Influence of Cross-Linking on the Molecular Relaxation of an Amorphous Copolymer Near Its Glass-Transition Temperature

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ABSTRACT: Temperature-dependent dielectric relaxation spectra of cross-linked styrene–butyl acrylate copolymers were measured at frequencies between 10 mHz and 1 MHz. The results were analyzed using the empirical Kohlrausch–Williams–Watts (KWW) and Havriliak–Negami (HN) formalisms. While the KWW and the HN formalisms were equally well able to fit the experimental data for the uncross-linked copolymer, the HN formalism provided superior fits at high levels of cross-linking. The fitting parameters obtained from the HN routine were used to interpret the data in terms of the model proposed by Schönhals and Schlosser that relates the molecular motion of the polymer with the HN parameters. In this model, $n = \alpha\beta$ is correlated with the local intramolecular dynamics of the polymer and is not influenced by the level of cross-linking. On the other hand, the parameter $m = \alpha$, which is related to the intermolecular correlations of the polymer chain segments, decreases with increasing level of cross-linking.

Introduction

Dielectric spectroscopy, along with other forms of Hertzian spectroscopy (e.g., rf, microwave, IR, UV),[1] has long been used to probe the molecular motions of polymers. The use of dielectric spectroscopy in particular has grown in recent years, driven by improved experimental convenience and a wider available frequency range. With the advent of broad-band dielectric spectroscopy, it is now possible to study the relaxation behavior of materials over very wide frequency ranges. As a recent example, Kremer and co-workers have analyzed the relaxation behavior of glycerol over 12 decades of frequency.[2] While the experimental capabilities have certainly increased in the last decade, it is still necessary to establish a theoretical model that is able to correlate the shape of the dielectric relaxation spectrum with dynamic motions of the polymer chains.

Background

The isothermal dielectric relaxation behavior in the frequency domain can be described by the complex relative permittivity

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \qquad (1)$$

where $\omega = 2\pi f$, f is the frequency in Hz, $i = (-1)^{1/2}$, and $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are the real and imaginary parts of the relative permittivity, respectively. Currently, the two most commonly used empirical functions to analyze the shape of dielectric loss curves are the Havriliak–Negami (HN) and the Kohlrausch–Williams–Watts (KWW) functions. However, in recent years there have been a number of papers published wherein researchers correlate the fitting parameters with molecular motions of the polymer chains.[3-5]

The first successful attempt to treat permittivity was developed by Debye.[6] However, the treatment developed by Debye predicted that a molecule would exhibit only a single relaxation time. For such a single relaxation process, the dielectric response can be described by eq 2 with $\alpha = 1$ $\beta = 1$ and τ as the Debye relaxation time.

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{(1 + (i\omega\tau)^\alpha)^\beta} \qquad (2)$$

Recognizing the limitation of the original work of Debye, Cole and Cole[7] reworked the treatment of Debye by setting $\beta = 1$ and allowing α to vary between $0 < \alpha \leq 1$. This function models materials that exhibit a broad but symmetrical distribution of relaxation times. While the properties of many molecules conformed to the expectations of this empirical model, many other materials, especially polymers, exhibited nonsymmetrical behavior.

To describe materials with an asymmetrical distribution of relaxation times, Davidson and Cole[8] modified eq 2 such that $\alpha = 1$ and now β was allowed to vary from $0 < \beta \leq 1$. By parameterizing the model in this way, it was possible to fit dielectric loss peaks exhibiting high-frequency tails.

In order to describe the shape of a broad and asymmetric relaxation curve, Havriliak and Negami[9] combined the Cole–Cole and the Davidson–Cole relationships. In this model, α and β are both able to vary between $0 < \alpha \leq 1$ and $0 < \beta \leq 1$. The typical representation of the HN function is shown in eq 2 with $\tau = \tau_{\text{HN}}$ as a mean relaxation time.

In this equation, α and β are adjustable fitting parameters (equal to unity for a single relaxation time), ϵ_0 and ϵ_∞ are the relaxed and unrelaxed relative permittivities, respectively, and τ is a relaxation time.

The value α is able to describe the symmetric broadening of the dielectric relaxation, while β is correlated to the asymmetric nature of the relaxation curve. On a log–log plot of the dielectric loss factor as a function of frequency, the slope of the dielectric loss peak on the low-frequency side (i.e., $\omega\tau \ll 1$) is proportional to α, and on the high-frequency side (i.e., $\omega\tau \gg 1$), the slope is proportional to the product $-\alpha\beta$.[3] The HN relationship with its five parameters gives an excellent description of the shape of the dielectric relaxation curve for many different polymeric materials.[2,3,10,11]

Additionally, a contribution from the dc conductivity is superimposed on the dielectric loss curve $\epsilon''(\omega)$, particularly at low frequencies. This contribution can be well described by a power law[12]

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$$\epsilon''_{\text{conduction}} = \frac{1}{2\pi\epsilon_0}\frac{\sigma_{\text{DC}}}{f^s} \tag{3}$$

with the parameter σ_{DC} associated with the dc conductivity and $s \approx 1$.

