On the Motional Coupling between Chain and Junction Dynamics in Thermoreversible Networks

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ABSTRACT: The dielectric relaxation of polar stickers capable of binary hydrogen bond complexation is studied theoretically and compared to experiment. In the model system, free and complexed units are considered in equilibrium. The theoretical evaluation shows that the dipole correlation function of complexes cannot be described by a simple exponential decay, as is usually assumed in dielectric spectroscopy. Complex reorientation and dissociation contribute simultaneously to the dielectric relaxation. The theoretical results are compared to experimental data obtained on polybutadiene which is functionalized at low concentration (x = 0.02, 0.03, and 0.04) by 4-phenyl-1,2,4-triazoline-3,5-dione (4-phenylurazole (PU)) units. From the comparison of recent dielectric and dynamic mechanical measurements, the relaxation times of the reorientation of dimeric complexes are calculated and compared with the lifetime of dimeric contacts. From the relaxation strength of the relaxation of complexed urazoles, the dipole moment is calculated and compared with the result of a force field calculation. Both methods reveal a slightly twisted structure of the dimeric complexes.

1. Introduction

Thermoplastic elastomers form an important class of polymers. The macroscopic properties of these systems can be realized by different molecular concepts. In block copolymers, microphase separation between soft and hard segments which differ in the glass temperature T_g form the structural concept. A different approach to realize the desired macroscopic properties is attaching a small number of hydrogen bond carrying groups to a nonpolar polymer backbone. In these thermoreversible networks, the macroscopic properties are governed by the "local" dynamics of the reversible junctions. On time scales shorter than the lifetime of the junctions, the network shows the viscoelastic properties of covalently cross-linked systems whereas at longer times only entanglements determine the viscoelastic behavior. A model system for a simple case of such a thermoreversible network is realized if a low concentration of 4-phenylurazole (PU) units is attached to polybutadiene. In this case the junctions are formed by binary hydrogen bond complexes of two phenylurazole units.[1,2] In the following, the nomenclature given in previous publications will be used. A polybutadiene ("PB") of a molecular weight M_n = 28 000 and a degree of modification X (mol % with respect to the number of double bonds of the polymer chains) is designated as "PB-28−PU−X".

While the junctions in hydrogen-bonded thermoreversible networks in general may consist of large dipolar clusters,[3−6] only binary hydrogen bond linkages are formed in the case of phenylurazole. To describe the global dynamics of such a thermoreversible network, Leibler, Rubinstein, and Colby developed the hindered reptation theory.[7] The overall relaxation will be governed by a relaxation process with a relaxation time that was predicted to be the lifetime of binary complexes. In recent dynamic mechanical measurements,[1] this relaxation process ($\alpha^{*}_{\mathrm{DMA}}$-relaxation) could be detected in the rubbery plateau regime. In their theory Leibler, Rubinstein, and Colby developed a correlation between the terminal relaxation time and the lifetime of binary stickers. This correlation was nicely confirmed by the dynamic mechanical measurements.

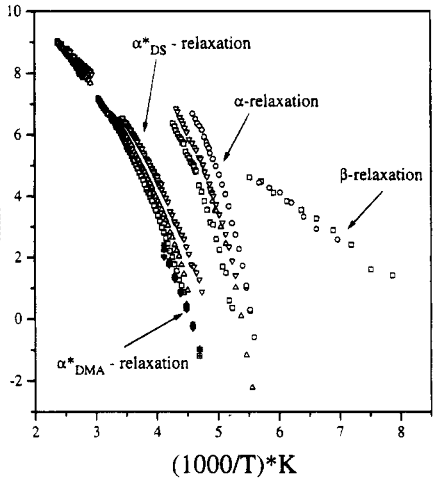

Figure 1. Activation plot for polybutadienes substituted by different amounts of phenylurazoles (0 mol %: O; 2 mol %: ▽; 3 mol %: △; 4 mol %: □; symbols with crosses; dynamic mechanical measurements;[1] open symbols: dielectric measurements[2]). The degree of modification refers to the number of double bonds of the polybutadiene chains.

By dielectric spectroscopy[2] a relaxation process (α^{*}_{DS}-relaxation) was detected in the same frequency regime. The intensity of this process showed the same dependence on the degree of functionalization as in the dynamic mechanical measurements. However, the data of dielectric and dynamical measurements did not coincide[1] (Figure 1). The characteristic deviations between the two data sets (see part 4) were not explained in our previous work.[1]

In the present work we give a quantitative treatment of the dielectric relaxation, using the correlation function approach as developed by Kubo,[8] Glarum,[9] Cole,[10]

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Table 1. Specification of the Individual Dipole Correlation Terms

terms	number	meaning
		Dipole correlation between open stickers at $t = 0$ and
$\langle \vec{M}_U(0)\cdot[\vec{M}_U(t)]_U\rangle$	1	open stickers at time t which had been uncomplexed at $t = 0$
$\langle \vec{M}_U(0)\cdot[\vec{M}_U(t)]_{U_2}\rangle$	2	open stickers at time t which had been complexed at $t = 0$
$\langle \vec{M}_U(0)\cdot[\vec{M}_{U_2}(t)]_{U_2}\rangle$	3	complexed stickers at time t which had been complexed at $t = 0$
$\langle \vec{M}_U(0)\cdot[\vec{M}_{U_2}(t)]_U\rangle$	4	complexed stickers at time t which had been uncomplexed at $t = 0$
		Dipole correlation between complexed stickers at $t = 0$ and
$\langle \vec{M}_{U_2}(0)\cdot[\vec{M}_{U_2}(t)]_U\rangle$	5	complexed stickers at time t which had been uncomplexed at $t = 0$
$\langle \vec{M}_{U_2}(0)\cdot[\vec{M}_U(t)]_{U_2}\rangle$	6	open stickers at time t which had been complexed at $t = 0$
$\langle \vec{M}_{U_2}(0)\cdot[\vec{M}_{U_2}(t)]_{U_2}\rangle$	7	complexed stickers at time t which had been complexed at $t = 0$
$\langle \vec{M}_{U_2}(0)\cdot[\vec{M}_U(t)]_U\rangle$	8	open stickers at time t which had been uncomplexed at $t = 0$

