

Dielectric α - and β -Relaxations in Uncured Styrene Butadiene RubberS. Cerveny,^{*,†} R. Bergman,[‡] G. A. Schwartz,[†] and P. Jacobsson[‡]

Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Depto. Física, LPMPyMC, Pabellón 1, Buenos Aires (1428), Argentina, and Department of Experimental Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

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ABSTRACT: The development of the dynamic glass transition in styrene-butadiene copolymers has been investigated by dielectric spectroscopy in the frequency range from 10^{-2} to 10^6 Hz. Two processes were detected and attributed to the α - and β -relaxations. The α relaxation time has a non-Arrhenius temperature behavior that is highly dependent on styrene content while the β relaxation time shows an Arrhenius behavior with an activation energy that is independent of styrene-content. Furthermore, the shape of the α -relaxation is strongly influenced by the styrene content while the shape of β -relaxation is not. We interpret these results as follows. The observed β -relaxation is primarily due to local motions of butadiene monomers and therefore not affected by the presence of styrene. The α -relaxation, on the other hand, is highly sensitive to the styrene content due to its cooperative character.

Introduction

Relaxation processes in polymers have been studied for a long time using several different techniques such as dynamical mechanical spectroscopy, NMR, and Brillouin light scattering. One of the most valuable tools for characterizing the behavior of polymer systems is, however, dielectric spectroscopy.¹ The characterization of the segmental motions of a polymer chain in the melt is frequently obtained in terms of relaxation times and activation energies from these measurements.

In polymeric systems, the dielectric response is usually dominated by the α -relaxation whose relaxation time dramatically increases when the temperature decreases toward the glass transition temperature, T_g . Besides the α -relaxation, additional relaxations called secondary relaxations or β -relaxations can be active on faster time scales. The β -process generally occurs in glass-formers of diverse chemical structure, and has very different properties compared to the α -relaxation. This secondary process exhibits an Arrhenius temperature dependence of its relaxation time, $\tau_\beta(T)$, in contrast to the much stronger temperature dependence of $\tau_\alpha(T)$. At high temperatures, where $\tau_\alpha \approx \tau_\beta$, the two relaxation processes are not well separated. However, as the temperature is lowered, the relaxations become separated due to the different temperature dependencies, so that a clear identification of the two distinct relaxations is possible.

In some cases, the secondary relaxation process can be assigned to motion of the side groups on the polymer chain. In this case, the β -relaxation is decoupled from the α -relaxation, and its behavior can be readily interpreted. More challenging to explain are β -processes occurring in glass-formers that have no side groups. Already several decades ago, Johari and Goldstein investigated such relaxations in low molar mass liquids.² The fact that β -relaxations occur independent of microstructure suggests that it is an intrinsic property of the glassy state.²

The poly-butadiene rubbers (BR) and their styrene copolymers (SBR) are the most important type of

synthetic elastomers and the most widely used in the rubber industry. The dynamics of uncured BR have been extensively studied using dielectric spectroscopy,^{3–5} neutron spin-echo,^{6,7} and NMR⁸ measurements. Results from dielectric measurements of random BR show that: i) there are two distinct peaks in the dielectric spectrum^{3–5} that are associated with the α - and β -relaxations, respectively; ii) the α peak is often well described by the empirical Havriliak–Negami function in the frequency domain; iii) the α -relaxation time, τ_α , follows a non-Arrhenius behavior; iv) the main influence on τ_α is the vinyl content;³ v) the temperature evolution of the secondary peak follows an Arrhenius behavior.^{3,4} The origin of this BR β peak is still unclear.

Few studies have been performed on uncured SBR⁹ (uncured means that there are no cross-links present in the samples), all concerning the behavior of the α -relaxation. On the other hand, there are many studies on cured (cross-linked) SBR by dynamical mechanical measurements, still focusing on the α -process.⁹ Studies of the secondary process have only been reported by Bartenev in an early publication.¹⁰ To our knowledge, until now there have been no reports on secondary processes on uncured SBR.

