Macromolecules **1996,** *29,* 129−134

Secondary and Segmental Relaxation in Polybutadienes of Varying Microstructure: Dielectric Relaxation Results

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Received December 16, 1994; Revised Manuscript Received August 3, 1995[⊗]

ABSTRACT: The dielectric behavior of polybutadiene copolymers with different compositions of 1,2 and 1,4 units is analyzed to study the influence of the microstructure on the relaxation spectrum, especially the β relaxation. The experimental data were obtained between 10^{-2} and 10^{6} Hz and temperatures above and below T_g. Above T_g, the relaxation spectra are described by the superposition of two processes, the main α relaxation at low frequencies and a β relaxation at high frequencies. The α relaxation has the typical Vogel−Fulcher−Tammann behavior and exhibits a quasi-linear shift of time scale upon change of the vinyl content. The high-frequency process shows Arrhenius behavior only in the case of the homopolymers. For the other samples with a mixture of microstructures, spectral broadening occurs and deviation from the Arrhenius behavior is observed. In these samples, the relaxation can be modeled by the simple assumption that the high-frequency process consists of a superposition of two separate processes, each with the properties of the β relaxation of one of the homopolymers. This suggests that secondary relaxations can relax quite independently from the segmental relaxation and are therefore restricted to a very local environment influenced by intramolecular interaction.

I. Introduction

The α relaxation is usually the dominating relaxation process in glass-forming amorphous systems.[1] The temperature dependence of the relaxation time shows a dramatic increase around T_g, leading to the glassy state at lower temperatures. In the case of polymers, this relaxation is attributed to segmental relaxation of the main chain, and cooperative relaxation is thought to lead to the glass transition.

Besides the α relaxation, especially in polymeric systems, additional relaxations on various faster time scales can be active, which are called secondary relaxation processes (β relaxation, γ relaxation, etc.). These processes have an Arrhenius temperature dependence of their characteristic time scale. However, in general, the corresponding values of the activation energy are too high and the preexponential factor is too low as to be associated with simple activated processes. They have traditionally been attributed to local relaxation of flexible parts, e.g., side groups, and in the absence of side groups to local motion in the main chain consisting of twisting or crankshaft motion.[1] However, in the context of some models of the glass transition,[2,3] secondary relaxation should originate from intermolecular interaction and, like the α relaxation, exist in all glass-forming systems.

It is well known that the microstructure has a strong influence on the glass transition temperature and the properties of the α relaxation.[1,4−7] On the other hand, detailed dielectric studies of polymers, e.g., polyacrylates,[1,8] have shown that the mobility of side chains, measured as the β relaxation, can be quite independent of the change of microstructure. In a main chain polymer, the situation might be different since any local motion must be inside of the main chain. However, as far as we know, there is a lack of systematic studies in the literature concerning this topic.

Here we report a dielectric study of the α and β relaxations in a series of polybutadienes with different and well-characterized microstructure. Five anionically polymerized polybutadienes (PB) consisting of a statistically uniform stereoirregular distribution of 1,4-cis, 1,4-trans, and 1,2 (vinyl) units (see Figure 1) were investigated. These polymers were prepared under conditions such that they mainly differ in vinyl content. Comparative experimental studies of polybutadienes have been reported recently on blends,[4] diblock copolymers,[9] and copolymers with randomly interchanging subunits.[5−7,10,11] Most work concentrated on the strong α relaxation, whose relaxation time is very sensitive to the vinyl content, and discussed the results in terms of models of the glass transition.[11,12] The extension of the frequency window to 10^{6} Hz and the temperature range down to 100 K makes it now possible to analyze both the α and β relaxations and determine how local reorientations influence each other in polybutadienes with changing microstructure.

II. Polymer Preparation and Characterization

The five polybutadienes were prepared following well-established high-vacuum procedures[13] by anionic polymerization. Details of synthesis and characterization are given elsewhere.[10] Purified *sec*-butyllithium was used in all cases as initiator. A cyclohexane/benzene mixture served as polymerization solvent. Diethyl ether, tetrahydrofuran, and dipiperidinoethane were used as polar modifiers. The number-average molecular weights, M_n, were measured by membrane osmometry in toluene at 37 °C. The values were obtained by

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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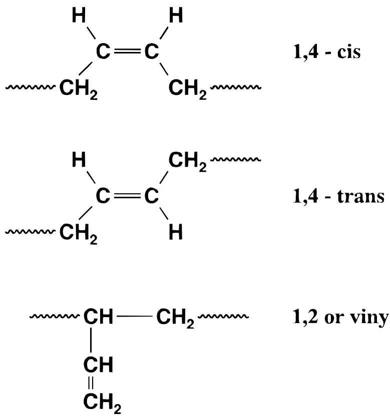

Figure 1. Chemical structures of the three repeating units in anionically prepared polybutadienes.

