Dielectric Relaxation Behavior of Styrene/Butyl Acrylate Copolymers near T_g

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ABSTRACT: The dielectric relaxation behavior of copolymers of styrene and butyl acrylate is investigated over a wide frequency range. The results are analyzed in terms of the free volume and configurational entropy theories. The calculated fractional free volume was nearly constant over the composition range studied while the volume expansion coefficient exhibits a maximum in the mid composition range. Even though the change in heat capacity at T_g varied linearly with composition, the free energy of activation calculated from the configurational entropy model reached a broad maximum in the mid composition range. In addition, the average dielectric relaxation time of the copolymers at T_g is not constant. In fact, the longest relaxation times were obtained for samples containing nearly equal amounts of styrene (S) and butyl acrylate (B). It is suggested that the SB diad has a relaxation time much longer than the relaxation times of the SS and BB diads.

Introduction

It is often necessary to modify an existing polymer in order to obtain desirable mechanical and physical properties. Among the simplest approaches is the introduction of a comonomer during the polymerization process. By control of the concentration and the rate of addition of the comonomer a wide variety of physical and mechanical properties can be realized that are intermediate between the individual constituents.[1,2]

The glass transition temperature (T_g) of random copolymers is observed to vary nearly linearly over the composition range, although situations do exist wherein the T_g vs composition curve is either convex or concave depending on the structure and steric considerations of the monomers.[3-5] The earliest approaches for predicting the T_g of a copolymer were reasonably successful and were based on simple additivity concepts related to either free volume or thermodynamic theories.[6,7] Barton[8] and Johnston[9] independently improved these models by accounting for the sequence distribution of the monomers and found better agreement between theory and experiment. Because the relationship between T_g and composition is monotonic, it is important to know how the fractional free volume, f_g, at T_g, and the volume expansion coefficient, α_f, at T_g vary with composition. Moreover, it will be possible to determine if the relaxation time, τ_g, at T_g, which is thought to be a constant (100 and 1000 s depending on the measurement technique), is indeed independent of composition.

Although there have been a considerable number of studies concerned with the dielectric and viscoelastic relaxation behavior of copolymers and polymer blends, few have considered how f_g and α_f vary with composition. From the results of the few studies that do exist, the results have in some cases been shown to vary nonlinearly as a function of composition,[10] while in other studies, monotonic variations in composition were observed.[11] Moreover, in many of these studies only a few copolymer compositions were measured and the experimental data were generally obtained over a limited frequency range. With the wider frequency range available using dielectric spectroscopy, an improvement in the precision of the values of f_g and α_f can be obtained. Furthermore, an analysis of the relaxation behavior of a series of copolymer compositions will allow us to determine how f_g and α_f vary with composition. In addition, because the relationship between T_g and composition can also be described by the configurational entropy model, the influence of composition on the free energy of activation can be determined.[12]

In this study, random copolymers containing styrene and butyl acrylate were prepared wherein the composition of the styrene was varied between 0 and 100 wt %. With the use of dielectric spectroscopy the motions of the dipoles at the glass transition temperature were probed in the frequency range between 10^{-1} and 10^6 Hz. This system was chosen because the contribution to the dielectric loss can be associated mainly with the butyl acrylate segment, because the dipole moment of the styrene segment is small (~0.4 D).[13]

Experimental Section

Sample Preparation. The copolymers were prepared by particulate-stabilized batch suspension polymerization techniques. The monomers and initiators were used as received without further purification. Polymerizations were run on a 200 g scale at 40% solids. The organic phase was emulsified with the aqueous phase by use of either a Waring blender or a microfluidizer. The resulting oil/water emulsion was then added to a three-neck, round-bottomed flask equipped with a condenser, stirrer, and nitrogen inlet and was polymerized at the appropriate temperature and reaction time. The resulting dispersions were then devolatilized, cooled, washed, and filtered. Reaction yields were generally greater than 95% based upon total solids.