Another model was introduced by Williams and Watts[13,14] that describes the shape of the dielectric relaxation curve by using a mathematical function first introduced by Kohlrausch. This model is often referred to as the Kohlrausch–Williams–Watts (KWW) function and commonly used in the form shown in eqs 4 and 5.

Using a similar definition of the dielectric function, the frequency domain function is given by

$$\Gamma(\omega) = \frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty -\dot{\Phi}(t)\exp(-i\omega t)\,\mathrm{d}t \tag{4}$$

where $\dot{\Phi}(t)$ denotes the time derivative of the time distribution function $\Phi(t)$.

The time distribution function, $\Phi^{\text{KWW}}(t)$, defined by the KWW model is

$$\Phi^{\text{KWW}}(t) = \exp\left[-\left(\frac{t}{\tau_{\text{KWW}}}\right)^{\beta_{\text{KWW}}}\right] \tag{5}$$

with $0 < \beta_{\text{KWW}} \leq 1$ and τ_{KWW} as the KWW relaxation time.

This function provides an excellent fit to the shape of the relaxation curve, especially for dielectric loss curves showing a high-frequency skewedness. Furthermore, it uses one less fitting parameter than the Havriliak–Negami function.

Although the shape of the primary relaxation curve is reasonably well described by both the HN function and the KWW function, both are historically empirical models with no correlation to molecular motions of polymer chains. Recently, Schönhals and Schlosser[3] proposed a model that can be applied to explain the shape of the dielectric relaxation curve near the glass-transition temperature (T_g). The authors suggest that the mobility of the polymer chain segments at T_g is controlled by both intra- and intermolecular interactions. Using a scaling hypothesis of the molecular dynamics, the model relates the high-frequency part (i.e., $\omega\tau \gg 1$) of the dielectric response to the local chain dynamics and the low-frequency dependence (i.e., $\omega\tau \ll 1$) to the intermolecular correlation between chains and their segments. Therefore, the HN parameter α can be correlated with the intermolecular dynamics and the product $\alpha\beta$ describes the very local intramolecular dynamics of the polymer.

Alternatively, Ngai and his co-workers have developed a model that results in an expression for $\Phi(t)$ that is similar to the KWW function shown in eq 5. In their model, $\Phi(t)$ is given by

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau^*}\right)^{1-n}\right] \tag{6}$$

where τ^* is the effective relaxation time and n is related to the intermolecular coupling between the relaxing species. This model has been utilized to successfully describe the relaxations of molecules in a number of systems.[4,15]

To test the models of Schönhals and Schlosser and of Ngai, a series of samples were prepared with varying degrees of cross-linker. In this way, the influence of the level of cross-linker on the molecular motions of the polymer can be studied. One might expect that the model that would fit these data would predict that the very local motion of the polymer should be essentially unaffected by the introduction of the cross-link sites. However, the large-scale cooperative motions of the polymer chains and its segments should be slowed in comparison to the uncross-linked polymer.

Experimental Section

Sample Preparation. Styrene–butyl acrylate (SB) divinylbenzene (DVB) polymers were prepared by particulate stabilized batch suspension polymerization techniques. The monomers and initiators were used as received without further purification. In order to keep the relaxation strength of our samples constant, the content of the butyl acrylate was kept constant at 25 wt %. 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-bottom 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-4 with an attached Perkin-Elmer 3600 data station. The temperature was calibrated with an indium standard. Samples were typically run between 253 and 423 K at 10 K/min. The midpoint of the transition is reported as the T_g of the copolymers.

Dielectric Spectroscopy. For the dielectric measurement, the samples were prepared as thin plates by pressing at elevated temperatures well above T_g. These specimens had diameters of 30 mm and thicknesses between 0.1 and 0.5 mm with a deviation of ±2 μm. A parallel-plate capacitor geometry was provided by mounting the samples between parallel brass plates.

The dielectric studies were performed using a commercially available instrument from Novocontrol that utilizes a Solartron-Schlumberger 1260 frequency-response analyzer and a Chelsea high-impedance preamplifier of variable gain. The frequency range covered in these experiments generally ranged from 10^{-2} to 10^6 Hz. The limits of the measured data ranged for tan(δ) between 10^{-4} and 10^3, for the conductivity (G) between 1 pS and 10 mS, and for the capacitance (C) between 1 pF and 10 nF with an accuracy of better than 3%. The temperature was controlled by a stream of temperature-controlled nitrogen gas passing the sample.