In this paper, we report on results from dielectric measurements on uncured styrene-butadiene rubber random copolymers with different composition of styrene units. We show that the relaxation time of the α -relaxation follows a typical VFT behavior and that the T_g values can be correlated with the styrene content. The β relaxation, on the other hand, shows an Arrhenius behavior that is independent of styrene content. This implies that the β -relaxation is a local BR process. We also compare our results to the properties of the β -process in 1,2-polybutadiene of low vinyl content.

Experimental Section

Materials. The polymer used in this investigation was a random copolymer of styrene-butadiene (SBR). Three samples with different styrene content were studied (SBR1, SBR2, and SBR3). The BR structure is the same in all the samples. The microstructure of the samples is specified in Table 1 and in Figure 1, we show the chemical structure for SBR.

Glass transition temperatures were determined using a Perkin-Elmer Differential Scanning Calorimeter DSC-7. All

* To whom correspondence should be addressed.

† Universidad de Buenos Aires, Buenos Aires.

‡ Chalmers University of Technology, Göteborg, Sweden.

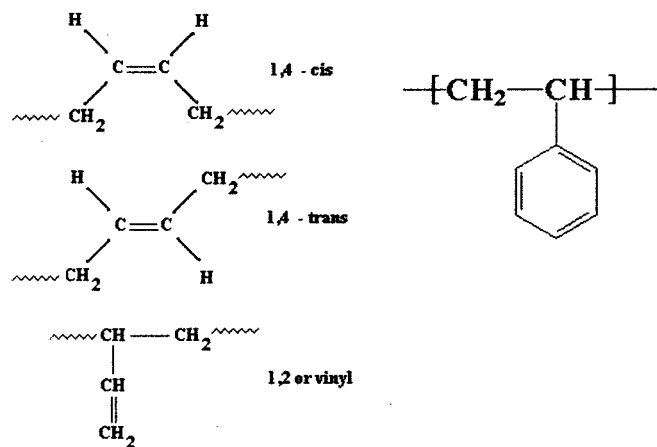


Figure 1. Microstructure of the styrene-butadiene rubbers studied in this work.

Table 1. Polymers Used in This Study

sample	styrene	Butadiene Microstructure			T_g [K] (DSC)
		% 1,2-vinyl	% 1,4-trans	% 1,4-cis	
SBR1	18	10	55	35	208
SBR2	23.5	10	55	35	213
SBR3	35	10	55	35	223

samples were sealed in aluminum pans and were run at a rate of 10 °C/min from -120 °C to 140 °C. The T_g values were determined at the inflection point. These results are also shown in Table 1.

Dielectric Measurements. A broadband, high-resolution dielectric spectrometer (Novocontrol Alpha), was used to measure the complex dielectric function, $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, in the temperature range of 140 to 270 K and in the frequency range from $f = 10^{-2}$ Hz to $f = 10^6$ Hz. During measurements the samples were placed between stainless steel parallel plate electrodes with a diameter of 30 mm. The samples were typically 2 mm thick.

Results and Discussion

Figure 2 shows a representative data set in the frequency domain from the SBR3 sample at different temperatures. The loss spectrum in this figure, ϵ'' , reveals a typical example of the observed temperature-dependence for the studied polymers. At 250 K, the relaxation curve shows only one relaxation peak. When the temperature decreases, (see curve at 230 K), a secondary peak appears on the high-frequency side of the ϵ'' peak. Two broad but well-separated relaxation processes can be seen at 220 K. At low temperatures (see curve at 180 K), only the secondary peak is present in the dynamic window of our instrument. The dielectric loss thus shows two maxima, the first one is due to the main α -relaxation and the second, smaller peak, at higher frequency is attributed to the β -relaxation of SBR.