Differential Scanning Calorimetry (DSC). DSC measurements were made with a Perkin-Elmer DSC-2 as described previously.[14] Heating rates of 1.25, 5, and 20 °C/min were used. At the higher heating rates for some of the samples the dielectric and DSC relaxation times overlap. At the lowest

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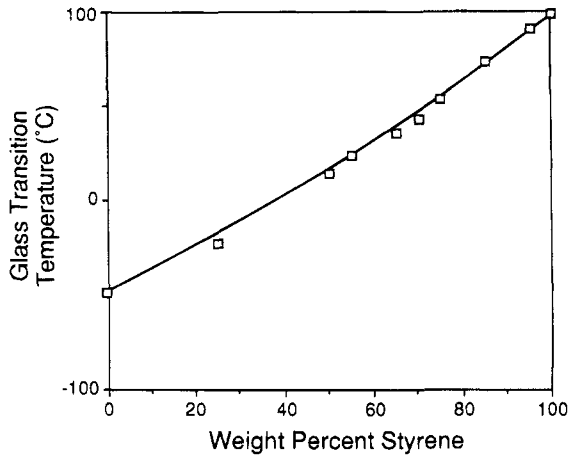

Figure 1. Composition dependence of T_g for the styrene–butyl acrylate copolymers. The line represents the best fit to the data using the Gordon–Taylor equation with $k = 0.79$.

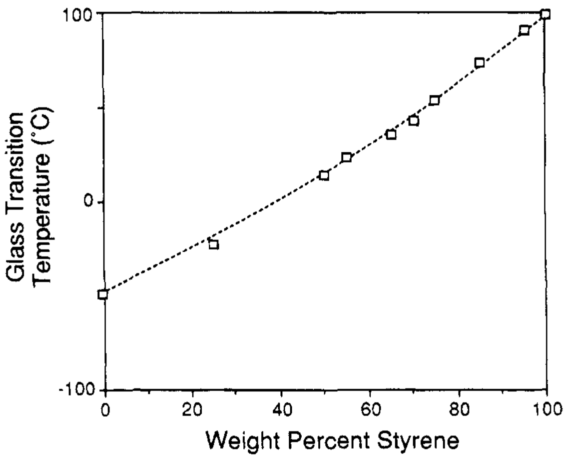

Figure 2. Composition dependence of T_g for the styrene–butyl acrylate copolymers. The line represents the best fit to the data using the Couchman equation.

heating rate, for all but the pure poly(butyl acrylate) sample, the relaxation time determined by DSC is lower than τ_D.

Dielectric Spectroscopy. The dielectric studies were made using a commercially available instrument from Novocontrol that uses the Solartron-Schlumberger 1260 frequency response analyzer and a Chelsa high-impedance preamplifier of variable gain. The frequency range covered in these experiments generally ranged from 10^{-1} to 10^6 Hz. The temperature was controlled by passing a stream of temperature-controlled nitrogen gas past the sample. Also, a HP 4192 Hewlett-Packard analyzer was used to measure the dielectric response of the copolymers between 10^2 and 10^6 Hz. In this case temperature was controlled by a Delta Design 9023 oven. In both cases the sample was ramped to the desired temperature and allowed to equilibrate before the frequency range was scanned.

Results and Discussion

In order to characterize these copolymers, ^{13}C and ^{1}H NMR were used to determine the sequence distribution of the copolymers. Previous studies had shown that it was possible to determine the sequence distribution of styrene–acrylate copolymers using a combination of these techniques.[15] However, because of the overlapping signals associated with tacticity and sequence distribution of the copolymer, it was not feasible to extract the concentrations of the diads with any degree of accuracy. Based on the analysis of the data, the results indicated that block copolymers were not formed. To estimate the concentrations of diads, the data of Brar et al. were utilized for the analysis described later.[15]

In Figure 1 the glass transition is plotted as a function of the concentration of styrene present in the copolymer. As is typical with most copolymers, this plot deviates slightly from linearity. The Gordon–Taylor equation shown in eq 1 has often been used to predict the T_g of

$$T_g = \frac{[w_1 T_{g1} + k(1 - w_1)T_{g2}]}{[w_1 + k(1 - w_1)]} \tag{1}$$

the copolymer based on the T_g of each of the homopolymers [T_{g1}(polystyrene) and T_{g2}(poly(butyl acrylate)), respectively] and the weight fraction of each of the species present.[16] The results show that a good fit to the Gordon–Taylor equation is obtained with a value of the fitting parameter, k, equal to 0.79. The fitting parameter is equal to the ratio α_s/α_{bm} where α_s and α_{bm} are the thermal expansion coefficients of styrene and butyl acrylate, respectively.