Results and Discussion

In a previous paper,[16] ^{13}C and ^{1}H NMR was used to characterize the sequence distribution of the styrene–butyl acrylate copolymers. Within the error of the analysis for a 75/25 styrene–butyl acrylate copolymer (i.e., SB75), the butyl acrylate was found to be incorporated randomly. Further, it was not anticipated that replacing the styrene with divinylbenzene influenced the random nature by which the butyl acrylate is incorporated into the polymer, although no direct evidence for this was obtained. As indicated in the Experimental Section, the styrene was replaced with an equivalent weight percentage of divinylbenzene. Therefore, the concentration of butyl acrylate, which has the higher dipole moment, remained constant throughout the series of samples studied.

In Figure 1, the T_g of the styrene–butyl acrylate copolymers is seen to increase with increasing concentration of the DVB cross-linker. This result is consistent with earlier studies of Ueberreiter and Kanig[17] and Glans and Turner.[18] In both papers, the T_g of the cross-linked polystyrene was seen to increase linearly with increasing level of the DVB cross-linker. The increase in T_g could be described by using a simple linear relationship that relates the cross-link density and T_g as shown in eq 7.

$$T_g(\xi) = T_{g0} + D\xi \tag{7}$$

Here T_{g0} is the glass-transition temperature for the uncross-linked sample, ξ is the cross-link density, and D

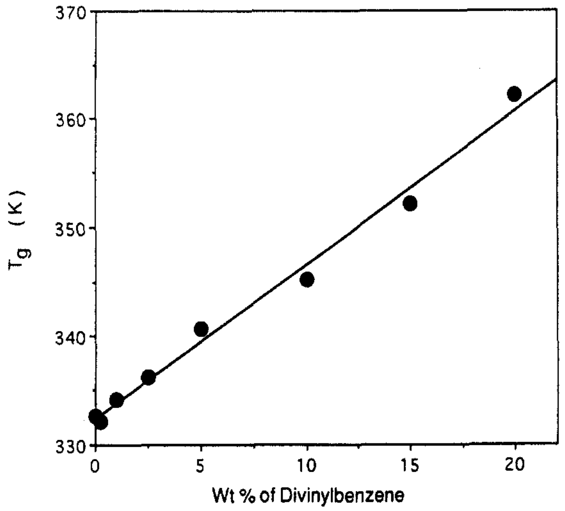

Figure 1. Dependence of the glass-transition temperature (T_g) on the amount of the divinylbenzene cross-linker for different styrene–butyl acrylate copolymers.

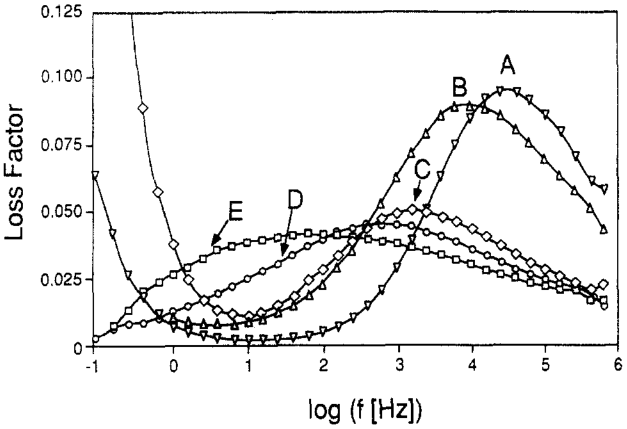

Figure 2. Typical dielectric relaxation spectra of the loss factor $\epsilon''(f)$ as a function of frequency at $T = 370$ K for different levels of cross-linking. (A) 0.0 wt %, (B) 2.5 wt %, (C) 5.0 wt %, (D) 10.0 wt %, (E) 15.0 wt % divinylbenzene.

is an empirical constant. The results show that the slope of the curve is $D = 1.41$ K/wt %.

Figure 2 shows the effects of cross-linking on the dielectric relaxation spectra of the polymers at a fixed temperature (370 K) above T_g. The position of the peak moves to lower frequency with increasing level of cross-linker, and the relaxation curve tends to broaden. In addition, a decrease in the intensity of the loss peak is observed with increasing level of cross-linker. The shift in the peak position to lower frequency is a manifestation of increasing the T_g of the polymer with increasing cross-link density. Qualitatively, the growth in the breadth would indicate a broader distribution of relaxation times.

In Figure 3 a more detailed comparison of the loss factor as a function of frequency for the pure SB75 copolymer (top) and a sample containing 10 wt % DVB cross-linker (bottom) is shown. The temperature range is between 340 and 400 K, corresponding to about 10, 20, 30, 40, and 50 K above T_g for each sample. Two characteristic features are present in both spectra sets. First, a large increase in the dielectric loss occurs at low frequency that is more pronounced for the un-cross-linked sample and is attributed to the dc conductivity, and second, a loss peak occurs whose position shifts to higher frequency with increasing temperature. A qualitative comparison of the data between the cross-linked and the uncross-linked samples indicates that the half-width of the relaxation peak for the cross-linked sample is broader than for the uncross-linked samples.