Table 1. Microstructure of the PB Samples: Composition As Measured by ^{13}C and ^{1}H NMR, Number-Average Molecular Weight by Membrane Osmometry, and Glass Transition Temperature by DSC

sample	% 1,2-vinyl	% 1,4-trans	% 1,4-cis	mol wt × 10^{-4}	T_g (K)
PB07	7	52	41	2.1	178
PB37	37	40	23	2.2	201
PB52	52	29	19	1.8	216
PB68	68	20	12	2.0	238
PB86	86	8	6	2.0	250
PB95	95			2.0	272

$(\pi/c)^{0.5}$ versus c plots, where π is the osmotic pressure and c is the concentration. Molecular weight distributions were analyzed by size exclusion chromatography. All polymers have polydispersity indices smaller than 1.05, indicating near-monodisperse distributions. The microstructural composition of the samples was determined by ^{13}C- and ^{1}H-NMR spectroscopy. The molecular characteristics of all polybutadienes along with their glass transition temperatures, measured by differential scanning calorimetry, are listed in Table 1.

In order to obtain long-term stability of the polybutadienes, small amounts of 4-methyl-2,6-di-*tert*-butylphenol were added. No effect of this antioxidant on the measured relaxation processes could be detected. Nevertheless, preparation of sample PB95 at around 80 °C led to a significant change in the relaxation behavior. Therefore, the polybutadienes were kept below 50 °C under an argon stream during their preparation. For convenience, samples PB07 and PB95, the two extremes in the amount of vinyl units, will be called homopolymers in the following. In contrast, the other samples will be referred to as (mixed) copolymers.

Dielectric Measurements. Dielectric measurements were carried out between 10^{-2} and 10^6 Hz with a Schlumberger 1260 frequency response analyzer equipped with a Chelsea dielectric interface with high-impedance preamplifier. Samples were held at a constant temperature with a stability better than 0.1 K.

The sample holder consisted of a parallel-plate capacitor (diameter 20 mm, distance between 50 and 100 μm). The distance could be kept constant by insertion of small Teflon spacers. Because this distance could not be determined to an accuracy higher than 10%, this is also the minimum error of the absolute value of the dielectric constant and loss. The samples had such a low dc conductivity that no conductivity contribution to the dielectric losses had to be subtracted.

III. Results and Discussion

Figure 2 shows the temperature-dependent loss spectrum of PB07, which serves as a typical example for the investigated polymers: at temperatures above T_g, two relaxations, the α relaxation at low frequencies and the β relaxation at high frequencies, are in the measured frequency window (see curve at 181 K). At higher temperatures, both processes approach each other and tend to merge. At lower temperatures, the α relaxation moves out of the frequency window at around T_g. Then only the β relaxation is left.

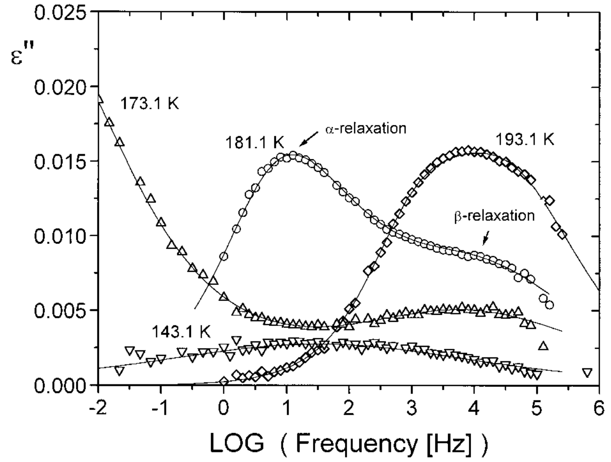

Figure 2. Imaginary part of the dielectric function of 1,4-polybutadiene (sample PB07) for different temperatures as indicated. The curves show two relaxational processes: the α relaxation at low frequencies and a β relaxation at high frequencies. Solid lines are fit curves as discussed in the Experimental Section.