In the time domain the α -relaxation of glass-forming materials can normally be described by the Kohlrausch-Williams-Watts (KWW) function¹¹

$$\phi(t) = \exp\left(-\frac{t}{\tau}\right)^{\beta_{\text{KWW}}} \quad (1)$$

where β_{KWW} is the Kohlrausch stretching exponent. β_{KWW} is between 1 and 0, being unity for a pure exponential relaxation. The stretching can be explained by the presence of a distribution of relaxation times. The distribution of relaxation times give rise to broadened responses in frequency domain as compared to the

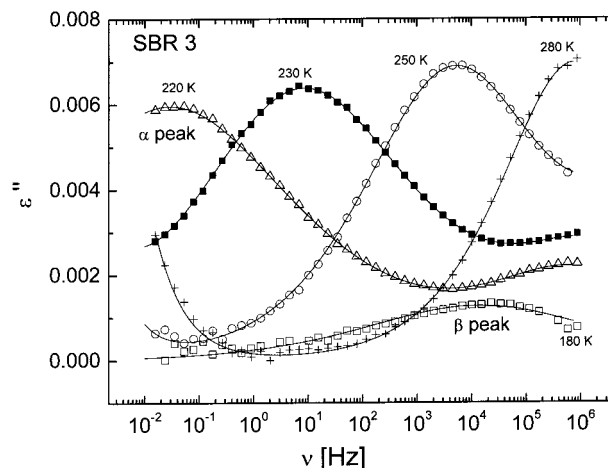


Figure 2. Imaginary part of the dielectric susceptibility of the sample SBR3 as a function of a frequency at several temperatures. The lines through the data are HN + CC fits (see the text). For clarity, only data taken at some representative temperatures are shown here.

simple Debye response which corresponds to a pure exponential relaxation. Since most dielectric data are collected in the frequency domain, semiempirical functions are usually used¹² for describing these broadened non-Debye responses.

Here, we described the α -relaxation by a Havriliak-Negami (HN) function¹³

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (i\omega\tau_{\text{HN}})^\alpha]^\gamma} \quad (2)$$

where ϵ_0 and ϵ_∞ are the unrelaxed and relaxed values of the dielectric constant, τ_{HN} is the relaxation time, and ω is the angular frequency. In eq 2 α and γ are adjustable fitting parameters ($0 < \alpha, \alpha \times \gamma \leq 1$). One disadvantage of eq 2 is that the shape parameters are coupled and therefore give unstable behaviors of the high frequency γ parameter. We have therefore also analyzed the α -relaxation using a recently proposed general susceptibility equation¹²

$$X''(\omega) = \frac{X_p''}{\frac{(1 - |a - b|)}{a + b} \left[b \left(\frac{\omega}{\omega_p} \right)^{-a} + a \left(\frac{\omega}{\omega_p} \right)^{-b} \right] + |a - b|} \quad (3)$$

where X_p and ω_p define the height and position of the peak, and a and b are internally independent shape parameters for the low and high frequencies, respectively. Both the HN and this function give good fits for the loss spectrum. Finally, we would like to note that the eq 3 is related to many other fit functions, for example the Jonscher equation.¹⁴ See ref 12 for more details.

The β -relaxation was described by a symmetrical Cole-Cole (CC) function¹⁵ which is a special case of eq 2 with $\gamma = 1$. The total loss spectrum was thus fitted as the sum of the imaginary part of the CC and HN functions or alternatively a sum of the CC function and eq 3. The fitting procedure was carried out on the imaginary part of the permittivity, ϵ'' . Some resulting curve-fits are shown in Figure 2 as solid lines.

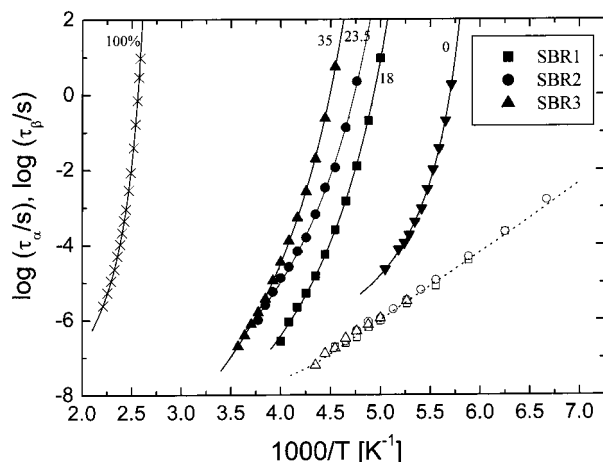


Figure 3. Temperature dependence of the relaxation times for the primary (solid symbols) and secondary processes (hollow symbols) of random copolymer SBR. Solid lines represent the fit of the HN equation to the α -relaxation and the CC equation to the β -relaxation. Each curve is labeled by the styrene content of the sample it represents. The datum of the sample at 0% was taken from ref 4 and the datum at 100% of styrene from ref 23.