The Couchman equation (eq 2), which is based on thermodynamic considerations, can also be used to

$$T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \tag{2}$$

predict the T_g of the copolymers.[17] Unlike the Gordon–Taylor equation there are no adjustable parameters. The T_g of the copolymer depends only on the glass transition temperature of the homopolymers, their associated heat capacities, and the concentration of each of the species present. The results shown in Figure 2 indicate that within experimental error, the variation with T_g is well described by this equation also.

Dielectric Spectroscopy. The complex permittivity is given in eq 3, where ϵ' is the permittivity, ϵ'' is the

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \tag{3}$$

loss factor, and $\omega = 2\pi f$ where f is the frequency. A typical plot of the loss factor as a function of frequency at selected temperatures for a few of the copolymers is shown in Figure 3. Two contributions to the loss factor are generally observed. At low frequency and high temperatures there is an increase in ϵ'' that is associated with dc conductivity. At higher frequencies a loss peak is observed that is associated with the relaxation caused by micro-Browinan motions of the polymer chains in the glass transition region.

The temperature and composition dependence of the relaxation process in the vicinity of the glass transition temperature can be described by the Williams–Landel–Ferry (WLF) formalism shown in equation 4.[11]

$$\log \frac{\tau(T)}{\tau(T_g)} = -\frac{C_1(T - T_g)}{C_2 + T - T_g} \tag{4}$$

As indicated in the Experimental Section, the onset of the glass transition was defined as T_g, and the T_g was determined by DSC at a heating rate of 1.25 K/min. A three-parameter nonlinear regression was used to obtain the best fit parameters for C_1, C_2, and the relaxation time, τ_g, at T_g. Plots of $\log f_m$ vs temperature are shown in Figure 4a–c. Values of C_1 and C_2 along with their standard deviations are shown in Table 1. The standard deviations of C_1 and C_2 are small because of the extensive frequency range covered in the dielectric experiments. It should also be noted that superimposed