Böttcher,[11] and Hill, Vaughan, Price, and Davies.[12] Previously, Schwarz[13] and Williams[14] already considered dielectric relaxation for systems in which opposing unimolecular ($A_1 \rightleftharpoons A_2$) and opposing bimolecular and unimolecular reactions ($A + B \rightleftharpoons AB$) occur, using a perturbation approach and a time correlation function (TCF) approach, respectively.

2. Theory

The relationship between the macroscopic complex dielectric function ϵ^* and the dipole correlation function ($\Gamma(t)$) for the permanent moment of a microscopic volume in a liquid which depends only on short-range interactions is given by[10,12,15–17]

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = L[\dot{\Gamma}(t)] \tag{1}$$

with

$$\Gamma(t) = \frac{\langle \vec{M}(0)\cdot\vec{M}(t)\rangle}{\langle \vec{M}(0)\cdot\vec{M}(0)\rangle} \tag{2}$$

where $\vec{M}(0)$ and $\vec{M}(t)$ are the sum of the dipole moments of the individual molecules for a macroscopic volume V at time $t = 0$ and time t, respectively ($\vec{M}(0) = \sum_{i=1}^{n}\vec{\mu}_i(0)$, $\vec{M}(t) = \sum_{i=1}^{n}\vec{\mu}_i(t)$). ϵ_∞ and ϵ_s are the plateau values of the real part of the dielectric function at high and low frequencies, respectively, and L is the Laplace transformation.

In a thermoreversible network based on binary complexes between polar stickers attached to a nonpolar or weakly polar backbone, the polymer backbone as well as the reversible junctions contribute to the dielectric behavior. The reversible junctions either consist of free units (U) or complexed stickers (U_2) which undergo a chemical exchange (chemical relaxation) according to

$$U + U \underset{k_-}{\overset{k_+}{\rightleftharpoons}} U_2 \tag{I}$$

This chemical equilibrium can be described by an equilibrium constant K which is given as $K = k_+/k_-$.

So far only few approaches have been taken to describe the dielectric relaxation in systems which undergo chemical relaxation[13,14] aside the reorientation of dipoles. The common treatment of dielectric relaxation is based on the assumption that the dipole correlation function shows a simple or stretched exponential decay induced by thermal fluctuations of permanent dipoles. In the case of equilibrium I, besides these thermal fluctuations of U and U_2 the chemical relaxation is a further relaxation mechanism. This problem will be treated by the correlation function approach.[8–10,14] For equilibrium I, the effective dipole moment at $t = 0$, $\vec{M}(0)$, can be written as the sum of the dipole moments of open urazole units U and complexed ones U_2:

$$\vec{M}(0) = \vec{M}_U(0) + \vec{M}_{U_2}(0) \tag{3}$$

with

$$\vec{M}_U(0) = \sum_{i=1}^{N_U(0)} \vec{\mu}_{U_i}(0) \tag{4}$$

$$\vec{M}_{U_2}(0) = \sum_{k=1}^{N_{U_2}(0)} \vec{\mu}_{U_{2_k}}(0) \tag{5}$$

After a time t, the dipole moments have changed to

$$\vec{M}(t) = \vec{M}_U(t) + \vec{M}_{U_2}(t) = [\vec{M}_U(t)]_U + [\vec{M}_U(t)]_{U_2} + [\vec{M}_{U_2}(t)]_{U_2} + [\vec{M}_{U_2}(t)]_U \tag{6}$$

where the first index denotes the molecule considered at time t and the second index denotes the state of this molecule at time $t = 0$. Thus $[\vec{M}_U(t)]_{U_2}$ stands for free urazole units U at time t which were complexed at $t = 0$. Now the average of the product $\vec{M}(0)\cdot\vec{M}(t)$ is formed by inserting eqs 3 and 6 into eq 2. $\langle \vec{M}(0)\cdot\vec{M}(t)\rangle$ can be written as the sum of the terms 1–8 given in Table 1.

There is no correlation between molecules that had been uncomplexed at $t = 0$ and molecules that had been complexed at $t = 0$. Therefore terms 2, 3, 5, and 8 vanish to zero. Furthermore, it can be assumed that complex formation and dissociation destroy any correlation that had existed before. This is the case if (i) uncomplexed molecules form with no orientation correlation to the original U_2 molecule (and vice versa) or if (ii) uncomplexed molecules having formed from a U_2 molecule immediately tumble. In parts 4a and 4b, it will be shown that the tumbling time of uncomplexed molecules is more than 4 orders of magnitude smaller than the relaxation time of complexed molecules. Thus the latter case is realized and cross correlations between uncomplexed urazoles (at $t = 0$) and complexed urazoles at time t that have been uncomplexed at $t = 0$ (term 4 = 0) and between complexed urazoles at $t = 0$ and uncomplexed urazoles that had been complexed at $t = 0$ can be neglected. Thus only terms 1 and 7 do not disappear and the dipole correlation function can be written as

$$\langle \vec{M}(0)\cdot\vec{M}(t)\rangle = \langle \vec{M}_U(0)\cdot[\vec{M}_U(t)]_U\rangle + \langle \vec{M}_{U_2}(0)\cdot[\vec{M}_{U_2}(t)]_{U_2}\rangle \tag{7}$$