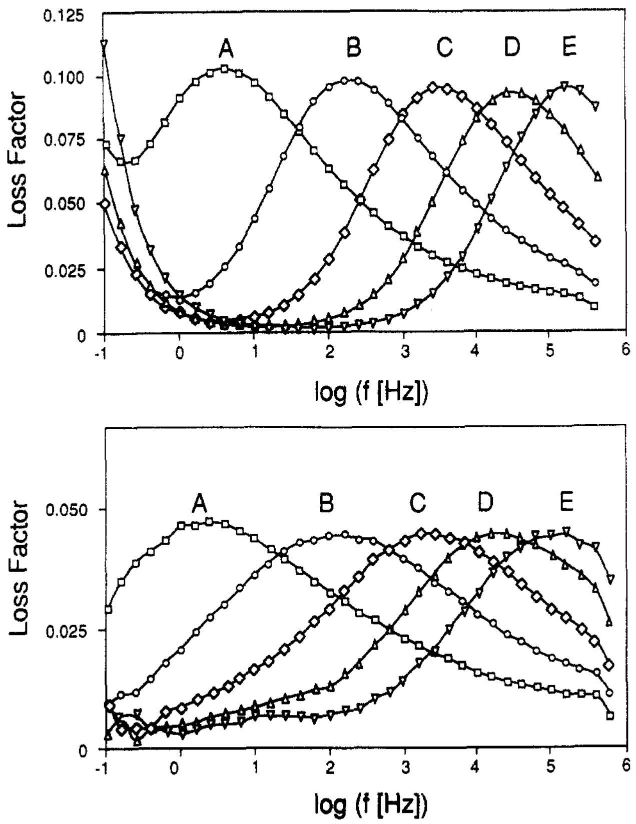

Figure 3. Dielectric loss spectra vs frequency at a series of different temperatures for (top) an uncross-linked 75/25 styrene–butyl acrylate copolymer at (A) 340 K, (B) 350 K, (C) 360 K, (D) 370 K, and (E) 380 K and (bottom) for a highly cross-linked 65/25 styrene–butyl acrylate copolymer with 10 wt % divinylbenzene at (A) 356 K, (B) 366 K, (C) 376 K, (D) 386 K, and (E) 396 K. The temperatures are approximately (A) 10 K, (B) 20 K, (C) 30 K, (D) 40 K, and (E) 50 K above T_g.

In Figure 4a, the peak frequency ($f = f_{\max}$) of the maximum in the dielectric loss spectrum is plotted vs temperature for samples with various cross-link densities. At a given temperature, the relaxation time increases with increasing concentration of cross-linker. This reflects the increase of T_g due to the slowing down of the molecular motion of the polymer chains.

The temperature dependence of the dielectric relaxation curves of the α-relaxation were analyzed by the Williams–Landel–Ferry (WLF) relationship shown in eq 8.

$$\log\left(\frac{\tau}{\tau_g}\right) = -\frac{C_1(T - T_g)}{C_2 + T - T_g} \qquad (8)$$

In this equation, T_g is the glass-transition temperature measured by DSC and is associated with a τ_g of about 10–10^2 s. The parameters C_1 and C_2 are related to the fractional free volume f_g (eq 9) and the thermal expansion coefficient α_f (eq 10) at $T \approx T_g$.[19] The WLF equation is generally applicable in the temperature range $T_g < T < T_g + 100$ K. B is assumed to be equal to unity and constant

$$f_g = \frac{B}{2.303C_1} \qquad (9)$$

$$\alpha_f = \frac{B}{2.303C_1C_2} \qquad (10)$$

for all discussions presented in this paper.[19]