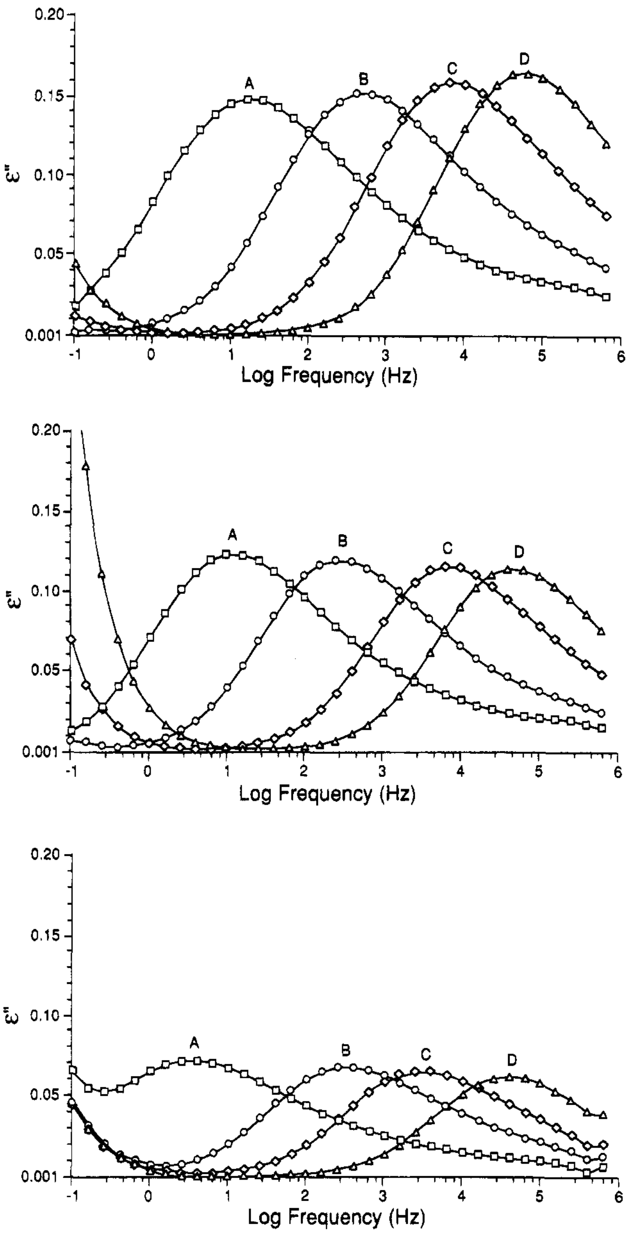

Figure 3. (a) Dielectric loss curves for SB55 at temperatures aproximately (A) 15, (B) 25, (C) 35, and (D) 45 deg above T_g. (b) Dielectric loss curves for SB70 at temperatures approximately (A) 20, (B) 30, (C) 40, and (D) 50 deg above T_g. (c) Dielectric loss curves for SB85 at temperatures approximately (A) 10, (B) 20, (C) 30, and (D) 40 deg above T_g.

on this plot are the data points obtained from various heating rates from the DSC experiments. In some cases the T_g's obtained from the DSC overlap data points from the dielectric data, with the lowest point always being the T_g determined at the 1.25 K/min heating rate. This is consistent with previous studies on polymer blends that indicate that the DSC data have the same temperature dependence as the dielectric data.[18]

Free Volume Approach. From the values of C_1 and C_2 it is possible to determine how the free volume and volume expansion coefficient vary with composition. The free volume of a polymer as a function of temperature, $f(T)$, can be expressed by

$$f(T) = f_g + \alpha_f(T - T_g) \qquad (5)$$

where f_g is the fractional free volume at T_g and α_f is the volume expansion coefficient at T_g. From the Doolittle equation which describes the relationship between the viscosity of a system and the temperature

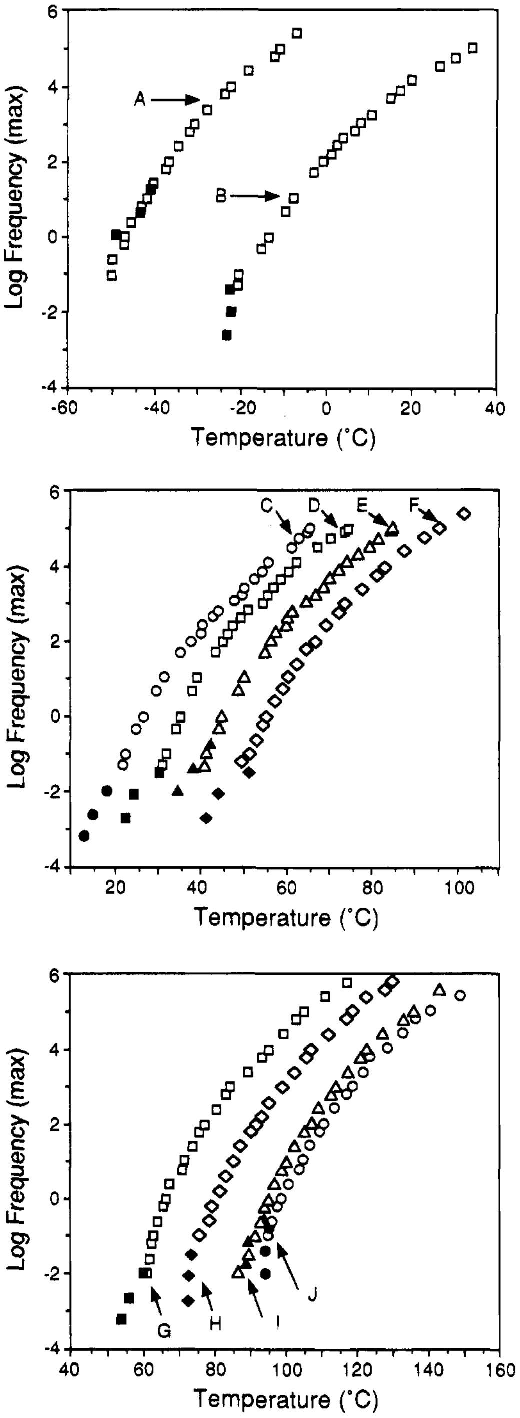

Figure 4. Temperature dependence of the relaxation curves for each of the copolymers: (a) (A) B100, (B) SB25; (b) (C) SB50, (D) SB55, (E) SB65, (F) SB70; (c) (G) SB75, (H) SB85, (I) SB95, (J) S100.