For the analysis of relaxation spectra in the frequency domain, spectra are often parameterized by the Havriliak–Negami (HN) function[14]

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{(1 + (i\omega\tau)^{\alpha})^{\gamma}} \qquad (0 < \alpha \le 1), (0 < \gamma \le 1) \quad (1)$$

where ϵ_∞ and ϵ_s are the limits of the real part of the dielectric function for infinite and zero frequency, respectively. For $\omega \ll \omega_{\max}$ and $\omega \gg \omega_{\max}$ (with $\omega_{\max}$ defined by the maximum of $\epsilon''(\omega)$), the HN function will reduce to power laws: for $\gamma = 1$ to the (in a log-frequency representation) symmetrical Cole–Cole[15] equation, and for $\alpha = 1$, $\gamma = 1$ to the simple Debye equation.[16] To characterize two relaxation processes, the sum of two HN functions can be taken. This method works well when both processes are separated; when they start to merge at high temperatures (see Figure 2), the fit gets difficult, because the parameters that determine the high-frequency spectrum of the α relaxation and the low-frequency spectrum of the β spectrum can be adjusted freely. To restrict the fit parameters, we have added two constraints: First, we assume the β relaxation to be symmetric and of a Cole–Cole form, which has been found for many polymeric systems[1] (i.e., $\gamma_{HN} = 1$). Second, we assume the α relaxation to be of a Kohlrausch–Williams–Watts (KWW) form:[17]

$$\Psi(t) = \Psi_0 \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{KWW}}\right] \qquad (0 < \beta_{KWW} \le 1) \quad (2)$$

It has been shown recently[18–20] that for many systems, the HN parameters α and γ are coupled such that the HN function can be approximated by a KWW function with

$$\gamma = 1 - 0.812(1 - \alpha)^{0.387} \quad (3)$$

$$\beta_{KWW} = (\alpha\gamma)^{0.813} \qquad (\beta_{KWW} \le 0.95) \quad (4)$$

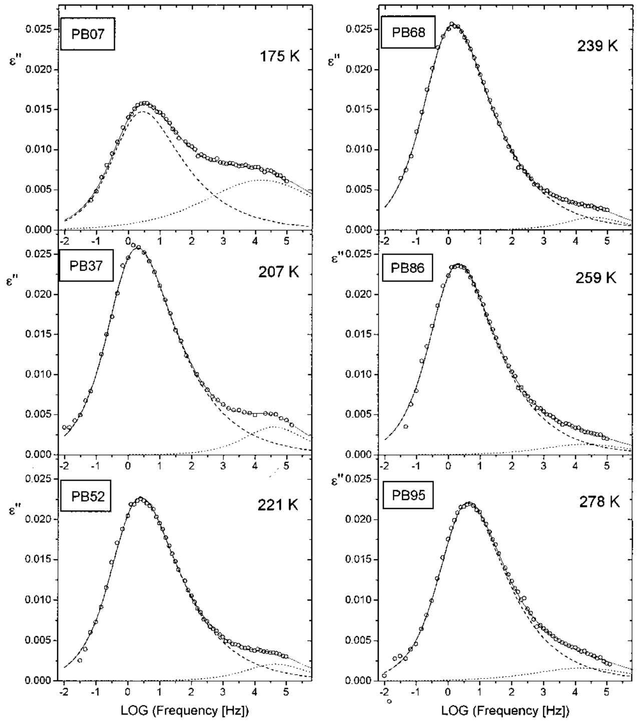

Figure 3. Dielectric loss spectra of all samples at temperatures close to T_g. The solid line is the sum of a fit with a KWW function (dashed line) and a Cole–Cole function (dotted line).

thus reducing the number of free parameters by 1. Therefore, in the following, the α relaxation has been described with the KWW-restricted HN function and the β relaxation with the Cole–Cole function, the overall relaxation spectra above T_g being composed of the sum of the two. Such fits are shown as solid lines in Figures 2 and 3. In any case, the sum of two merging and probably interacting relaxation processes should be considered only as a first approximation to a more realistic procedure involving some kind of convolution, especially in the region where the α and β relaxations merge.