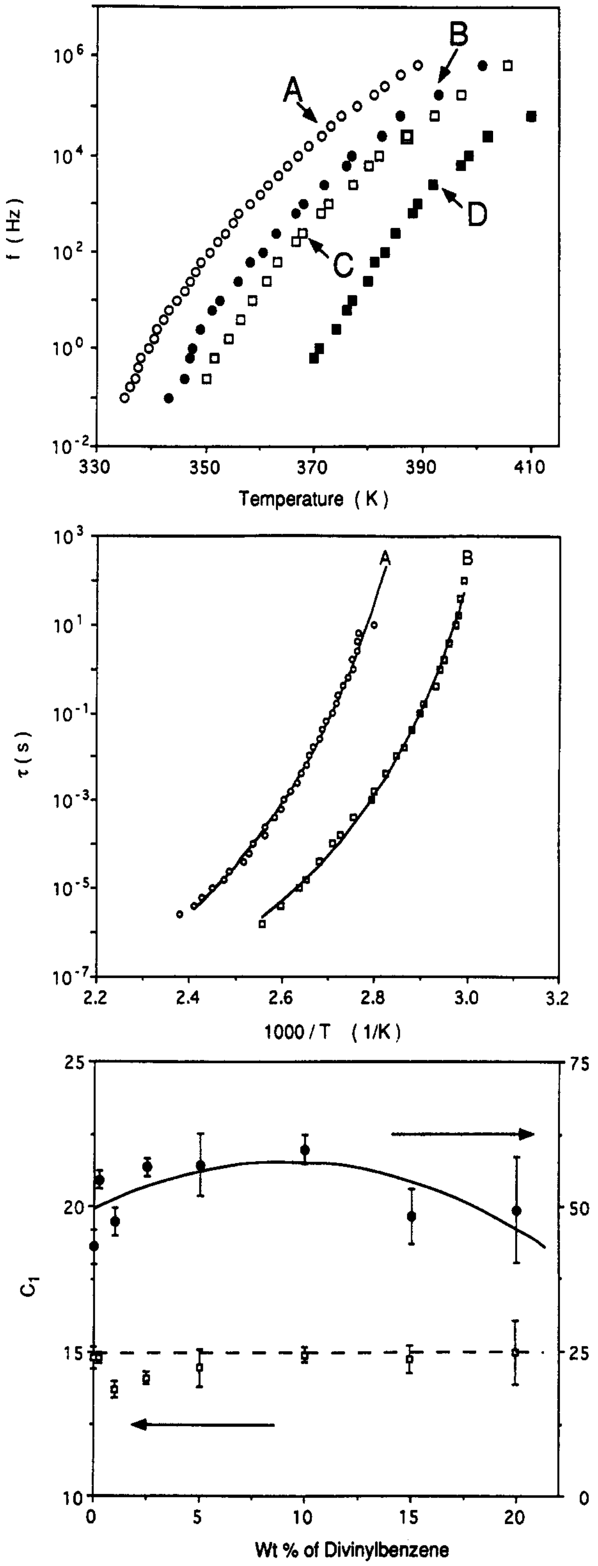

Figure 4. (a, top) Temperature dependence of the frequency of the peak maximum ($f = f_{max}$) extracted from dielectric loss spectra at four different levels of cross-linker: (A) SB75 (0 wt %), (B) SB70 (5 wt %), (C) SB65 (10 wt %), and (D) SB55 (20 wt %) divinylbenzene. (b, middle) WLF plot of the maximum's relaxation time τ (A) of a highly cross-linked SB60 (15 wt % divinylbenzene) and (B) of a pure styrene–butyl acrylate SB75 copolymer. The lines represent the results of the calculation according to equation 8. (c, bottom) Dependence of the WLF parameters C_1 and C_2 on the concentration of divinylbenzene.

In Figure 4b, the temperature dependence of the relaxation time τ, extracted from the peak position of the dielectric loss spectra, is plotted for pure SB75 and SB60 with 15 wt % DVB. The corresponding WLF-fits are plotted for the two samples. The results indicate that the experimental data fit the WLF relationship very well, with the best-fit WLF parameters listed in Table 1.

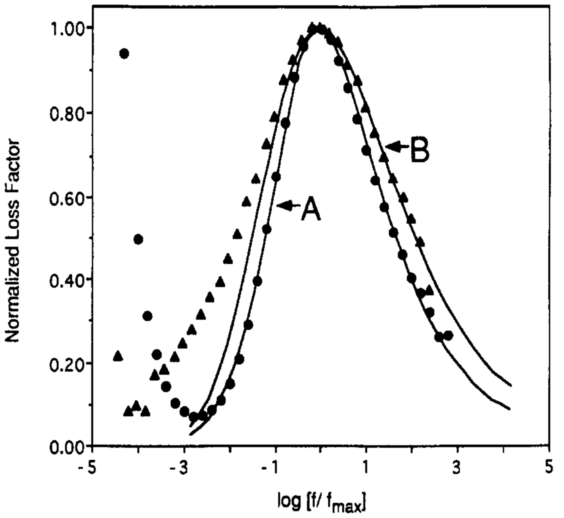

Figure 5. (A) Normalized dielectric loss spectra $\epsilon''(f)/\epsilon''_{max}$ vs f/f_{max} of a uncross-linked styrene–butyl acrylate copolymer (SB75) at $T = 360$ K. The data were fitted to the KWW function with a $\beta_{KWW} = 0.38$. (B) Normalized dielectric loss spectra $\epsilon''(f)/\epsilon''_{max}$ vs f/f_{max} of a highly cross-linked styrene–butyl acrylate copolymer (SB65) with 10 wt % divinylbenzene at $T = 375$ K. The data were fitted to the KWW function with a $\beta_{KWW} = 0.23$.