Table 1. WLF Parameters

% styrene	T_g (°C)	C_1	std dev	C_2	std dev
0	-49.0	14.5	±1.1	70.0	±9.0
25	-23.2	13.5	±0.4	62.0	±3.5
50	13.6	15.4	±0.5	42.0	±4.8
55	23.0	15.0	±0.2	37.7	±2.0
65	35.4	14.5	±0.3	38.0	±2.5
70	42.3	13.6	±0.1	43.0	±1.2
75	54.0	14.8	±0.3	43.0	±2.0
85	73.0	14.5	±0.3	49.6	±2.4
95	90	14.0	±0.5	54.1	±3.2
100	98	12.5	±0.5	56.4	±4.0

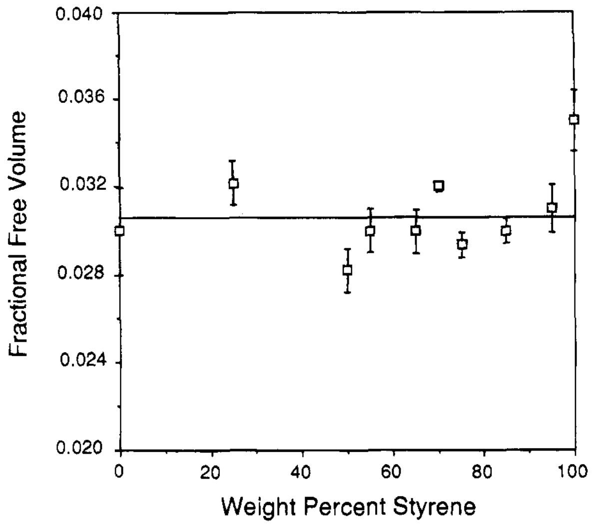

Figure 5. Fraction free volume vs percent styrene.

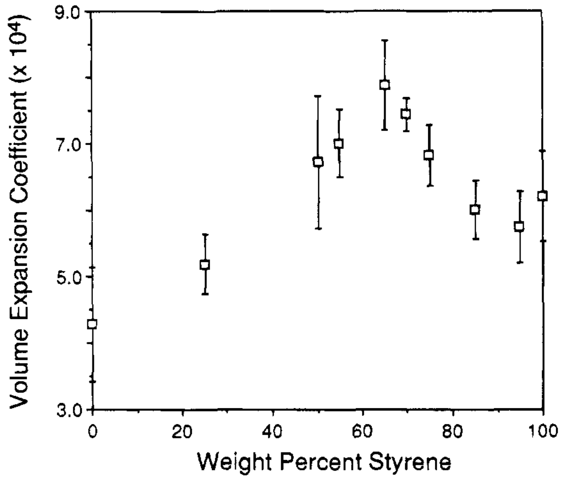

Figure 6. Volume expansion coefficient vs the percentage styrene.

dependence of the free volume, it is possible to relate the WLF constants to f_g and α_f, as shown in eqs 6 and 7.[11] B is an empirical constant used in the Doolittle equation and for this analysis is assumed to be unity and independent of composition.

$$f_g = B/2.303C_1 \tag{6}$$

$$\alpha_f = B/2.303C_1C_2 \tag{7}$$

As shown in Figure 5, the fractional free volume at T_g for the copolymers is nearly constant and independent of composition. The average fractional free volume at T_g is 0.030 ± 0.002 and is slightly larger than the universal constant of 0.025. The volume expansion coefficient is plotted vs composition in Figure 6. The results show that the expansion coefficient, α_f, goes through a maximum slightly above the mid composition range. The fact that α_f goes through a maximum is perhaps surprising in that the volume expansion coefficient is expected to be a monotonic function of composition. In these copolymers, contributions to the volume expansion would be expected from both the chain backbone and the side chain motions of the butyl acrylate segments.