The dependence of the relaxation spectrum on vinyl content is shown in Figure 3, where the spectra are displayed at selected temperatures close to T_g. The broken lines are the KWW and Cole–Cole functions corresponding to the α and β relaxations, respectively. One can see that the α relaxation in PB07 has a much lower value of the relaxation strength, and the contribution of the β relaxation at high frequencies is decreasing with vinyl content. The relaxation strength of the β relaxation in PB07 is about 4 times higher than in PB95. This point will be discussed below.

α Relaxation above T_g. The analysis of the α relaxation gives the following results: The main influence of the vinyl content is the well-known change of T_g and therefore the relaxation time τ_{KWW}. This is represented in Figure 4, where the relaxation time is fitted with the Vogel–Fulcher–Tammann (VFT) equation, $\log \tau = A + B/(T - T_0)$ (values B and T_0 listed in Table 2). Extrapolation of this formula to a relaxation time of 100 s gives a dielectric estimate of the glass transition temperature, which is plotted in Figure 5 and has an almost linear dependence on vinyl content. Although the spectrum of the α relaxation narrows at higher temperatures, the value of the Kohlrausch parameter β_{KWW} in this high-temperature range could be strongly affected by the way of analysis used because of the merging of the α and β relaxations. Therefore we have characterized the shape of the α relaxation by the value of β_{KWW} at temperatures where τ_{KWW} is about 0.1, for which the α peak is in the frequency window and the α and β relaxations are relatively well separated (see Figure 3). The values of β_{KWW} so obtained are shown in Figure 5. Within the error bars, a constant value 0.42 ± 0.01 is found for all samples. However, a systematic increasing of β_{KWW} with increasing vinyl content is envisaged. This finding is different from results obtained from recent mechanical relaxation measurements, which found a decrease of β_{KWW} with increasing vinyl content.[5] Although the values of β_{KWW} obtained could be influenced to some extent by the different way of analysis (the mechanical data are analyzed by construction of master functions and by fitting to a single KWW process), the differences in this parameter as obtained from mechanical and dielectric techniques are a remarkable fact.

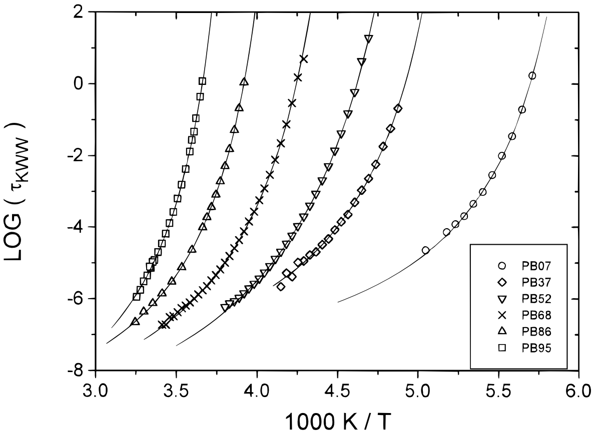

Figure 4. Activation plot of the α relaxation of the different samples. The solid lines represent a fit with the VFT equation. The fit values are listed in Table 2.

On the other hand, in agreement with the previous studies, all samples investigated have only one α relaxation. This is different for diblock copolymers[9] and sometimes even homopolymer blends,[4,21] where two distinct α relaxations were detected, revealing concentration heterogeneities. Additionally, we do not find spectral broadening of the α relaxation for the copolymers investigated. This suggests that the random copolymers are sufficiently homogeneous on the relevant length scale of the α relaxation. Therefore, subsequent substitution of one monomeric part through another leads to a smooth variation of the main dynamical properties as displayed in the relaxation time.