$[\vec{M}_U(t)]_U$ and $[\vec{M}_{U_2}(t)]_{U_2}$ can be expressed as

$$[\vec{M}_U(t)]_U = \sum_{i=1}^{N_U(0)} \vec{\mu}_{U_i}(t)[P_U(t)]_U \tag{8}$$

and

$$[\vec{M}_{U_2}(t)]_{U_2} = \sum_{j=1}^{N_{U_2}(0)} \vec{\mu}_{U_2 j}(t)[P_{U_2}(t)]_{U_2} \qquad (9)$$

where $[P_U(t)]_U$ is the probability that a urazole that was uncomplexed at $t = 0$ is still uncomplexed at time t and $[P_{U_2}(t)]_{U_2}$ is the probability that a urazole unit that was complexed at $t = 0$ is still complexed at time t. Thus $[P_U(t)]_U$ and $[P_{U_2}(t)]_{U_2}$ are concerned with the survival of molecules U at time t that were U at $t = 0$ and of molecules U_2 at time t that were U_2 at time $t = 0$. U molecules at $t = 0$ that associated to U_2 at $0 < t' < t$ and redissociated again to form U at $t = 0$ do not contribute to dielectric relaxation because any correlation between U at $t = 0$ and t was assumed to be destroyed by the association–dissociation process. The same agreement holds for complexed stickers U_2 that originate from a dissociation–association process. Under these conditions, $[P_U(t)]_U$ is obtained from $U + U \rightarrow U_2$ (with no reverse) and $[P_{U_2}(t)]_{U_2}$ from $U_2 \rightarrow U + U$ as

$$[P_U(t)]_U = \frac{1}{1 + k_+ t c_U^0} \qquad (10)$$

$$[P_{U_2}(t)]_{U_2} = e^{-t/\tau_{U2}^{ch}} \qquad (11)$$

with $\tau_{U_2}^{ch} = 1/k_-$ as the lifetime of complexed stickers and c_U^0 as the concentration of uncomplexed stickers. From eq 8 and assuming that $U + U \rightarrow U_2$ occurs without change in orientation of each U (not physically reasonable), it follows that

$$\langle \vec{\mu}_U(0) \cdot \vec{\mu}_U(t) \rangle = \vec{\mu}_U^2 [P_U(t)]_U = \vec{\mu}_U^2 \frac{1}{1 + k_+ c_U^0 t} \qquad (12)$$

which is well behaved but does not give a "Debye" process on Laplace transformation. If however the assumption is made that U molecules tumble many times before they connect into U_2 molecules (as will be shown in part 4b), then

$$\langle \vec{\mu}_U(0) \cdot \vec{\mu}_U(t) \rangle = \vec{\mu}_U^2 e^{-t/\tau_U} \qquad (13)$$

where τ_U is the relaxation time of molecular reorientation of uncomplexed (U) molecules.

Now let us consider the U_2 molecules. If they simply tumble without dissociation (case A), the dipole correlation function is given by

$$\langle \vec{\mu}_{U_2}(0) \cdot \vec{\mu}_{U_2}(t) \rangle = \vec{\mu}_{U_2}^2 e^{-t/\tau_{U2}} \qquad (14)$$

with τ_{U_2} as the relaxation times of molecular reorientation of complexed (U_2) molecules.

In eqs 13 and 14 we have assumed a simple exponential decay of the dipole correlation functions (Debye approximation). The effect of a symmetrically and asymmetrically broadened relaxation time distribution will be treated later.

On the other hand, if U_2 molecules dissociate slowly (and then immediately tumble as U molecules as will be shown in part 4b), then chemical relaxation dominates the dipole correlation term of U_2 molecules (case B):

$$\langle \vec{\mu}_{U_2}(0) \cdot \vec{\mu}_{U_2}(t) \rangle = \vec{\mu}_{U_2}^2 e^{-t/\tau_{U2}^{ch}} \qquad (15)$$

where $\tau_{U_2}^{ch} = 1/k_-$. So at $t = 0$ there are a certain number of U molecules and similarly U_2 molecules with a dipole correlation function

$$\langle M(0) \cdot M(t) \rangle = N_U^{eq} \vec{\mu}_U^2 e^{-t/\tau_U} + N_{U_2}^{eq} \vec{\mu}_{U_2}^2 e^{-t/\tau_{U2}} \qquad \text{(case A)} \qquad (16)$$

or

$$\langle M(0) \cdot M(t) \rangle = N_U^{eq} \vec{\mu}_U^2 e^{-t/\tau_U} + N_{U_2}^{eq} \vec{\mu}_{U_2}^2 e^{-t/\tau_{U2}^{ch}} \qquad \text{(case B)} \qquad (17)$$

with N_U^{eq} and $N_{U_2}^{eq}$ given by the equilibrium constant $K = N_{U_2}^{eq}/(N_U^{eq})^2$. Besides these two extremes ($\tau_{U_2} \ll \tau_{U_2}^{ch}$ (case A) and $\tau_{U_2} \gg \tau_{U_2}^{ch}$ (case B)), the case that chemical relaxation and reorientation of U_2 molecules contribute simultaneously to the decay of the dipole correlation function ($\tau_{U_2} \approx \tau_{U_2}^{ch}$) shall be considered. Then the dipole correlation function is given by

$$\begin{aligned}\langle M(0) \cdot M(t) \rangle &= N_U^{eq} \vec{\mu}_U^2 e^{-t/\tau_U} + N_{U_2}^{eq} \vec{\mu}_{U_2}^2 e^{-t\tau_{U2}} e^{-t/\tau_{U2}^{ch}} \\ &= N_U^{eq} \vec{\mu}_U^2 e^{-t/\tau_U} + N_{U_2}^{eq} \vec{\mu}_{U_2}^2 e^{-t/\tau_{U2}^*} \qquad (18)\end{aligned}$$