The results obtained from analysis of the temperature dependent dielectric data indicate that the values obtained for the WLF coefficients C_1 and C_2 are very similar to values previously reported for polystyrene using viscoelastic measurement techniques. In previous studies the value of the fractional free volume at T_g is reported to be $f_g = 0.033$[10,19] and the value of the volume expansion coefficient to be 6.6×10^{-4}/°C and 7.2×10^{-4}/°C, respectively.[10,19] These values compare well with $f_g = 0.0345$ and $\alpha_f = 6.1 \times 10^{-4}$/°C obtained using the dielectric data.

For copolymers of styrene with n-hexyl methacrylate it had previously been shown that f_g increases with increasing concentration of the n-hexyl methacrylate.[19] However, it is difficult to draw conclusions from this study because only two copolymers were analyzed. In the paper by Halary et al. the authors reported that f_g exhibited a nearly S-shaped dependence on concentration.[10] In none of the previous studies did the authors find that the fractional free volume was nearly constant as in this study. In the paper by Ahuja, it was determined that for styrene–methyl methacrylate copolymers, f_g reached a minimum at 50% styrene concentration.[20] However, only two copolymers were studied and the uncertainties in C_1 and C_2 were not reported.

In two of the previous studies the authors found that the volume expansion coefficient varied nearly linearly as a function of composition.[10,19] In this study we find that α_f reaches a maximum in the mid composition range. Because the Gordon–Taylor equation yielded a value of $k = 0.79$ for the ratio α_s/α_{bm}, the results indicate that α_{bm} contributes more to f_g than α_s. Thus if the relaxation times were governed by the same α_{bm} and α_s as T_g, then the volume expansion coefficient (α_f) at T_g should be a monotonic function of composition. However, we have shown that α_f is not a monotonic function of composition and, in fact, passes through a maximum. Therefore, it must be concluded that the relaxational α_f determined from C_1 and C_2 is not equal to the thermal expansion coefficient that determines T_g.

Configurational Entropy Model. The temperature dependence of the dielectric relaxation times can be analyzed by the Adam–Gibbs equation, which assumes that the configurational entropy determines the average relaxation time.[12] It is believed that the relaxation time is related to cooperative rearrangement of many segments. An expression for the relaxation time is given in terms of the thermally activated transition state Arrhenius equation in combination with the assumption that the relaxation process occurs by cooperative rearrangement of the segments.[21]

The configurational entropy $\Delta S_c(T)$ is given in eq 8. T_2 is the temperature at which the configurational

$$\Delta S_c(T) = \Delta C_p \ln \frac{T_g}{T_2} \tag{8}$$

$$\Delta u = \frac{2.3C_1C_2\Delta C_p}{S_c^*} \tag{9}$$

entropy goes to zero. The activation free energy for cooperative rearrangement, $\Delta\mu$, is given in eq 9, where it is assumed that S_c^* is the critical entropy required for rearrangement and equals $R \ln 2$. Because it has been previously shown that T_g and ΔC_p are monotonic functions of composition, it is expected that ΔS would also vary in this manner. However, $\Delta\mu$ may not vary linearly. The results of this analysis indicate that the free energy of activation $\Delta\mu$ varies with composition, as shown in Figure 7. The highest values of $\Delta\mu$ are at either end of the composition range. Although the

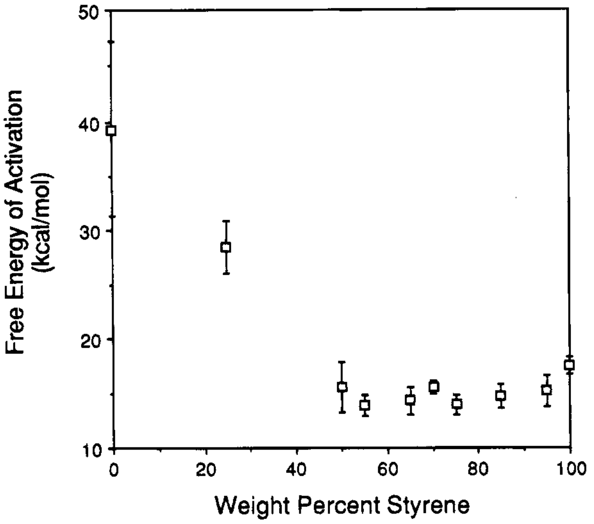

Figure 7. Free energy of activation vs the concentration of styrene.