***β* Relaxation below T_g.** The samples with vinyl content higher than 37% have a β relaxation much weaker than the α relaxation (as shown in Figure 3). For temperatures much above T_g, it is almost impossible to separate for these samples the β process from the α process. Therefore we analyze the β spectrum in the sub-T_g region, where the α relaxation is outside the measuring window. As a first approach, a fit was made to each spectrum with a single Cole–Cole function. Figure 6a shows β spectra for the two homopolymer cases (PB07, PB95) and one mixed system (PB68) at temperatures where the maximum of the loss process is in the middle of the measured frequency window. Besides the decrease of the relaxation strength with increasing vinyl content already mentioned above, there is an increased broadening of the spectra in the case of the copolymer system in comparison to the homopolymers. Due to the low intensity of the β process, a

Table 2. Result of Fit with One α and One β Relaxation[a]

	α relaxation			β relaxation			
sample	$T_{g,100s}$[b] (K)	B[c]	T_0[c] (K)	E_A[d] (kJ/mol)	τ_0[d]	$\bar{\Delta\epsilon}$[e]	$\bar{\alpha}$[e]
PB07	171	142	158	37	3.0×10^{-6}	0.028 ± 0.001	0.28 ± 0.02
PB37	198	207	180	?[f]		0.027 ± 0.001	0.18 ± 0.02
PB52	211	326	186	?[f]		0.018 ± 0.002	0.20 ± 0.02
PB68	230	291	207	?[f]		0.014 ± 0.001	0.20 ± 0.02
PB86	250	262	228	?[f]		0.013 ± 0.001	0.19 ± 0.02
PB95	268	285	246	41	9.8×10^{-14}	0.008 ± 0.001	0.25 ± 0.01

[a] E_A = activation energy, τ_0 = prefactor of Arrhenius equation. $\bar{\Delta\epsilon}$ and $\bar{\alpha}$ are medium values of the Cole–Cole parameters for the temperatures below T_g. [b] Temperature at which the relaxation time of the α relaxation equals 100 s. [c] VFT parameters. [d] Arrhenius parameters. [e] Cole–Cole parameters. [f] Not well defined.

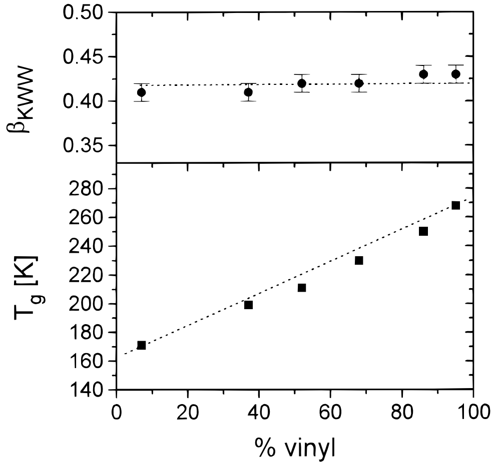

Figure 5. T_g and shape parameter of the α relaxation as a function of vinyl content: T_g is determined at a relaxation time of 100 s, and the Kohlrausch parameter β_{KWW} is determined at temperatures just above the glass transition at $T \approx T_g/0.9$.

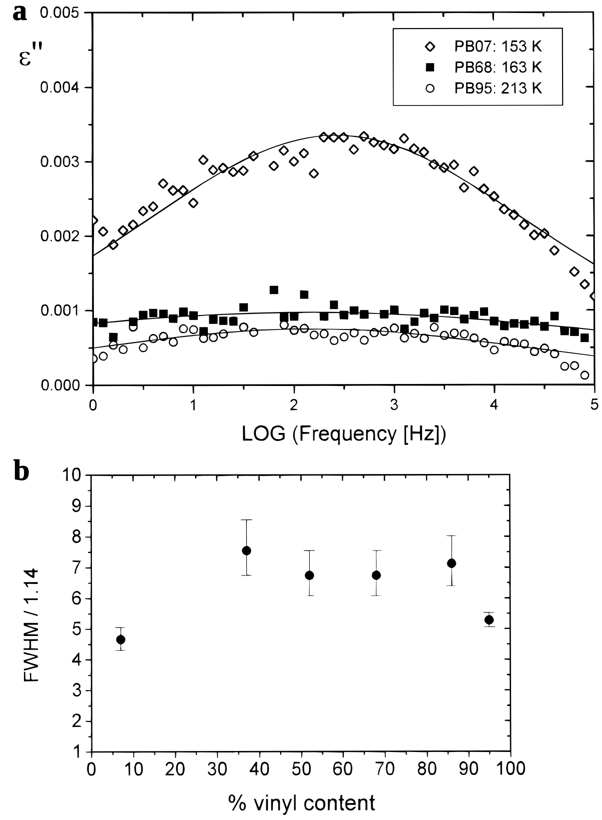

Figure 6. (a) β relaxation of three polymers for temperatures at which the main part is in the middle of the frequency window. From top to bottom, the vinyl content increases, resulting in a lowering of the intensity. Notice that the width of the Cole–Cole curve (solid line) is broadest for PB68. (b) Width of the β spectrum as determined with a fit of one Cole–Cole function. In contrast to the homopolymers, the copolymers have a much broader spectrum.

temperature-dependent analysis of the broadening was not possible. Instead, average values were determined for the FWHM (full width at half-maximum), which was calculated from the Cole–Cole parameters. The values given in Figure 6 together with the corresponding uncertainties, show the systematic increase of width for the copolymer systems in comparison to the homopolymer systems.