Table 1. WLF (Williams–Landel–Ferry) Fitting Parameters for the Styrene–Butyl Acrylate Samples with Different Levels of Divinylbenzene Cross-linker

DVB, wt %	T_g, K	$\log(\tau_g) \pm \Delta\log(\tau_g)$, s	$C_1 \pm \Delta C_1$	$C_2 \pm \Delta C_2$
0.0	331	1.9 ± (0.11)	14.7 ± (0.4)	43.5 ± (2.9)
0.25	332	1.0 ± (0.03)	14.8 ± (0.2)	54.6 ± (1.6)
1.0	334	1.1 ± (0.06)	13.7 ± (0.3)	47.4 ± (2.3)
2.5	336	0.5 ± (0.02)	14.1 ± (0.2)	56.8 ± (1.5)
5.0	340	0.9 ± (0.10)	14.4 ± (0.6)	57.3 ± (5.4)
10.0	345	0.9 ± (0.05)	14.9 ± (0.3)	59.8 ± (2.5)
15.0	352	0.9 ± (0.10)	14.8 ± (0.5)	48.3 ± (4.9)
20.0	362	1.6 ± (0.26)	15.0 ± (1.1)	49.4 ± (9.2)

The results shown in Figure 4c indicate that, within experimental uncertainty, the fractional free volume at T_g associated with the parameter C_1 is constant at all levels of the cross-link density studied. The parameter C_2 seems to change slightly over the concentration range investigated. There might be a broad maximum around 10 wt % DVB cross-linker.

In Figure 5 (curve A), a normalized master curve $\epsilon''(f/f_{max})$ of pure SB75 is shown along with the best fit obtained from the KWW function. A value $\beta_{KWW} = 0.38$ obtained from those data is in good agreement with the results of previous studies of this material.[16] Figure 6A shows a typical Havriliak–Negami fit to the same data. The fitting parameters α and β are 0.74 and 0.36, respectively. The experimental data for the uncross-linked copolymer can be fitted equally well both to the HN and KWW function.

The normalized dielectric loss curve for the styrene–butyl acrylate copolymer containing 10 wt % of the cross-linker is shown in Figure 5 (curve B). The results clearly show that the loss curve is broader than that of the uncross-linked polymer shown in curve A. It is interesting that it is not possible to fit the data using a single β_{KWW} parameter. Even a very small value of $\beta_{KWW} = 0.23$, associated with a very broad and skewed relaxation distribution, fits only the high-frequency side of the data well. The superposition of two or more KWW functions with different β_{KWW} would possibly yield a better fit to the data; however, we did not attempt this. The low-frequency side of the loss curve is broadened far too much to fit the model. Because the

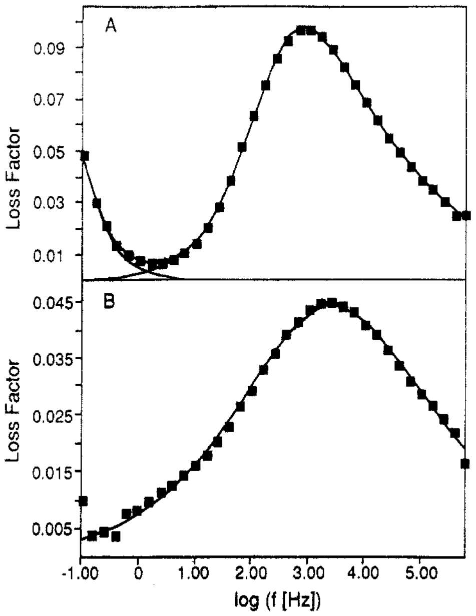

Figure 6. (A) Dielectric loss spectra $\epsilon''(f)$ of a uncross-linked styrene–butyl acrylate copolmer (SB75) at T = 360 K (i.e., T_g + 30 K). The results are obtained by using the HN function with the parameters α = 0.74, β = 0.36, and τ = 186 μs. (B) Dielectric loss spectra $\epsilon''(f)$ of a highly cross-linked styrene–butyl acrylate copolymer (SB65) with 10 wt % divinylbenzene at T = 375 K (i.e., T_g + 30 K). The results are obtained by using the HN function with the parameters α = 0.30, β = 0.39, and τ = 100 μs.

fitting function describes the experimental data so poorly, it was not possible to analyze the data further and apply the coupling model of Ngai. Therefore, we attempted to fit the HN function to the data.