with

$$\frac{1}{\tau_{U_2}^*} = \frac{1}{\tau_{U_2}} + \frac{1}{\tau_{U_2}^{ch}} \qquad (19)$$

as the inverse relaxation time of an "overall" relaxation which consists of two contributions, the time τ_{U_2} of reorientations of U_2 and the lifetime of dimeric contacts $\tau_{U_2}^{ch}$. Thus this relaxation encloses the contribution from (i) orientation fluctuations of intact complexes U_2 and (ii) the dissociation of these complexes. Inserting eq 18 together with

$$\langle \vec{M}(0) \cdot \vec{M}(0) \rangle = N_U^{eq} \vec{\mu}_U^2 + N_{U_2}^{eq} \vec{\mu}_{U_2}^2 \qquad (20)$$

into eq 2, we obtain

$$\Gamma(t) = \frac{N_U^{eq} \vec{\mu}_U^2 \exp\left(\frac{-t}{\tau_U}\right)}{N_U^{eq} \vec{\mu}_U^2 + N_{U_2}^{eq} \vec{\mu}_{U_2}^2} + \frac{N_{U_2}^{eq} \vec{\mu}_{U_2}^2 \exp\left(\frac{-t}{\tau_{U_2}^*}\right)}{N_U^{eq} \vec{\mu}_U^2 + N_{U_2}^{eq} \vec{\mu}_{U_2}^2} \qquad (21)$$

The complex dielectric constant is obtained by inserting eq 21 into eq 1:

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{N_U \vec{\mu}_U^2}{N_U \vec{\mu}_U^2 + N_{U_2} \vec{\mu}_{U_2}^2} \frac{1}{1 + i\omega\tau_U} + \frac{N_{U_2} \vec{\mu}_{U_2}^2}{N_U \vec{\mu}_U^2 + N_{U_2} \vec{\mu}_{U_2}^2} \frac{1}{1 + i\omega\tau_{U_2}^*} \qquad (22)$$

Thus the complex dielectric function contains two relaxation processes, one with a relaxation time τ_U describing reorientations of uncomplexed molecules U and one with the overall relaxation time $\tau_{U_2}^*$ of dimeric stickers. The overall relaxation time $\tau_{U_2}^*$ contains both chemical relaxation and reorientation processes if $\tau_{U_2} \approx \tau_{U_2}^{ch}$ or is determined by either reorientation ($\tau_{U_2} \ll \tau_{U_2}^{ch}$) or chemical relaxation ($\tau_{U_2} \gg \tau_{U_2}^{ch}$). The latter process is a first-order molecular reaction and must follow an Arrhenius law. The fluctuations of complexes U_2 must be coupled to the motion of adjacent chain segments and thus are expected to show a WLF behavior.

So far only the mean relaxation time of the α*-relaxation was considered. Further important information can be obtained from the relaxation time distribution which determines the peak shape of the dielectric relaxation. Let us first consider the case $\tau_{U_2}^{ch} \gg \tau_{U_2}$, where the reorientation process dominates the overall relaxation. Reorientations of dimeric association complexes couple to the cooperative motion of the polymer matrix. Thus it depends on the relaxation time distribution of chain dynamics whether symmetrically or asymmetrically broadened peaks are obtained. On the other hand, if $\tau_{U_2}^{ch} \ll \tau_{U_2}$, i.e., if chemical relaxation dominates the overall relaxation, the truly local dissociation leads to a rather narrow relaxation time distribution of the overall relaxation.

Finally let us consider $\tau_{U_2}^{ch} \approx \tau_{U_2}$. In this case the mean overall relaxation time $\tau_{U_2}^{*}$ which is obtained from the inverse frequency at maximum loss is given by eq 19. But it is important to notice that for the low- and high-frequency side of the relaxation peak, the condition $\tau_{U_2}^{ch} \approx \tau_{U_2}$ must not necessarily be fulfilled. Again, the two limiting cases $\tau_{U_2}^{ch} \ll \tau_{U_2}$ and $\tau_{U_2}^{ch} \gg \tau_{U_2}$ have to be considered. In Figure 2 a superposition of the narrow distributed chemical relaxation (open squares) and the broader distributed reorientation (open circles) of dimeric association complexes is shown. At the low-frequency side chemical relaxation is always faster than reorientations. At the high-frequency side the opposite case is realized; i.e., reorientations are always faster than chemical relaxation. As the faster relaxation mechanism dominates the overall relaxation, a relaxation peak as indicated by the solid line results. As can be seen in Figure 2, this peak is asymmetrically broadened at the high-frequency side.

From ϵ_s and ϵ_∞ of this relaxation the dipole moment of urazole complexes can be calculated according to the Kirkwood–Fröhlich equation:[11]

$$\mu_{U_2}^2 = \frac{9kT}{4\pi x_{U_2} N_0 g}\epsilon_0 \frac{(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{\epsilon_s(\epsilon_\infty + 2)^2} \qquad (23)$$

with g the Kirkwood correlation factor, N_0 the number of stickers, and x_{U_2} the molar fraction of closed stickers.