Table 2. Results of Fit from VFT Equation for α -Relaxation

sample	D	T_0 [K]	$\log(\tau_0)$	$T_{g,100s}[K]^a$	m^b
SBR1	6.1 ± 0.5	165.0 ± 2.0	-11.54 ± 0.30	197 ± 3	84 ± 3
SBR2	6.4 ± 0.4	167.0 ± 4.0	-10.60 ± 0.46	204 ± 3	69 ± 3
SBR3	7.4 ± 0.4	176.0 ± 2.0	-12.11 ± 0.22	216 ± 2	76 ± 2

^a The value of $T_{g,100s}$ was calculated as extrapolation to a relaxation time of ~ 100 s. ^b The value of m was calculated from eq 5.

The α -Relaxation. The temperature dependence of the relaxation times, τ_α , for the α -process are shown in Figure 3. Literature data for pure BR (0% of styrene) and data for polystyrene (PS) (100% of styrene) are also included in Figure 3.

The temperature dependence of τ_α is clearly non-Arrhenius, with an apparent activation energy that increases with decreasing temperature. This behavior can be described by the empirical Volger-Fulcher-Tamman (VFT) equation¹⁶

$$\tau_\alpha = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right) \quad (4)$$

where τ_0 is the relaxation time in the high-temperature limit. The temperature where the relaxation time would diverge, T_0 , is often identified with the Kauzmann temperature¹⁷ and D parametrizes the departure from Arrhenius behavior and is useful to distinguish between strong and fragile glasses (high or low D respectively).¹⁸ Extrapolation of this formula to a relaxation time of ~ 100 s gives a dielectric estimate of the glass transition temperature, $T_{g,100s}$. The values of the parameters obtained by fitting eq 4 to the α -relaxation times are given in Table 2.

From Figure 3 we can see, as expected from Table 1, that the integration of styrene into the butadiene decreases the chain flexibility. In addition, it could be expected that the fragility, D , changes with the styrene content. Indeed, from Table 2, we see that D shows some variation with the styrene content. When discussing the fragility it is usual to use the parameter m , instead of D , because the former is well established to correlate

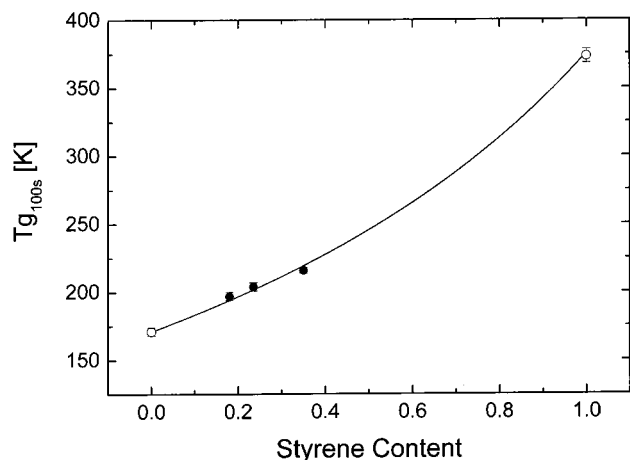


Figure 4. Dependence of the glass transition temperature (T_g) on the amount of styrene units. The values for T_g were determined at a relaxation time of 100 s. The line represents the fit using the Gordon-Taylor equation. The point at 0% was taken from ref 4 and the data at 100% of styrene from ref 23.

with the intermolecular cooperativity of the segmental relaxation.^{19–21} In terms of the VFT parameters, the fragility is given by²²

$$m = \frac{DT_0}{T_{g,100s} \ln(10)} \left(1 - \frac{T_0}{T_{g,100s}}\right)^{-2} \quad (5)$$

The values of m calculated from D values and eq 5 are shown in Table 2. The values of m , 146 at 0% of styrene content and 152 at 100%, were taken from ref 24. From these values, we see that the fragility is affected by the styrene content. However, more studies are necessary to verify and explain the apparent minima at around 20% styrene content.

