior evidence of this in the literature. Wide-Angle-X-Ray-Scattering studies[10] on HPI/HPB blends found that the average molecular interchain spacing was much larger than expected from the weighted-average of the interchain spacings of the homopolymers when the blend was miscible, but was equivalent to the weighted-average when the blend was immiscible. Those authors concluded that the wider spacing between chains in miscible blends was evidence that the chains are spread farther apart when HPI chains are mixed with HPB chains (compared to the spacing between chains when all chains are either HPI or HPB), resulting in an increase in free volume to accommodate the new packing order. They also showed that the single glass-transition temperature (T_g) of the blend was lower than predicted by the Gordon-Taylor equation. Although not specifically discussed, differential scanning calorimetry (DSC) scans were shown which, when analyzed by this author for this work, suggested that the single T_g of one miscible blend was broader than those of the homopolymer polydienes used in that blend. Other[11,12] DSC and Visco-Elastic studies have shown that HPI/HPB miscible blends exhibit a single T_g that is broader than the T_g's of the homopolymers, indicative of micro-phase segregation. This micro-phase segregation provides increased free volume and allows more chain segmental mobility. One theory[13] pointed out that the original random phase approximation (RPA) theory, which assumes incompressibility, cannot account for this excess volume change upon mixing, and offered an alternative model that accounts for this effect. This accommodation of a new packing order, manifesting itself as an increase in the distance between PI and PB chains, indicates that even though the blend may be miscible on the macro-scale (as evidenced by Electron Microscopy (EM) and DSC experimental data), these chains may not be miscible on the molecular-scale. For example, if a miscible HPI/HPB blend, exhibiting one sharp T_g intermediate between those of the two polydienes, is analyzed for its Solid-State Nuclear Magnetic Resonance (SS-NMR) ^{13}C spectrum at a temperature that is greater than the T_g of the higher-T_g polydiene, sharp baseline-resolved

resonance peaks for the two polydienes are seen, indicating a completely liquid-like miscible blend. But as the temperature is lowered to the T_g of the higher-T_g polydiene but still above the blend T_g, there will be an abrupt change in the NMR resonance peaks of that polydiene, broadening and disappearing like a solid, while the resonance peaks of the lower-T_g polydiene remain sharp and liquid-like, indicating that even though the blend is miscible and has one T_g on the macro-scale, the two polydienes are acting as if they were distinct phases, i.e., immiscible on the molecular-scale.

It seems clear that an increase in free volume is consistent with a decrease in T_g, and logically leads to the suggestion of an increase in chain flexibility. Why is flexibility increasing? If, as previous studies suggest, individual chains of the two polydienes are not miscible on the molecular-scale, the repulsive forces between unlike chains result in added free volume, which in turn provides the space for more segmental mobility, resulting in more flexibility. Thus, an increase in free volume because of molecular-scale immiscibility appears to be the cause of increased flexibility in blends that are miscible on the macro-scale. The molecular-scale immiscibility, in turn, occurs because of the chemical differences between the vinyl groups of each polydiene.

Except for those with very high vinyl contents, the flexibility (as evidenced by the inverse of average statistical segment length) of these two polydienes, in miscible blends with each other, is controlled by the influence that the vinyl content of one polydiene has on the flexibility of the other polydiene. A close inspection of Table III reveals that in miscible blend systems of one HPI of any vinyl content with DPB with different vinyl contents, the flexibility of DPB increases as its vinyl content increases but the flexibility of that HPI decreases. In miscible blend systems of one DPB of any vinyl content with HPI with different vinyl contents, the flexibility of HPI decreases as its vinyl content increases but the flexibility of that DPB increases. In other words, in HPI/DPB miscible blends, either polydiene can have any flexibility depending on the vinyl content of the other polydiene with which it is blended (and to a lesser extent on the assumed effect that blend ratio has on the two polydienes). This suggests that a matrix effect on the flexibility of each polydiene exists for miscible HPI/DPB blends. There is scant discussion in the literature of matrix effects on miscible blends of polyisoprene and polybutadiene. The dielectric relaxation of low volume fractions of HPI miscibly blended with HPB[7] found that there was no appreciable matrix effect on HPI chain configurations. Nonetheless, in this work, the results can be interpreted as both polydienes being more flexible when entangled with each other, with each flexibility

being influenced by the other polydiene, and the vinyl content dependencies of this influence of one polydiene on the other being directionally-opposite. For HPI and DPB, the average statistical segment length of a polydiene chain may not be an inherent physical property, rather its flexibility is greatly influenced by the flexibility of the other polydiene chains with which it is entangled. This suggests that the average statistical segment length of a polydiene chain must be considered in terms of what polydiene chains it is entangled with, even when those other chains are the same as the chain in question, i.e., a homopolymer.

CONCLUSIONS

The observed[1] nonmonotonic relationship exhibiting a minimum for HPI/DPB miscible blends is explained by three factors: (1) the decreased average square statistical segment length that both polydienes exhibit when miscibly blended; (2) the opposite directional changes in average square statistical segment length that occur as vinyl content changes when the two polydienes are blended; and (3) the influence of the blend ratio of the blend, as evidenced by the segregation of the blend systems into groups that have average square statistical segment lengths that are mainly influenced by the average square statistical segment length of one or the other polydiene.