Comparing the relaxation times of samples with different vinyl contents at the same temperature, as in Figure 7a, gives an interesting result: The relaxation time τ is in the case of PB52 not intermediate between the relaxation times of the homopolymer samples but almost identical to the one of PB07. This finding is very different from the one obtained for the α relaxation, which, for the same samples, is shifted to a glass transition temperature almost in between the homopolymer glass transition temperatures. A comparable shift for the β relaxation would, when taking a medium value for the activation energy of PB07 and PB95, be around 2 decades in frequency, which is far beyond the experimental uncertainty. Following this analysis procedure by fitting a single Cole–Cole function to the β spectra at different temperatures, an activation plot is obtained as shown in Figure 7b: Whereas for the homopolymers the typical activation for a secondary relaxation in the form of an Arrhenius function ($\tau = \tau_0 \exp[-E_A/kT]$) results (with values listed in Table 2), the relaxation times of the copolymers do not conform with a straight line. This strange behavior is not a consequence of low resolution: PB95 has the lowest relaxation strength and yet has a very good Arrhenius behavior. On the other hand, many relaxation times determined for PB37, PB52, and PB68 are almost identical with the ones of PB07, which cannot be accidental.

The relaxation strength of the samples is almost constant below T_g and increases at higher temperatures, presumably because of the influence of the α relaxation. The average values below T_g are shown in Figure 8 and give an almost linear dependence of the relaxation strength on vinyl content. Looking at the composition of the systems, they consist not of two, but of three components: vinyl, cis, and trans units. However, whereas the vinyl and cis units have about the same dipole moment (1-butene and *cis*-2-butene both have $\mu \approx 0.3$ D[22]), the trans group has no dipole moment. Thus in PB07 mainly cis units and in PB95 mainly vinyl units will contribute to the dielectric loss. Apparently the vinyl group needs more volume for local reorientation, leading to increased molecular hindrance and a lower value of the relaxation strength. Identifying the β relaxation with local reorientation of a subgroup could