Usually a random copolymer of two monomers with different glass transition temperatures (T_g) has an intermediate glass transition temperature. Sometimes T_g varies linearly over the composition range although in most cases the T_g versus composition curve is concave or convex depending on the structure of the monomers. The Gordon-Taylor²³ equation has often been used to predict the T_g of the copolymers based on the T_g of each homopolymer

$$T_g = \frac{\omega_1 T_{g1} + k(1 - \omega_1) T_{g2}}{[\omega_1 + k(1 - \omega_1)]} \quad (6)$$

where the subscripts 1 and 2 refer to the pure polymers and ω is the weight fraction of pure polymer. The parameter k describes the departure from linear behavior.

In Figure 4 the glass transition temperature is plotted as a function of the styrene content present in the copolymer. The values at 0% and 100% styrene content were taken from ref 3 and 23, respectively. As is typical with most copolymers, this plot deviates from linearity. This behavior is in accordance with the study by White and Lee²⁵ in the same material. In Figure 4, we show the best fit to the data using the Gordon-Taylor equation with $T_{g1} = T_g$ (polystyrene) and $T_{g2} = T_g$ (polybutadiene) and $k = 1.7$.

Next we turn to the shape of the dielectric loss attributed to the α -relaxation. The fitted values of the a -parameter of eq 3 are shown in Figure 5a as a function of the temperature for all samples. The value of a is

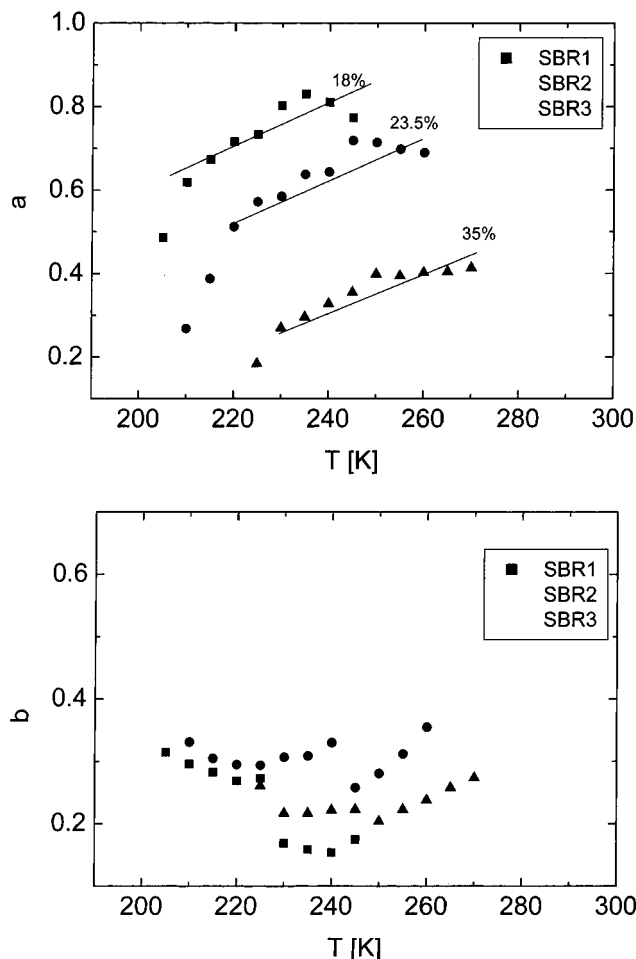


Figure 5. (a) Temperature dependence of the a -parameter from eq 3. The solid lines are guides to the eye and indicate the general trend of the temperature dependence. (b) Temperature dependence of the b -parameter from eq 3.

clearly increasing with temperature. In addition, we note that the a -value decreases (relaxation spectrum broadens) with the addition of styrene possibly due to increasing intermolecular coupling and complexity. In Figure 5b we show the less pronounced variation of the b -parameter of eq 3 as a function of the temperature. The HN shape parameters have similar behaviors, however, with larger scatter.

The shape parameters of the dielectric curves can be interpreted in terms of the dynamic model proposed by Schönhals and Schlosser.²⁶ In the low-frequency region, the power law exponent (a or α) is related to long-range intermolecular motions. In the high-frequency region, the power law exponent (b or γ) is related to more local motions. Our results therefore indicate that the styrene mainly affects the long-range motions.