3. Data Analysis

Sample preparation and experimental details of dielectric spectroscopy are given in previous work.[2] The data were fitted by the sum of two Havriliak–Negami functions[18]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (i\omega\tau)^{\alpha})^{\beta}} \qquad (24)$$

where the parameters α and β ($0 \le \alpha,\beta \le 1$) describe the symmetric and asymmetric broadening of the relaxation time distribution, τ is the mean-relaxation time derived from the reciprocal frequency ω at maximum loss ϵ''_{max}, and Δε is the relaxation strength. The first Havriliak–Negami function describes the α*-relaxation whereas the second describes the dynamic glass transition of the polybutadiene chains, which occurs at higher frequencies than the α*-relaxation. For the analysis of the parameters α and β, only those curves where the α*-relaxation is located completely within the experimental frequency window of 10^2–10^7 Hz were analyzed. For these curves, the loss maximum of the dynamic glass transition (α-relaxation) is outside the experimental frequency window. Therefore, the relaxation times of the α-relaxation were calculated from the Williams–Landel–Ferry equation

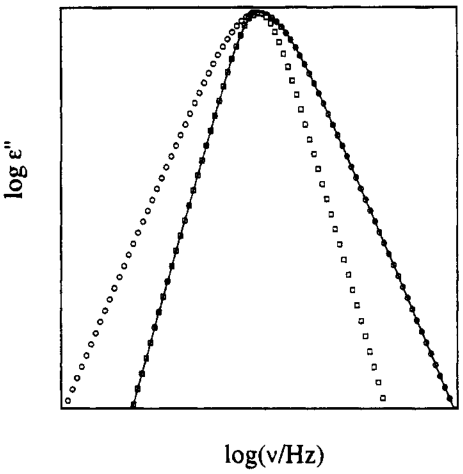

Figure 2. Simulated curves of chemical relaxation (□) and reorientation (○) of dimeric association complexes for $\tau_{U_2}^{ch} \approx \tau_{U_2}$. The solid line represents the resulting overall α*-relaxation that results from a superposition of these relaxations.

$$\log(\tau(T)/\tau(T_g)) = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \qquad (25)$$

where C_1 and C_2 are constants ($C_1 = 15.0$, $C_2 = 29.0$ K for PB-28–PU-2 and $C_1 = 15.0$, $C_2 = 31.2$ K for PB-28–PU-4) and T_g is the glass transition temperature of the functionalized polybutadienes obtained by fitting the experimental data with the WLF equation where $\tau(T_g) = 100$ s was kept constant ($T_g = 177.5$ K for PB-28–PU-2 and $T_g = 182.5$ K for PB-28–PU-4).[2] For all curves α, β, and Δε of the α-relaxation were kept constant (α = 0.4 and β = 1 for both samples, Δε(PB-28–PU-2) = 0.02 and Δε(PB-28–PU-4) = 0.04).

4. Comparison with Experimental Results

(a) Relaxation of the Complexed Urazoles. Polybutadiene functionalized by urazole as polar stickers shows a dielectric relaxation process (α*-relaxation) (Figure 1) in addition to the dynamic glass transition (α-relaxation). According to part 2, the relaxation time of this process may be expressed by the overall relaxation time of binary stickers $\tau_{U_2}^{*}$ as given in eq 19. According to previous measurements[2] the relaxation strength of this relaxation process increased with decreasing temperature. This is in agreement with a shift of the chemical equilibrium I toward a larger fraction of binary complexes with decreasing temperature. Thus the molar fraction of urazole complexes x_{U_2} increases and leads to an increase of the relaxation strength $\Delta\epsilon = \epsilon_s - \epsilon_\infty$ according to eq 23. Similarly, increasing the degree of substitution leads to an increase in x_{U_2} and thus Δε (Figure 3).

From the relaxation strength it is possible to calculate the dipole moment $\mu_{U_2}^{exp}$ of a dimeric urazole complex U_2. In table 2, the values of ϵ_s as obtained from the Havriliak–Negami fits[18] (solid lines, Figure 4) and the corresponding dipole moments $\mu_{U_2}^{exp}$ are given for three

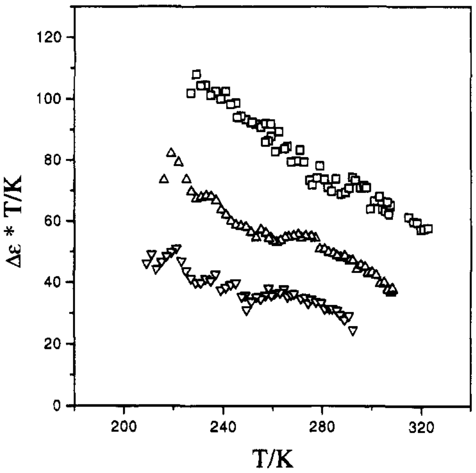

Figure 3. Product of relaxation strength and temperature as a function of temperature for polybutadienes substituted by different amounts of phenylurazole (2 mol %: ▽; 3 mol %: △; 4 mol %: □).

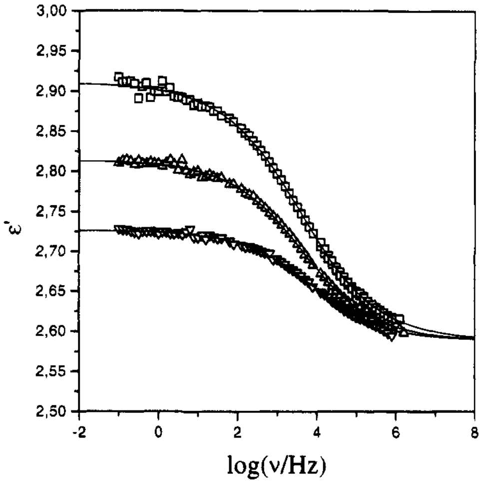

Figure 4. Real part of the complex dielectric function for polybutadienes substituted by different amounts of phenylurazole (2 mol %: ▽, $T = 253$ K; 3 mol %: △, $T = 257$ K; 4 mol %: □, $T = 263$ K). The solid line represents a fit according to the Havriliak–Negami function (eq 24).[18]

