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ORIGINAL CONTRIBUTION

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The molecular dynamics of thermoreversible networks as studied by broadband dielectric spectroscopy

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Abstract Polybutadienes modified by a small number of 4-phenyl-1,2,4-triazoline-3,5-dione form thermoreversible networks via hydrogen bonding between the polar stickers. The molecular dynamics of systems with different contents of polar stickers are investigated by broadband dielectric spectroscopy in the frequency regime of 10^{-1}–10^9 Hz. Unmodified polybutadiene shows two relaxation processes, the α-relaxation which is correlated to the dynamic glass transition of the polybutadiene, and a β-relaxation corresponding to a local relaxation of polybutadiene segments. In the polar functionalized systems, besides these two relaxations, an additional relaxation process (called α^*-relaxation) is observed, which occurs at lower frequencies than the α-process. While the β-relaxation remains unaffected by the functionalization the cooperativity of the α-relaxation increases by the formation of reversible junctions and slows down considerably. This indicates a decreased mobility of the polymer matrix. At the same time the dipole moment of relaxing units contributing to the α-relaxation is increased by free phenyl urazole units. The α^*-relaxation is assigned to the local complex dynamics resulting from the dissociation and formation of dimeric contacts. Hence, for this dynamic process, the absolute value of the dipole moment fluctuates with time and causes a dielectric absorption. This interpretation is in agreement with the hindered reptation model of Leibler, Rubinstein and Colby and simultaneous measurements of infrared dichroism and birefringence.

Key words Thermoreversible networks – dynamics – dielectric spectroscopy – hydrogen bonding

Introduction

Contrary to covalent networks, where crosslinks between chain molecules are realized by chemical bonds, in thermoreversible networks the polymer chains are connected by reversible contacts. In previous papers, urazoyl substituted polybutadienes have been introduced as a model system of thermoreversible networks [1–4]. In the most simple case the thermoreversible junctions are formed by binary hydrogen bond contacts between two polar stickers [(4-phenyl-3,5-dione1,2,4-triazolidin-1-yl)-units (abbreviated as 4-phenylurazole- or PU-units) attached to polybutadiene] (Fig. 1).

While in thermoreversible networks like ionomers, the reversible crosslinks are formed by ionic clusters which are not well defined in number and size, the formation of strictly binary contacts gives the possibility to handle this hydrogen bond network as a model system for the theoretical description of the dynamics in such systems (Fig. 1) [5–7].

The most advanced theoretical approach to describe the molecular dynamics in such thermoreversible networks has been developed by Leibler et al. on the basis of a hindered reptation model (LCR-model) [7]. This model correctly predicts the increase of the terminal relaxation time of the stickered chains in comparison to chains without specific enthalpic contacts. In addition, the model predicts an additional relaxation process at temperatures above the glass transition, which results from the breaking and forming of reversible contacts, i.e., the local complex dynamics. At frequencies which are higher than the characteristic frequency of the complex dynamics, the complexes act like covalent junctions, while at lower frequencies they will just retard the terminal relaxation.

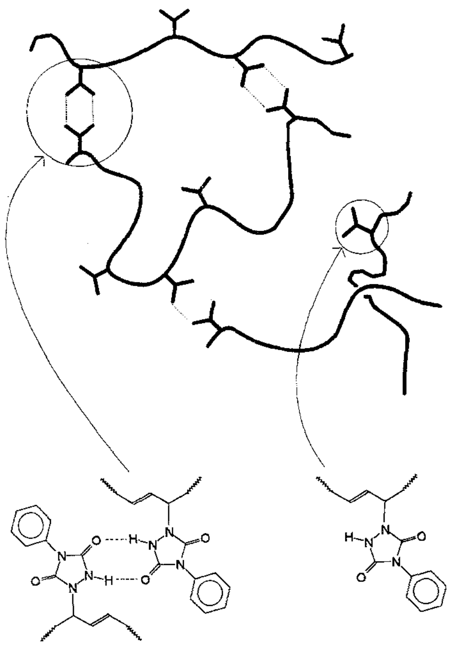
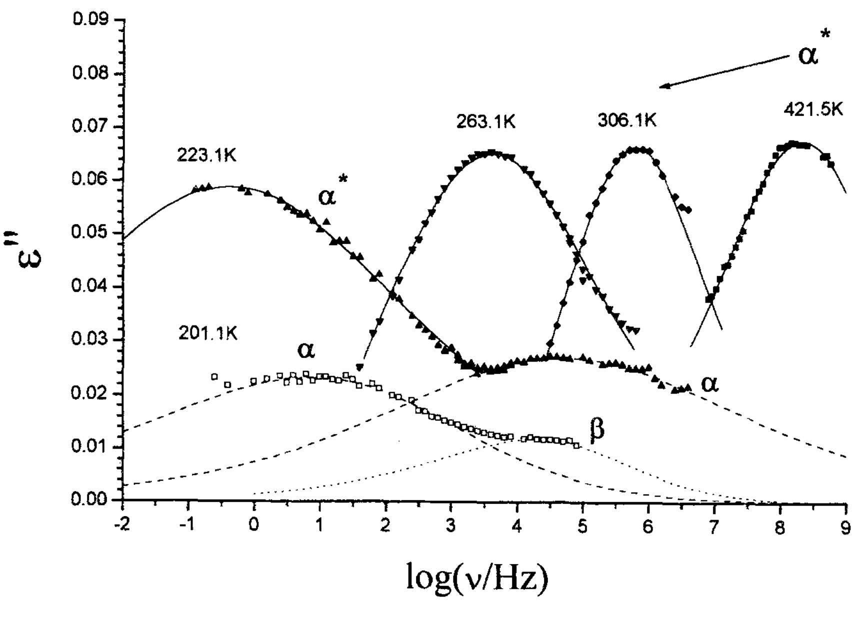