Broadening of relaxation spectra in mixtures of two glass-forming liquids was observed in dielectric measurements already in the 1970s by Shear and Williams.²⁷ They attributed this broadened distribution to variability in local dipole concentration. Later Wetton et al.²⁸ developed a model based on concentration fluctuation of dipoles for the analysis of the broadened distribution of relaxation times in polymer blends. Recently Miura et al.²⁹ have analyzed dielectric relaxation curves of poly *o*-chlorostyrene (PoCS) and its blends with PS. In this study, they found that the spectrum of the random copolymers becomes broader

at lower temperatures. This implies that the random copolymers of the same composition could exhibit different degrees of broadening depending on the size of heterogeneities. The shape of the relaxation dispersion of the polymer blend was broader than that of the copolymer due to mixing heterogeneity in the former at the segmental level. The temperature dependence of the shape parameters, a and b , in our samples are in accordance with those presented by Miura et al. for copolymers.²⁹ Thus, it is plausible that some of the broadening of the spectra is due to fluctuations in local dipole concentrations.

The β -Relaxation. The SBR molecule contains several molecular units that may contribute to the dielectric loss. These groups are vinyl, cis, and styrene units (the trans group has no dipolar moment). It is known that the vinyl and cis units have about the same dipolar moment and this moment is larger than the dipolar moment for styrene.³⁰ Hence, mainly cis and vinyl units will contribute to the dielectric loss.

Our dielectric measurements of all SBR samples show a β -relaxation that is much weaker than the α -relaxation and appears at low temperatures and high frequencies. Since the data looks symmetric, the β -relaxation peak was fitted by a Cole–Cole function¹⁵ i.e., $\gamma = 1$ in eq 2.

The α parameter, related to the width of β -relaxation, shows a linear increase with temperature as we show in Figure 6a. This is in accordance with what is normally found for β -relaxations. It is noteworthy that the behavior is independent of styrene content.

The normalized β -relaxation strength of the samples is almost temperature independent below T_g and the value decreases with increasing styrene content as we show in Figure 6b. This is of course expected since the main part of the dielectric loss comes from the BR monomers.

From Figure 3 we note that the most probable relaxation time, τ_β , obtained from CC-fits to our data, has an Arrhenius temperature dependence

$$\tau_\beta(T) = \tau_{\beta\infty} \exp\left(\frac{E_\beta}{kT_0}\right) \quad (7)$$

where $\tau_{\beta\infty}$ corresponds to a molecular vibration time and E_β has a magnitude that is identifiable with a real energy barrier.

The activation energy obtained from the slope of the line in Figure 3 is $E_\beta = (8.2 \pm 0.3)$ kcal/mol for all samples. Typically, E_β is less than 10 kcal/mol which suggests that the β -relaxation is related to local motions. This means that the average energy barrier is due to the polybutadiene monomers and the random styrene units do not affect the β -process. The observed β -process thus originates in local motions of the BR monomers. Reassuringly, the value of E_β is in accordance with the activation energy for the β -process of polybutadiene with the same microstructure. It is important to note that this activation energy is significantly lower than for the β -process of PS which is about 34 kcal/mol.²³

This behavior is different from other copolymers cited in the literature such as Poly (*n*-butyl methacrylate-styrene)^{31,32} where the activation energy of the β -processes depends on styrene content. In those studies, the trace in the Arrhenius diagram shifted to higher frequencies for increasing styrene contents. Thus, we can conclude that the randomness of chemical config-