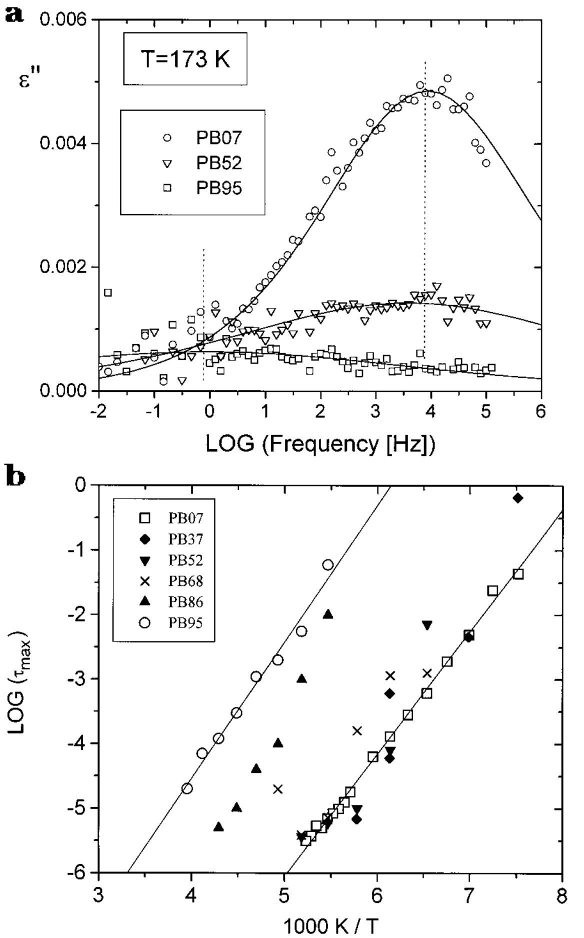

Figure 7. (a) β-Relaxation spectra for three samples at 173 K. The solid lines represent a fit with one Cole–Cole function. The peak frequencies of PB95 and PB07 are indicated as broken vertical lines. Notice that the maximum of the spectrum of PB52 has the same peak frequency as PB07. (b) Activation plot of the relaxation times obtained with a fit of one Cole–Cole function to the β spectrum: while the homopolymers (open symbols) follow well an Arrhenius behavior, the copolymers do not. Notice that for PB37, PB52, and PB68, some points lie between the relaxation time points of PB07.

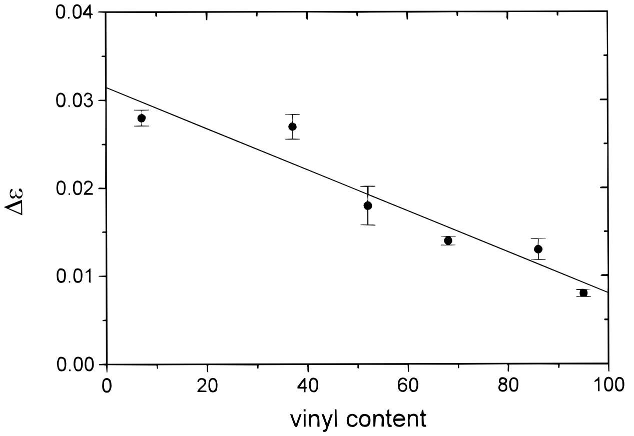

Figure 8. Average β relaxation strength $\Delta\epsilon$ for temperatures below T_g as a function of composition.

also explain the broadening of the spectra and the failure of the Arrhenius behavior for the copolymers, assuming that the β spectra in the copolymer systems consist not of one, but of two distinct processes that are difficult to resolve. The fact that the β relaxation of PB07 is much stronger than of PB95 would then explain why the maximum of the loss spectrum of the copolymers is sometimes identical with the maximum of PB07: when the relaxation time of the cis unit is in the measurement window, the cis contribution will dominate the spectrum and determine the maximum frequency.

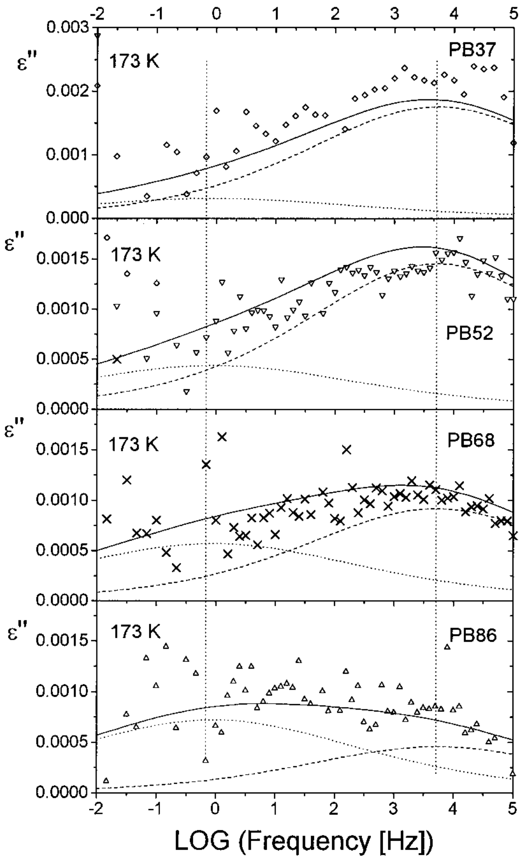

Figure 9. Relaxation spectra for the copolymers at 173 K. The solid lines are a simulation under the assumption of two independent contributions which are indicated by broken/dotted lines. The vertical lines represent the relaxation frequency of these β relaxations.