entropy analysis incorporates the experimental ΔC_p data, $\Delta\mu$ and α_f vary similarly as a function of composition because of contributions from C_1 and C_2. Further, because C_2 is related to $T_g - T_2$ and the configurational entropy at T_g, the results indicate that the samples with the highest configurational entropy occur at the ends of the composition range. The lowest configurational entropy is calculated for those samples that have nearly a 50/50 ratio of styrene to butyl acrylate. This implies that the flex energy (eq 10) is highest in the mid composition range. This observation is not consistent with the fact that the glass transition temperature deviates negatively from linearity.[22]

Distribution of Relaxation Times. The dielectric relaxation behavior in the vicinity of T_g is dominated by micro-Brownian motion of the polymer chains and can be characterized by a number of empirical equations. In this study we have chosen to use the distribution function proposed by Kohlrausch–Williams–Watts (KWW).[23–25]

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon^\infty} = \int_0^\infty \exp(-j\omega t)\left[\frac{-d\varphi(t)}{dt}\right] dt \qquad (10)$$

$$\varphi(t) = \exp(-t/\tau)^\beta \qquad (11)$$

where ϵ_0 and ϵ_∞ represent the static and the limiting high-frequency dielectric constants, respectively. τ is the relaxation, and β is a parameter that provides a measure of the distribution of relaxation times. The results shown in Figure 8 indicate that β increases from 0% to about 60% styrene content. At higher styrene content β is nearly independent of concentration. Because the value of β is increasing, the results indicate that there is a narrowing of the breadth of the relaxation curves as the concentration of styrene increases.

The average retardation time, $\langle\tau\rangle$, can then be calculated from eq 12 and as shown in Figure 9 is a nonlinear function of composition.

$$<\tau> = \left(\frac{\tau_0}{\beta}\right)\Gamma\left(\frac{1}{\beta}\right) \qquad (12)$$

The results show that the relaxation time goes through a maximum in the mid composition range. The data suggest that the large-scale cooperative motion of the dipoles in the polymer is slower in regions where styrene–butyl acrylate diads predominate.

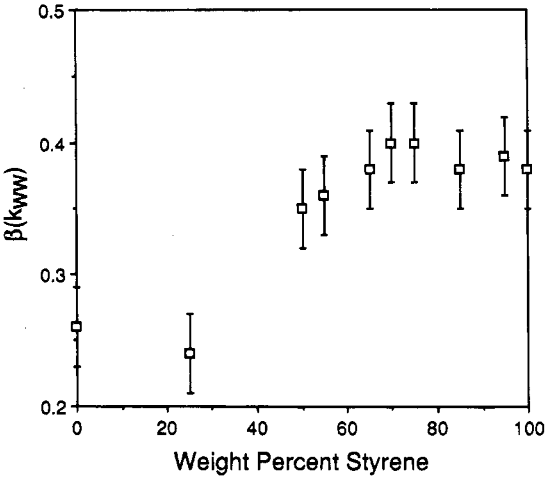

Figure 8. KWW β vs concentration of styrene.

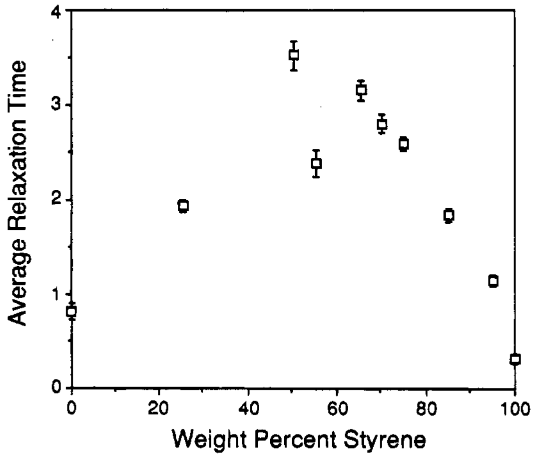

Figure 9. Average relaxation time vs concentration of styrene.

In summary, the dielectric relaxation times as a function of temperature and frequency depend on the copolymer composition in a complicated fashion. T_g shows a slight minimum where the SB diads are at a maximum. The relaxation times at T_g are a maximum where the concentration of SB diads is a maximum. The fractional free volume (determined by C_1) is a constant, independent of composition, while α_f, which is proportional to $1/C_1C_2$, reaches a maximum at the mid composition range.