Table 2. Plateau Values ϵ_s of the Real Part of the Dielectric Function for Polybutadienes with Different Amounts of Polar Stickers (Figure 4) and Dipole Moments $\mu_{U_2}^{exp}$ Resulting from the Kirkwood–Fröhlich Equation (Eq 23)

deg of modification/ mol %	ϵ_s	T/K	N_0/m³	$\mu_{U_2}^{exp}$/D
2	2.73	253	2.03×10^{26}	0.62
3	2.81	257	3.05×10^{26}	0.59
4	2.91	263	4.07×10^{26}	0.56

degrees of modifications (with $\epsilon_\infty = 2.59$ and a molar fraction of closed stickers x_{U_2} of 0.6, as estimated from dynamic mechanical[1] and IR measurements[19]). As the complexity of our system does not allow us to calculate the Kirkwood–Fröhlich factor, we assume a value of 1, which means that we assume no interactions between different urazole complexes. A mean dipole moment $\mu_{U_2}^{exp}$ of 0.59 D for all degrees of modifications (within the experimental error with respect to ϵ_s, ϵ_∞, and x_{U_2}) *evidences that this assumption is reasonable. If there* existed any interactions between urazole complexes, these interactions and thus the Kirkwood–Fröhlich factor should depend on the degree of modification.

There are several approaches to calculate the dipole moment of a dimeric urazole complex theoretically ($\mu_{U_2}^{th}$). First we have to find the spatial arrangement of the urazole units within the dimeric complex, and in a second step we have to calculate the dipole moment. One possibility is to use the structure obtained by WAXS measurements[6] of urazoles which carry a carboxylic group in the para position of the phenyl ring. These measurements evidence that the polar units form an ordered supramolecular arrangement, in which the hydrogen bond complexes are coplanar with respect to the urazole rings. If one takes this arrangement as a basis of a dimeric phenylurazole complex (this was done in previous work[2]), a theoretical calculation leads to a dipole moment $\mu_{U_2}^{th}$ of zero for this complex. Another possibility is to use the optimized geometry of a dimeric urazole complex obtained by force field calculation. A dipole moment $\mu_{U_2}^{th}$ of 1.6 D results for this arrangement. The reason for the nonvanishing dipole moment lies in a twisted arrangement of the two urazole units within the dimeric complex. In this case the dipole moments of two uncomplexed urazole units (calculated as $\mu_{2U}^{th} = 2.6$ D) do not compensate each other. The experimental value $\mu_{U_2}^{exp} = 0.59$ D is in between these two theoretical estimates. This indicates a slightly twisted arrangement of the two urazoles.

From the maxima of the dielectric loss curves, the overall relaxation times $\tau_{U_2}^*$ are obtained. As was pointed out in previous work[2] (see also Figure 1), the temperature dependence of the relaxation can be described by a WLF equation. As already mentioned in part 2, this results from the fact that the overall relaxation with $\tau_{U_2}^*$ includes orientation fluctuations of intact complexes U_2 (τ_{U_2}) (eq 19) which must be coupled to the motion of adjacent chain segments.

It was already pointed out in the previous section that there exist two limiting cases, where either the dielectric relaxation is governed completely by reorientations of complexes U_2 ($\tau_{U_2} \ll \tau_{U_2}^{ch}$) or by the dissociation of U_2 ($\tau_{U_2} \gg \tau_{U_2}^{ch}$). Using the dynamic mechanical data, it is now possible to establish which of the two cases is realized. As was pointed out in the work of Leibler, Rubinstein, and Colby,[7] the dissociation of dimeric stickers should lead to a dispersion maximum in the loss modulus curve $G''(\nu)$. The relaxation time of this process was predicted to be the lifetime of complexes U_2 ($\tau_{U_2}^{ch} = 1/k_-$; see equilibrium I). In our previous work,[1] we were able to study this process in dynamic mechanical measurements. The relaxation occurring at time $\tau_{U_2}^{ch}$ was designated as the α_{DMA}^*-relaxation. As was pointed out by McCrum, Read, and Williams,[20] dielectric spectra are retardation spectra whereas the storage and loss modulus spectra in dynamic mechanical measurements correspond to relaxation spectra. The correlation between the dielectric "relaxation time" τ_{DS} (which is a retardation time) and the dynamic mechanical relaxation time (the inverse frequency of the loss modulus maximum) τ_{DMA} is given by

$$\tau_{DMA} = \frac{\epsilon_\infty}{\epsilon_s}\tau_{DS} \qquad (26)$$

As can be seen for a single temperature in Figure 4 and can be verified for all experimental temperatures, the expression $\epsilon_\infty/\epsilon_s$ is close to unity. Therefore if we assume that U_2 complexes alleviate stress and electrical polarization in an equal way, the relaxation times obtained

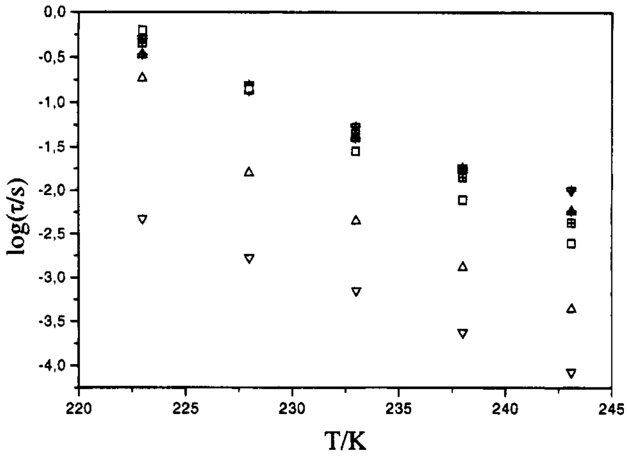

Figure 5. Temperature dependence of the relaxation time $\tau_{U_2}^{ch}$ (symbols with crosses) obtained by dynamic mechanical measurements[1] and τ_{U_2} (open symbols) obtained from eq 19 for polybutadienes with different degrees of substitution (2 mol %: ▽; 3 mol %: △; 4 mol %: □).