The above outlined idea implies in principle a splitting of the relaxation spectrum in two separate components. Such a splitting of the β relaxation has been observed earlier for the side chain polymer PMMA with a stereoblock of isotactic/syndiotactic units.[8] There, the splitting was accompanied by a shift in relaxation time of the isotactic group and explained by introduction of free volume by the syndiotactic units with the result of a change of activation energy. Our results indicate no change of the relaxation time of the cis units. We therefore have made a model for the mixed polymers at 173 K under the following simplifying assumptions: First, the β relaxation of the samples PB07 and PB95 can be assumed originating from local relaxations of the cis and vinyl groups, respectively. Second, these relaxations occur in the copolymers independently and contribute as a sum to the overall relaxation spectrum without change of time scale, shape, and intensity. According to these assumptions, the relaxation time has been calculated from the Arrhenius plot, a constant spectral width has been used which was the average value listed in Table 2, and the relaxation strength was taken from the values shown above for the homopolymers.

In Figure 9, the results of such a calculation at 173 K are displayed together with the relaxation spectra for the copolymers with different compositions. The solid lines are the sum of the part from the vinyl groups (dotted line) and the cis groups (dashed line) with peak frequencies at 0.9 and 5980 Hz, respectively. Compared to the simplicity of the model, the simulated curves agree qualitatively well with the data. Particularly, they reproduce that the maximum of the spectrum is up to a content of 68% almost unchanged.

IV. Conclusion

The variation of microstructure on a monomeric length scale in PB main chain polymers has a strong effect on the relaxation time of the α relaxation. On the relevant length scale of the α relaxation, the copolymers seem to be homogeneous. In contrast, the local β relaxations seem not to be influenced by the change of the glass transition but only by the content of each relaxational unit in the copolymer. This means that the observed β relaxations are influenced mainly by the local environment of each monomeric unit without strong interaction between neighboring groups.

Acknowledgment. The authors wish to acknowledge financial support from the "Stiftung Volkswagenwerk", the European Community by network project contract ERBCHRXCT92000, and the Accíones Integralas Hispano-Alemanas 50A (1994).

References and Notes

(1) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: London, 1967.

(2) Johari, G. P.; Goldstein, M. *J. Chem. Phys.* **1970**, *53*, 2372.

(3) Götze, W. In *Liquids, Freezing and the Glass Transition*; Hansen, J. P., Levesque, D., Zinn-Justin, J., Eds.; North-Holland: Amsterdam, 1991.

(4) Quan, X.; Johnson, G. E.; Anderson, E. W.; Lee, H. S. *Macromolecules* **1991**, *24*, 6500.

(5) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 5315.

(6) Ni, S.; Yu, F.; Shen, L.; Qian, B. *J. Appl. Polym. Sci.* **1989**, *37*, 729.

(7) Ni, S.; Yu, F.; Shen, L.; Qian, B. *J. Appl. Polym. Sci.* **1990**, *41*, 13.

(8) Ishida, Y. *J. Polym. Sci., Part B* **1967**, *5*, 745.

(9) Quan, X.; Johnson, G. E.; Anderson, E. W.; Bates, F. S. *Macromolecules* **1989**, *22*, 2451.

(10) Zorn, R.; McKenna, G. B.; Willner, L.; Richter, D., submitted to *Macromolecules*.

(11) Zorn, R.; Mopsik, F. I.; McKenna, G. B.; Willner, L.; Richter, D., to be published.

(12) Colmenero, J.; Alegría, A.; Santangelio, P. G.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 407.

(13) Morton, M.; Fetters, L. J. *Rubber Rev.* **1975**, *48*, 359.

(14) Havriliak, S.; Negami, S. *J. Polym. Sci., Polym. Symp.* **1966**, *14*, 89.

(15) Cole, R. H.; Cole, K. S. *J. Chem. Phys.* **1941**, *9*, 341.

(16) Böttcher, G. J. F.; Bordewijk, P. *Theory of Electric Polarisation*; Elsevier: Amsterdam, 1978.

(17) Kohlrausch, R. *Ann. Phys.* **1847**, *12*, 393.

(18) Alvarez, F.; Alegría, A.; Colmenero, J. *Phys. Rev. B* **1991**, *44*, 7306.

(19) Alvarez, F.; Algería, A.; Colmenero, J. *Phys. Rev. B* **1993**, *47*, 125.

(20) Hofmann, A. Ph.D. Thesis, University of Mainz, 1993.

(21) Alegría, A.; Colmenero, J.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 4486.

(22) McClellan, A. L. *Tables of Experimental Dipole Moments*; W. H. Freeman and Co.: San Francisco, 1963.

MA946419P