Influence of Sequence Distribution. Because it is possible that the relaxation times at T_g depend on the local sequence distribution of the segments in much the same way Johnston demonstrated T_g is, we attempted to test this hypothesis by modeling the average relaxation time in terms of the concentration of the diads. The approach we take is similar to that described by Barton[8] and Johnston[9] and further refined by Havlicek et al.[26] wherein they predict the T_g of a copolymer based on the T_g of the homopolymers and the alternating copolymer and a weighted fraction of the various diads present. Johnston suggested that for a copolymer, the glass transition temperature of the AA diads would be similar to that of the T_g of homopolymer A, and similarly, the BB diads would have a T_g similar to homopolymer B because they would experience much of the same interactions. However, the formation of AB diads would result in new interactions and would be

Table 2. Comparison of Calculated and Measured T_gs

% styrene	measd T_g (°C)	calcd T_gs
50	13.6	12.3
55	23.0	20.7
65	35.4	34.7
70	42.3	42.4
75	54.0	50.1
85	73.0	72.5
95	90.0	88.2

expected to have their own T_g. Similar to Johnston we write an equation to describe the glass temperature in terms of the concentration of diads determined by NMR. We used the data of Brar et al. to calculate the concentration of diads for the compositions we studied because we felt their results were more consistent.[15] In this equation the glass transition temperature of the copolymer is given by

$$T_g = [c_{ss}]T_{gss} + 2[c_{sb}]T_{gsb} + [c_{bb}]T_{gbb} \tag{13}$$

Since we know the glass transition temperatures of the poly(butyl acrylate) and PS, it is simple to solve for the T_g of the styrene–butyl acrylate diad. The best fit indicates that $T_{gsb} = 5.9 \pm 3$ °C. The glass transition temperature of the SB25 sample was not included in this analysis. Table 2 shows the values of the T_g's of the copolymers and those predicted by eq 13.

We consider an approach similar to that discussed above to account for the fact that the relaxation times in the mid composition range exhibit a maximum. It is assumed that we can write an equation to predict the relaxation time of the copolymer by taking into consideration the sequence distribution. Further, we assume that the relaxation time of the SS and BB diads are the same as the homopolymers and the relaxation phenomenon is governed by both inter- and intramolecular interactions. Therefore, by taking into account the concentration of the diads, the relaxation time of the SB diad can be calculated from the equation below.

$$\tau_{tot} = [c_{ss}]\tau_{ss} + 2[c_{sb}]\tau_{sb} + [c_{bb}]\tau_{bb} \tag{14}$$

The results indicate that the relaxation time for the styrene–butyl acrylate diad is approximately 250 (log $\tau = 2.39 \pm 0.6$) s. Because the relaxation time is longer than either homopolymer, it might have been expected that the T_g would deviate positively from linearity (see Figure 4); however, this was not observed experimentally. The $\tau(T_g)$ values are largest in the mid composition range because the T_g's are lower than the simple additivity relationship. The effect of different diads on the relaxation behavior is usually interpreted as an intramolecular effect, as in the Gibbs–DiMarzio theory.[27] However, the analysis applied here could be accounted for by either intramolecular or intermolecular effects. At the present time, we know of no methods of separating the inter- from intramolcular effects on T_g. In the future, molecular modeling may offer a means of separating the intra- from the intermolecular effects on the properties and relaxations.

Conclusions

In this paper we studied the relaxation behavior of a series of copolymers of styrene and butyl acrylate using dielectric spectroscopy. Within experimental error it was found that the fractional free volume at T_g was independent of composition while the volume expansion coefficient went through a maximum in the mid composition range. Similarly, the average relaxation time at T_g and the distribution of relaxation times were not monotonic functions of composition, but rather exhibited maxima in the mid composition ranges. Using an approach similar to that of Johnston it was demonstrated that the glass transition temperature of the styrene–butyl acrylate diad was approximately 6 °C. Moreover, we used a similar methodology to calculate the average relaxation time of the SB diad. Calculations indicated that the average relaxation time was about 250 s for the SB diad. Of course these results are only approximate because the diad concentration was calculated from literature data.

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