Fig. 1 Schematic representation of a thermoreversible network with binary contacts

In dynamic mechanical measurements [3, 8], the relaxation associated with the complex dynamics was detected at frequencies of about 10^4 rad/s at 273.15 K. In the original dynamic mechanical measurements by de Lucca Freitas and Stadler [3], only a small frequency range could be covered. The construction of an isothermal mastercurve was necessary to evaluate the mechanical data over a broad temperature range. This implies that the system should show thermorheologically simple behavior. The analysis of the local complex dynamics from dynamic mechanical experiments will thus bear some uncertainties.

Broadband dielectric spectroscopy [11] easily allows to cover 10 decades in frequency at an individual temperature. In the hydrogen bond networks based on phenylurazole units, large molecular dipoles are present. Dielectric spectroscopy offers the opportunity to study not only the dynamics of the polybutadiene segments but also the dynamics of binary contacts. In this context, the most interesting question is whether the predicted dynamics of binary contacts at relaxation times slower than the dynamic glass transition can be observed by dielectric spectroscopy.

Fig. 2 Dielectric loss curves for polybutadiene, modified by 4 mol% of phenylurazole. The lines are fits according to the Havriliak-Negami relaxation function (Eq. (1)), corresponding to the α^*-relaxation (solid line), the α-relaxation (dashed line) and the β-relaxation (dotted line)



Experimental section

Samples

The preparation of polybutadiene with a molecular weight $M_n = 28000$ g/mol by anionic polymerisation is described elsewhere [9]. 4-Phenyl-1,2,4-triazoline-3,5-dione was obtained by oxidation of 4-phenyl-1,2,4-triazolidine-3,5-dione using NO_2 as oxidizing agent according to the literature prescriptions [10]. The subsequent functionalization of the polybutadiene by various amounts of 4-phenyl-1,2-4-triazoline-3,5-dione was carried out via an en-reaction [1]. Table 1 summarizes the samples, prepared for the present study.

Dielectric spectroscopy

The dielectric measurements were carried out in the frequency range of 10^{-1}–10^9 Hz. To cover the entire frequency range, three different measurement devices were employed: i) a Solartron Schlumberger frequency response analyzer 1260; ii) a Hewlett Packard impedance analyzer HP4192A, and iii) a coaxial line reflectometer HP4191 A. The sample was kept between two gold-plated electrodes (diameter 20 mm) with a spacing of 50 ± 1 μm maintained by two glass fibres. Temperature adjustment with a resolution of ± 0.01 K was realized by using a temperature-controlled nitrogen gas jet and a custom made cryostat [11].

For the quantitative analysis the generalized relaxation function according to Havriliak-Negami [12] is used:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left(1 + (i\omega\tau)^\alpha\right)^\beta} \,. \tag{1}$$

In this equation, the parameters α and β ($0 \leq \alpha,\beta \leq 1$) describe the symmetric and asymmetric broadening of the relaxation time distribution, τ is the relaxation time, and $\Delta\varepsilon$ is the relaxation strength. In cases where two overlapping relaxation processes appear the experimental data are described by the superposition of two Havriliak-Negami functions. The accuracy in the determination of the fit parameters α and β is ± 0.05 and in τ and $\Delta\varepsilon \pm 10\%$. From the frequency ν_{max} at maximum loss ε_{max} of a relaxation process the relaxation time $\tau_{max} = 1/2\pi\nu_{max}$ can be deduced.