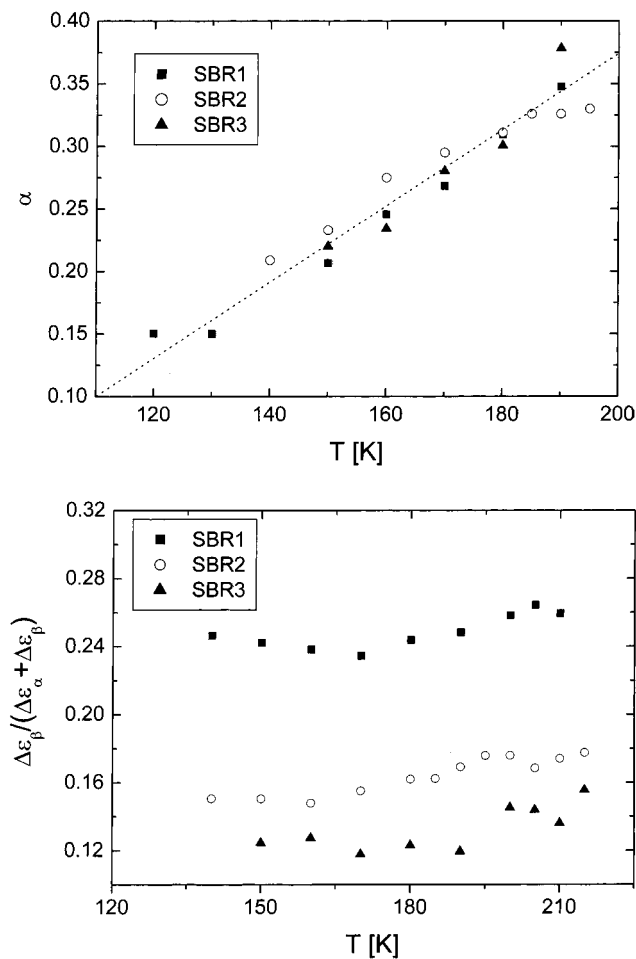


Figure 6. (a) Temperature dependence of the CC shape parameter (α) obtained from the fitting of eq 2 (with $\gamma = 1$) to the β -relaxation for the indicated samples of different styrene content. (b) Normalized amplitude of the β -relaxation as a function of the temperature for the samples with different styrene content.

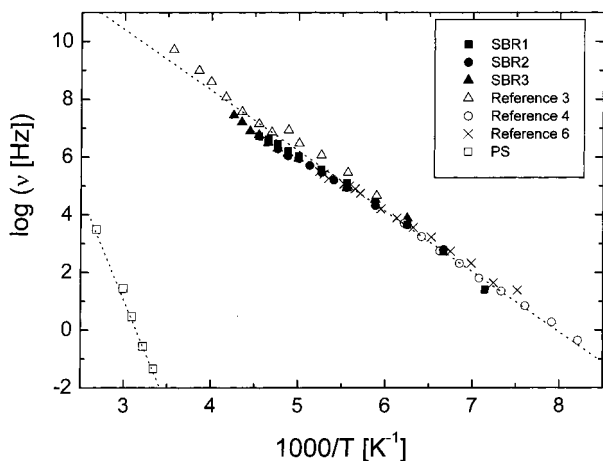


Figure 7. Arrhenius diagram of the β -relaxation of SBR (data from the present work), PS (data from ref 22) and PB (data from refs 2, 4, and 6).

uration of styrene, in our samples, does not cause different environments for the β -process.

In Figure 7, we show relaxation rate data for polybutadiene with low vinyl content from other sources: neutron scattering (Δ , ref 6) and dielectric measurements (\times ref 3; \circ ref 4). We also include data of the β -relaxation for polystyrene from ref 31. The similarity

to the β -relaxation observed in SBR confirms that the local environment seen by the BR monomer in SBR random copolymer must be almost identical to the environment seen by the monomer in polybutadiene.

Conclusions

In this paper we report results from broadband dielectric spectroscopy studies of the relaxational dynamics of uncured styrene-butadiene rubber. Two relaxation processes have been identified: the structural α -relaxation, and a secondary β -process. The temperature behavior of relaxation times, fragility, and shape parameters were analyzed. In particular, we found the following:

- 1) The α -relaxation time (along with T_g) increases with the styrene content. The styrene thus stiffens the system.
- 2) The fragility of SBR is lower than for both polystyrene and polybutadiene.
- 3) The styrene content influences the shape of the α -relaxation at both low and high frequencies.
- 4) The β -relaxation time and shape is independent of styrene content. However, the amplitude of the β -process decreases when the styrene content increases. This shows that the observed β -relaxation is to be identified with local motions of the butadiene segments.

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