from the loss modulus in dynamic mechanical experiments and those obtained from dielectric loss curves can be compared directly. In Figure 1, the temperature dependence of the relaxation times $\tau_{U_2}^{ch}$ (α_{DMA}^*-relaxation) are shown in comparison to the dielectric data. Three major differences between dielectric and dynamic mechanical data are obvious. First, $\tau_{U_2}^{ch}$ (α_{DMA}^*-relaxation) seems not to depend on the degree of modification (and thus T_g) of the samples. Second, the temperature dependence of the $\tau_{U_2}^{ch}$(α_{DMA}^*-relaxation) can be described by an Arrhenius law within the frequency range covered by dynamic mechanical measurements. Third, the relaxation times $\tau_{U_2}^{ch}$ (α_{DMA}^*-relaxation) are larger than those of the corresponding dielectric process. The first two observations follow immediately from the hindered reptation theory,[7] which postulates that

$$\tau_{U_2}^{ch}(\alpha_{DMA}^*\text{-relaxation}) = 1/k_- \qquad (27)$$

k_- is the rate constant of a molecular dissociation which follows an Arrhenius law and is independent of the glass temperature T_g of the polymer matrix as long as temperatures not too close to the glass transition temperature are considered. The third observation can be explained by eq 19. It can easily be deduced from this equation that $\tau_{U_2}^*$ must be smaller than $\tau_{U_2}^{ch}$.

Now from eq 19 and $\tau_{U_2}^{ch}$(α_{DMA}^*-relaxation) the relaxation time of thermal fluctuations of dimeric complexes (τ_{U_2}) can be calculated. In Figure 5, τ_{U_2} and $\tau_{U_2}^{ch}$ are shown as a function of temperature. For the sample with 2 mol % of polar stickers the reorientation of a dimeric complex (and adjacent polybutadiene segments) is about 100 times faster than the dissociation of such a complex. For PB-28–PU-3 the reorientation is already much slower and for PB-28–PU-4, the relaxation time of reorientation and the lifetime of dimeric complexes are almost of the same magnitude. As was pointed out in the theoretical part, the reorientation of complexes couples to the segmental dynamics of the polybutadiene chains (α-relaxation). As T_g increases with the number of urazole groups, this leads to an increase of the reorientation time of the complexes.

Thus in the case of the sample with 2 mol % of polar stickers, the α*-relaxation is almost completely governed by the reorientation of dimeric association complexes, whereas in the case of the sample with 4 mol % of polar stickers, both relaxation mechanisms contribute equally to the relaxation.

As was shown for the first case the relaxation time distribution of the segmental motion of the polymer matrix (α-relaxation) determines the relaxation time distribution of the α*-relaxation. As the α-relaxation of polybutadiene can be fitted by eq 24 with $\beta = 1$,[2] symmetrically broadened peaks are expected for PB-28–PU-2. On the other hand, for the sample with 4 mol % polar units, an asymmetrically broadened relaxation time distribution should be obtained. In Figure 6, the normalized relaxation peaks of the two samples with 2 and 4 mol % of polar stickers and the corresponding fits (dotted and solid line) are shown for a fixed distance to the glass temperature $T - T_g = 95$ deg. Whereas the asymmetry parameter β is 1 for the PB-28–PU-2 sample, which corresponds to a symmetrically broadened relaxation time distribution, in the case of the PB-28–PU-4 sample an asymmetrically broadened curve with $\beta = 0.46$ is observed. In Figure 7 the parameters α and β of the Havriliak–Negami fitting function (eq 24)[18] are plotted as a function of temperature for samples with 2 and 4 mol % of polar stickers (only those relaxation peaks that were located completely in the experimental frequency range were taken for this analysis). For all these temperatures the assumptions made in the theoretical part are confirmed.

(b) Relaxation of Uncomplexed Urazoles. In the previous section, the theoretical considerations were based on the assumption that the reorientation of uncomplexed urazoles was much faster than the association process. Now, with the data of dielectric spectroscopy, it is possible to provide experimental evidence for this assumption.

So far we have not considered the segmental dynamics of the polymer backbone. If we take into account this relaxation process, eq 22 transforms into

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{N_U^{eq}\vec{\mu}_U^2}{N_U^{eq}\vec{\mu}_U^2 + N_{U_2}^{eq}\vec{\mu}_{U_2}^2 + N_{PB}\vec{\mu}_{PB}^2}\frac{1}{1 + i\omega\tau_U} + \frac{N_{U_2}^{eq}\vec{\mu}_{U_2}^2}{N_U^{eq}\vec{\mu}_U^2 + N_{U_2}^{eq}\vec{\mu}_{U_2}^2 + N_{PB}\vec{\mu}_{PB}^2}\frac{1}{1 + i\omega\tau_{U_2}^*} + \frac{N_{PB}\vec{\mu}_{PB}^2}{N_U^{eq}\vec{\mu}_U^2 + N_{U_2}^{eq}\vec{\mu}_{U_2}^2 + N_{PB}\vec{\mu}_{PB}^2}\frac{1}{1 + i\omega\tau_\alpha} \qquad (28)$$

(local β-relaxations are not considered here).

Now let us consider two limiting cases. First we assume that the reorientation of uncomplexed urazoles couples to the segmental dynamics of polybutadiene, i.e., that $\tau_U \approx \tau_\alpha$. In this case we expect only one additional relaxation process in dielectric spectroscopy besides the relaxation of dimeric urazole units. The relaxation strength of this process should depend on the number and the dipole moment of uncomplexed urazoles (N_U^{eq}, $\vec{\mu}_U$) and polybutadiene segments (N_{PB}, $\vec{\mu}_{PB}$). If no such coupling would occur, two relaxation processes, one with relaxation time τ_U and one with relaxation time τ_α, should be detected in dielectric spectroscopy. In this case the relaxation strength of the α-relaxation should not depend on the number of free stickers.