As shown in Figure 6B, much better agreement between the measured data and the model is obtained for a highly cross-linked sample with 10 wt % DVB using the HN fitting routine. In this case, the fitting parameters are α = 0.30 and β = 0.39. By using the Havriliak–Negami function, we are able to describe the dielectric data of cross-linked samples much better than with the KWW routine, especially in the low-frequency region.

In Figure 7, the values of α are plotted as a function of temperature for samples containing up to 20 wt % divinylbenzene. Up to 1 wt % cross-linker, the value of α appears to be independent of the concentration of cross-linker. Further, at low concentrations of cross-linker, there appears to be only a slight temperature dependence of α.

At concentrations of 2.5 wt % cross-linker and above, the isothermal values of α are strongly dependent on the concentration of the cross-linker. Further, the value of α for the samples containing a higher cross-linker amount (e.g., 10 wt % DVB) is temperature dependent. By copolymerizing with the divinylbenzene, it is believed that a homogeneous polymer was prepared. However, there exists a distribution of molecular weights between the cross-link sites. Although grossly oversimplified, one may speculate that the relaxtions of the segments near the chain ends have a different activation energy than those further away. This would result in a distribution of activation energies that might result in the observed temperature dependence of the α parameter. Thus, as the temperature increases, the dielectric loss peak narrows, which is reflected by the growth of the value of α with increasing temperature. In addition, as shown in Figure 7, there is little change observed for the product $\alpha\beta$ for different concentrations of divinylbenzene over a wide temperature range (as compared to the value of α). In view of the model by Schönhals and Schlosser, the results suggest that the local environments of the polymer are not influenced by changes in the level of cross-linker.

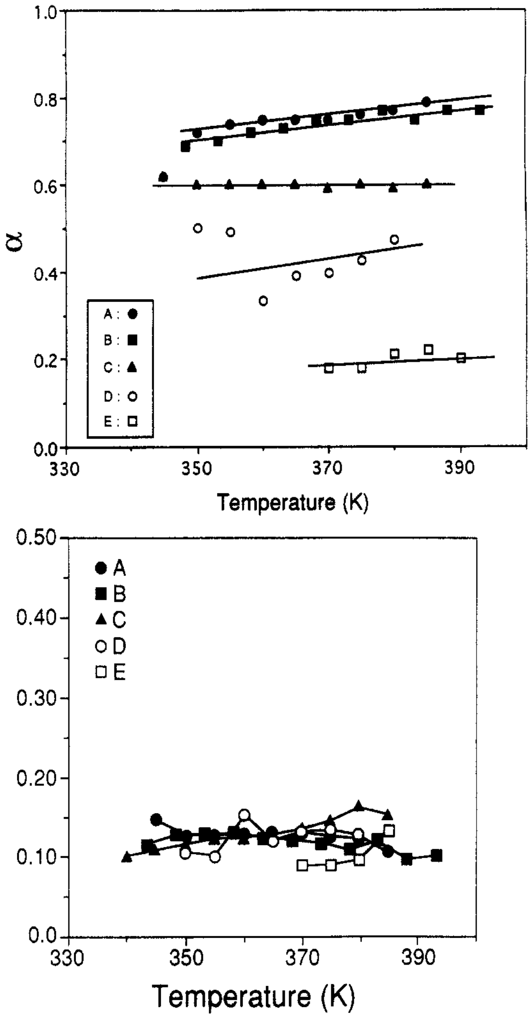

Figure 7. Temperature dependence of the fitting parameters α (top) and $\alpha\beta$ (bottom) of the HN function for copolymers with different levels of cross-linker. (A) SB75 (0.0 wt %), (B) SB74 (1.0 wt %), (C) SB72.5 (2.5 wt %), (D) SB65 (10.0 wt %), and (E) SB55 (20.0 wt %) divinylbenzene. The lines are only guides to the eyes and have no physical interpretation. Analysis of the data indicates that the error associated with α is ±5% and $\alpha\beta$ is ±10%.

Taking into account the change of T_g due to an increased level of cross-linker and normalizing for this difference allows us to define a normalized temperature ($T_N = T_g$ + 30 K). As shown in Figure 8, the value of α at temperature T_N decreases from 0.74 for the uncross-linked styrene–butyl acrylate polymer to 0.3 at 20 wt % cross-linker. The large changes in the value of this HN fitting parameter reflect the increase in the low-frequency broadening of the dielectric loss curve. The results shown in Figure 8 also indicate that the product $\alpha\beta$ is not influenced by the cross-linker. This suggests that the cross-linker has little effect on the local motions of the polymer chains associated with the high-frequency behavior of $\epsilon''(\omega)$. The results also indicate that the high-frequency behavior is unaffected by the level of cross-linker. In fact, for the most part, the value of $\alpha\beta$ is independent of both cross-link density and temperature.