Results

Two relaxation processes are observed in the dielectric spectra of unmodified polybutadiene ($M_n = 28000$ g/mol), the α-relaxation corresponding to the dynamic glass transition, and a β-relaxation attributed to local segmental motions [13]. This β-relaxation has only a very weak relaxation strength ($\Delta\varepsilon < 0.035$). The analysis of the temperature dependence shows that the α relaxation of the neat polybutadiene can be described as a William–Landel–Ferry (WLF)-or Vogel–Fulcher–Tammann (VFT)-process, while the β-relaxation has a temperature independent activation energy (Arrhenius-type behavior) (Fig. 3).

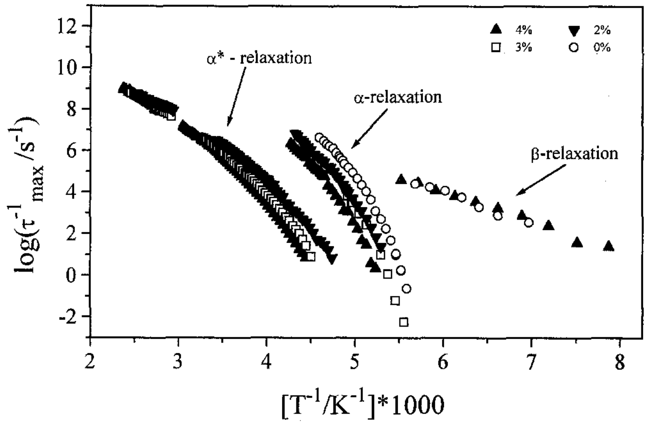


Fig. 3 Activation plot for polybutadiene, modified by 0,2,3 and 4 mol% of phenylurazole

After functionalization of the polybutadiene with phenylurazole groups, an additional relaxation occurs, the α^*- relaxation. Figure 2 shows the dielectric loss curves of polybutadiene functionalized by 4 mol % of polar units (PB-28-PU-4). At low temperatures the α-relaxation and the weak β-process at high frequencies are observed. In addition and in contrast to the unmodified polybutadiene a new relaxation process (α^*) with a considerably stronger dielectric strength $\Delta\varepsilon \approx 0.4$ occurs at frequencies below the α-relaxation (see curve at 233.1 K and higher temperatures).

In Fig. 3 the temperature dependencies of the characteristic relaxation times are plotted as a function of the reciprocal temperature for polybutadienes with various degrees of functionalization (0, 2, 3 and 4 mol%). In the following sections the different relaxation processes will be discussed in detail:

β-relaxation

The β-relaxation has only been analyzed for the unsubstituted polybutadiene PB-28-0 and the polymer containing one sticker every 25 repeating units (average substitution) (PB-28-PU-4). The experimental data can be described by an Arrhenius process with an activation energy of 27.3 kJ/mol. As can be seen in Fig. 3, the temperature dependence of the β-relaxation is not affected by the polar stickers. Neither the Havriliak–Negami parameter α nor the relaxation strength $\Delta\varepsilon$ are influenced by the functionalization of the polybutadiene.

α-relaxation

The α-relaxation of PB-0 is assigned to the dynamic glass transition of the polybutadiene. In comparison to the behavior of unsubstituted polybutadiene, the α-process of the functionalized polymers is slightly shifted to higher temperatures with increasing degree of substitution. The experimental data of the α-relaxation, shown in Fig. 3, can be described by the WLF equation

$$\log\left(\frac{\nu_{\mathrm{ref}}}{\nu_{\max}}\right) = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \tag{2}$$

Table 1 summarizes the WLF parameters C_1 and C_2 as well as the glass temperature T_g defined as the temperature where $\tau_{\mathrm{ref}} = 1/2\pi\nu_{\mathrm{ref}} \approx 10^2$ s. The results of the corresponding analysis based on the Vogel-Fulcher-Tamman (VFT) equation are also given in Table 1.

In agreement with corresponding DSC data [14] the glass transition temperature and the WLF-constant C_2 increase with the degree of modification. The increasing degree of functionalization and, consequently, the increased number of reversible contacts reduces the mobility of the system as a whole. As a consequence, the dynamics of the system freeze at higher temperatures and show a higher value of the apparent activation enthalpy.