How these three factors combine determines whether the flexibility of the blend will fall on one side or the other of the minimum. (1) The flexibility of blends with low total vinyl content to the left of the minimum is dominated by the flexibility of DPB but the domination decreases as total vinyl content increases. As total vinyl content increases in this region, flexibility increases for DPB and decreases for HPI, and even though the relative contribution by the flexibility of DPB to the flexibility of the blend is decreasing and the relative contribution by the flexibility of HPI is increasing, the rate of flexibility increase is greater for DPB than the rate of flexibility decrease for HPI, and the net result is that the blend becomes more flexible. (2) The flexibility of blends in the region of the minimum is not dominated by the flexibility of either HPI or DPB. As total vinyl content increases in this region, flexibility does not change much for either HPI or DPB, the net result being that the blends do not change much in flexibility. (3) The flexibility of blends of high total vinyl content to the right of the minimum is dominated by the flexibility of HPI and the domination increases as total vinyl content increases. As total vinyl content increases in this region, flexibility is almost constant for HPI and decreases for DPB. Even with the

relative contribution by the flexibility of HPI to the flexibility of the blend increasing and the relative contribution by the flexibility of DPB decreasing, the rate of flexibility decrease for DPB dominates the almost zero rate of flexibility decrease for HPI, and the net result is that the blend becomes less flexible.

Increases in flexibility of the two polydienes in miscible blends are due to immiscibility on the molecular-scale, resulting in an increase in free volume through chain repulsion and more space for the chain segments to rotate. A chemical effect due to vinyl content appears to be the cause of molecular-scale immiscibility, resulting in a matrix effect on flexibility.

RECOMMENDATIONS

These results were based on probably the largest set of blend average square statistical segment length data ever developed for this subject, encompassing the widest range of polydiene compositions and blend ratios ever studied. Even so, conclusions were drawn on a minimum of results. For this reason, it is recommended that this work should be extended to include a wider range of polydiene vinyl contents and blend ratios to better define the relationships and generate subsequent results based on a wider range of parameters with better precision and accuracy.

Solid-State Nuclear Magnetic Resonance has been used to evaluate miscible blends of polyisoprene and polybutadiene.[14] Further work is warranted because the SS-NMR ^{13}C spectra for polyisoprene and polybutadiene are sufficiently different that the major resonance peaks of the two polydienes are baseline-resolved even when miscibly blended. Since the peak-width is related to the flexibility (and, hence, the average statistical segment length) of that polydiene, this experiment could be an independent check on whether the average statistical segment length changes for either polydiene in miscible blends. For this experiment, deuteration of either polydiene is not needed, making it much easier to procur and study polydienes over a wide range of vinyl contents in blends over a wide range of blend ratios.

Blend identities, volume fractions and average square statistical segment lengths were furnished by R N Thudium.

APPENDIX

CHOICE OF REFERENCE UNIT CELL (ν_0) DEFINITION

The original[1] publication used a concentration-independent form of the reference unit cell molar volume to calculate χ and $\overline{b^2}$,

$$\nu_0 = (\nu_I \nu_B)^{1/2}. \tag{A.1}$$

TABLE A.I
Adjusted χ

Blend system	Blend ratio (HPI/DPB)	$\chi \times 10^5$		
		$\nu_0 = (\nu_I \nu_B)^{1/2}$	$\nu_0 = f(\Phi_i)$	$[(\nu_I\nu_B)^{1/2}]/[f(\Phi_i)]$
7-xxxx-9	32/68	93.1	88.1	1.06
	52/48	−0.476	−0.469	1.01
	72/28	−260	−268	0.97
7-xxxx-26	32/68	86.3	81.7	1.06
	52/48	−13.8	−13.6	1.01
	72/28	********	*******	**************
7-xxxx-70	32/68	−251	−237	1.06
	52/48	−264	−261	1.01
21-xxxx-9	32/68	277	262	1.06
	52/48	258	255	1.01
	72/28	252	260	0.97
21-xxxx-26	32/68	131	123	1.07
	52/48	177	175	1.01
	72/28	********	*******	**************
21-xxxx-39	52/48	98.6	97.2	1.01
	72/28	73.4	75.6	0.97
21-xxxx-70	32/68	73.4	75.6	0.97
	52/48	−370	−365	1.01
	72/28	−135	−139	0.97
44-xxxx-39	32/68	95.8	90.7	1.06
	52/48	253	249	1.02
44-xxxx-70	32/68	−437	−413	1.06
	52/48	−236	−232	1.02
	72/28	−591	−609	0.97

Since the results in that work were based on a considerable range in blend ratio, it would have been preferable to use the concentration-dependent reference unit cell molar volume,[15]

$$\nu_0 = [(\Phi_I/\nu_I) + (\Phi_B/\nu_B)]^{-1}. \qquad (A.2)$$

Equations (A.1) and (A.2) are equivalent in only certain cases, e.g., when $\nu_I = \nu_B$, at $\Phi_I = \Phi_B = 0.5$. This is the case for most reported studies but not the case for the study[1] on which this work is based. To investigate whether an appreciable error is introduced by the use of eq. (A.1), the original[1] calculated values of χ were adjusted to reflect using eq. (A.2). For illustration purposes, the results for $T = 318°\text{K}$ are listed in Table A.I. Comparing the results based on the two equations, the absolute value of χ changed by no more than 1–6%, and no change in the trends in the data was evident. No changes in the conclusions from the original[1] publication regarding the significance of χ are required. For the calculations using $\overline{b^2}$, the same percentage change is anticipated; no adjustments to $\overline{b^2}$ need be made since this level of error is of the same magnitude as experimental error in $\overline{b^2}$.

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