In previous dielectric measurements,[2] the α-relaxation of substituted polybutadienes was investigated in

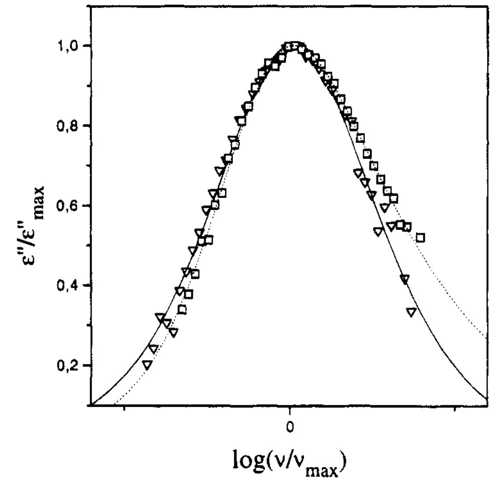

Figure 6. Normalized relaxation peaks for PB-28−PU-2 (▽) and PB-28−PU-4 (□) at a fixed interval to the glass transition temperature of the samples. The lines represent fitting curves that result from the sum of two Havriliak−Negami functions (eq 24)[18] (solid line: PB-28−PU-2; dotted line: PB-28−PU-4).

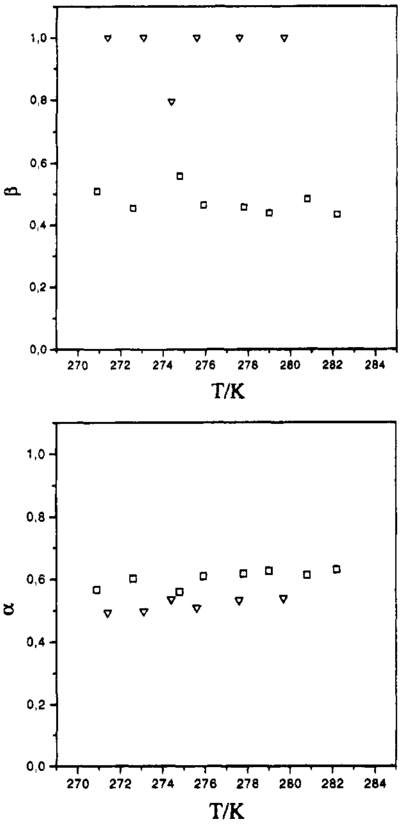

Figure 7. Parameters α and β of the Havriliak−Negami fitting function (eq 24)[18] as a function of temperature for samples with 2 (▽) and 4 (□) mol % of polar stickers.

detail (Figure 1). The relaxation strength of this process increased with temperature and degree of modification. This demonstrated the correlation between the relaxation strength and the number of free urazole units. Thus the relaxation of uncomplexed urazoles and polybutadiene segments is directly coupled (i.e., $\tau_U \approx \tau_\alpha$).

If one now considers the relaxation times of the dielectric α-relaxation (PB-28−PU-4) at 191 and 234 K (Figure 1), one finds 0.44 and 4.4×10^{-7} s, respectively. The inverse values of these relaxation times give us the time constant that describes the decay of the dipole correlation function induced by reorientations based on thermal fluctuations (eq 13).

The decay of the dipole correlation function via the association processes (eq 10) is controlled by the association rate constant.

$$k_+ = k_- \frac{x_{U_2}}{x_U^2 c_0} \qquad (29)$$

with c_0 as the concentration of urazoles.

Describing the temperature dependence of $\tau_{U_2}^{ch}$ (Figure 5) by an Arrhenius law (activation energy ΔH = 112.5 kJ/mol, frequency factor A = 26.6), average values for k_- can be deduced as $k_- = 1.32 \times 10^{-3}$ s^{-1} at 191 K and 30.90 s^{-1} at 234 K (for PB-28−PU-4). If we assume a molar fraction of closed stickers of 0.8 at 191 K and 0.7 at 234 K, we find that k_+ varies between 0.039 L/(mol·s) at 191 K and 356.1 L/(mol·s) at 234 K. Inserting values into eq 10 and comparing the result with that obtained by inserting the τ_α into eq 13 immediately lead to the conclusion that the decay of the dipole correlation function is entirely determined by thermal fluctuations of uncomplexed urazoles at both temperatures.

5. Conclusions

Based on the correlation function approach, it was possible to deduce theoretical expressions for the relaxation behavior of reversible contacts in thermoreversible networks. According to these calculations, there are two relaxation paths for the dielectric relaxation of the reversible contacts, the relaxation via thermally induced reorientations and dissociation. For phenylurazole-substituted polybutadiene in which reversible contacts are formed via dimeric hydrogen bond complexes, it was possible to decouple both relaxation paths by comparison of the dielectric and dynamic mechanical data and to calculate the relaxation time of the reorientation and dissociation of dimeric urazole complexes as a function of temperature. It could be shown that at low degree of modification (2 mol % referred to the number of monomers per chain) reorientation occurs much faster than dissociation, whereas at higher degrees of modification (4 mol % referred to the number of monomers per chain), both relaxation times are of the same magnitude. From the relaxation strength of the dielectric relaxation, the dipole moment of dimeric complexes was calculated and compared to the results of a force field calculation. Both methods indicate a slightly twisted structure of the dimeric complexes. From the lifetime of dimeric complexes, the rate constant of association of uncomplexed urazoles was calculated. A comparison with the dielectric α-relaxation revealed that the reorientation of uncomplexed urazoles occurs much faster than association.

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