The shape of the dielectric loss curves can be interpreted in terms of a dynamic model introduced by Schönhals and Schlosser.[3] In this model, the parameters m and n are used to characterize the shape of the dielectric loss function ($\epsilon''(\omega)$). In the low-frequency limit, the frequency dependence can be scaled as

$$\epsilon''(\omega) \propto \omega^{m} \qquad \omega \ll \tau^{-1} \tag{11}$$

and in the high-frequency limit it can be scaled as

$$\epsilon''(\omega) \propto \omega^{-n} \qquad \omega \gg \tau^{-1} \tag{12}$$

with τ as the relaxation time according eq 2.

In the high-frequency limit, the dielectric loss spectrum is described by $n = \alpha\beta$, and the motion would be expected to be small scale and very local in nature. Therefore, the very local motions of the butyl acrylate segments should be unaffected by the addition of the cross-linker. The results shown in Figure 7 and Figure 8 are consistent with this prediction. The value of α which is equivalent to m is related to large-scale intermolecular correlations. It is expected that α would decrease with increasing level of cross-linking, corresponding to a broadening of the low-frequency side of $\epsilon''(\omega)$ and reflecting the fact that the cross-linker modifies the large-scale interchain motions. As shown in Figure 7 and particularly in Figure 8, α decreases substantially with increasing concentration of divinylbenzene. In this study, α varied from 0.74 to 0.30 at concentrations of the DVB cross-linker between 0 and 20 wt %. Therefore, the trends in the experimental results appear to be consistent with the principles of the model of Schönhals and Schlosser.

The detailed physical interpretation of the model is not yet clear, in particular that concerning local changes in the polymer near the glass transition. If it is simply the motion of a single molar volume of the repeat unit that relaxes, one could argue that there may be multiple environments that the chains experience. Those that are close to the cross-link sites are in extremely restricted environments, while those more centrally located between cross-link sites relax in a manner more similar to the uncross-linked polymer. Therefore, the relaxation time of a single segment of the polymer chain may be related to the proximity of the butyl acrylate to the cross-link site. A distribution in the local environment of the single relaxing segments gives rise to a broadening of the dielectric relaxation spectrum.

Conclusions

We have investigated the influence of cross-linking on the molecular dynamics of styrene–butyl acrylate copolymers. The concentration of the divinylbenzene cross-linker was varied between 0 and 20 wt % while keeping the concentration of the higher dipole moment copolymer segment (i.e., the butyl acrylate) constant. The glass-transition temperature of the copolymer was found to increase linearly with increasing concentration of cross-linker, which is consistent with the results of Ueberreiter et al. The results of the WLF analysis indicated that both the fractional free volume and the volume expansion coefficient are nearly unaffected by cross-linking.

The results also showed that the Havriliak–Negami and the Kohlrausch–Williams–Watts formalisms could equally well describe the dielectric loss spectrum for the uncross-linked copolymer. However, as the cross-link density increased, the KWW function was not able to fit the low-frequency side of the dielectric loss curve. With the HN function, it was possible to describe the changes occurring particularly at low frequency, with increasing cross-link density.

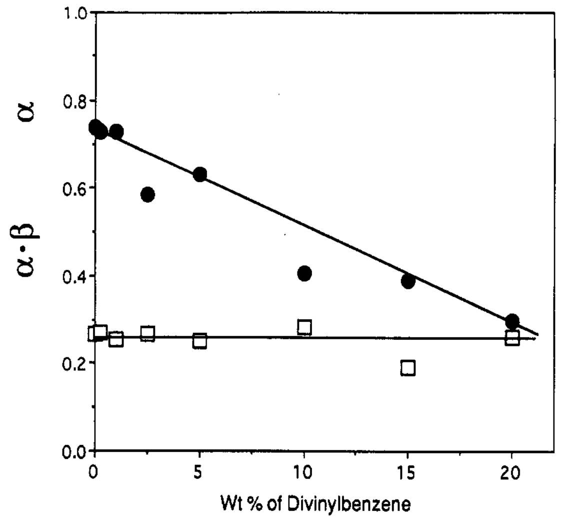

Figure 8. Dependence of the HN parameter α (●) and the product $\alpha\beta$ (□), respectively, on the concentration of DVB cross-linker at the normalized temperature ($T_N = T_g + 30$ K).

We found that the product of the two shape parameters ($\alpha\beta$) obtained from the HN function was nearly independent of cross-link density. On the basis of the model proposed by Schönhals and Schlosser, the results suggest that the local motions of the butyl acrylate groups were uninhibited by the addition of cross-linker. Furthermore, the analysis of the results indicated that α decreased with increasing concentration of the cross-linker. On the basis of the model, the results indicated that a slowing down of the long-range molecular motions is occurring with increasing cross-linking of the polymer resulting in the experimentally observed broadening of the low-frequency side of the dielectric relaxation curve.

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References and Notes

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