Figure 4 shows the analysis of the relaxation strength ($\Delta\varepsilon \cdot T$) of the α-process as a function of temperature for PB-0 and PB-28-PU-4. For conventional glass forming materials [5, 16], a slight decrease of the product of relaxation strength and temperature is characteristic, reflecting the decreasing cooperativity of the observed dynamic process at higher temperatures. This is verified for the unsubstituted polybutadiene. In the case of the functionalized polybutadienes the opposite behavior is found. The effective dipole moment seems to increase with increasing temperature. The corresponding behavior is observed in the analysis of $\Delta\varepsilon \cdot T$ of the α-relaxation as a function of the degree of modification at a constant difference to the glass transition temperature (T-$T_g = 24$ K) (Fig. 5). These results can be understood by taking into consideration the effect of functionalization. The functional stickers are present either as unimers or complexed dimers (Fig. 1). The urazole dimers are centrosymmetric and should not have any resulting dipole moment. In contrast, the unimer will have any resulting dipole moment. The local motion of the uncomplexed stickers which are linked to the polymer chain is observed together with the α-relaxation. On raising the temperature the equilibrium

$$\overset{\substack{|\mu| = 0\\ \vec{\mu} = 0}}{\mathrm{U}_2} \; \underset{k_+}{\overset{k_-}{\rightleftharpoons}} \; \overset{\substack{|\mu| > 0\\ \vec{\mu}(t) > 0}}{2\mathrm{U}} \tag{3}$$

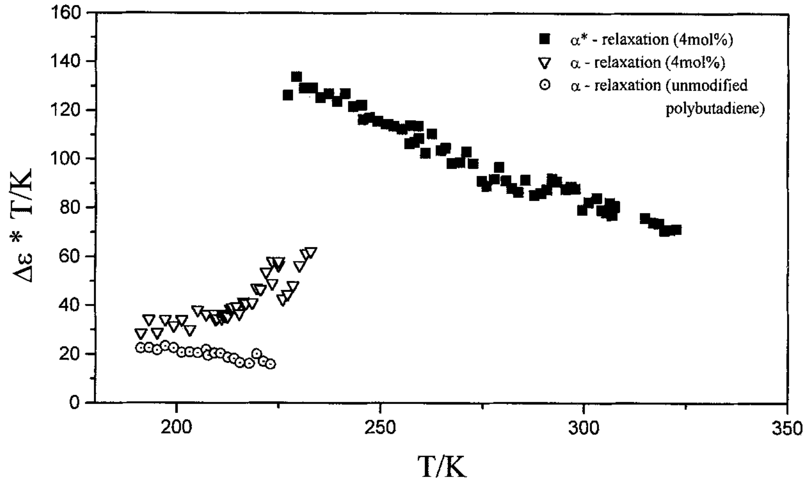
is shifted to the right (Eq. (3)), increasing the fraction of free urazole units. As a result, the effective dipole moment expressed as the product of the relaxation strength and temperature increases. The increase in $\Delta\varepsilon \cdot T$ of the α-relaxation with the degree of substitution (Fig. 5) is also a consequence of the increased number of free units. However, as the result of "Le Chatelier's principle", this increase of $\Delta\varepsilon \cdot T$ is less than proportional, because the equilibrium given in Eq. (3) is shifted to the left upon increasing the concentration of polar stickers.

Further information about the contribution of the stickers to the α-relaxation is obtained from the analysis according to the Havriliak-Negami equation (Eq. (1)). The parameter α characterizes the symmetric broadening of the relaxation time distribution. At a fixed difference to the glass transition temperature ($T - T_g = 24$ K), the relaxation time distribution shows a considerable broadening with increasing degree of modification (Fig. 6, Table 2). This behavior demonstrates an increasing cooperativity of the α-relaxation with increasing degree of functionalization and reflects the effect of the network formation which increases the cooperativity of the motion of chain segments by connecting different chains.

Table 1 WLF and VFT constants of the α-relaxation of polybutadienes of different degrees of functionalization

Sample		PB-28-0	PB-28-PU-2	PB-28-PU-3	PB-28-PU-4
Degree of modification [mol%]		0%	2%	3%	4%
WLF-constants	C_1	14.7	15.0	15.3	15.0
$2\pi\nu_{\mathrm{ref}} \approx 0.01\ \mathrm{s}^{-1}$	C_2	22.3	29.0	30.1	31.2
	T_g	174.7	177.7	178.7	182.5
VFT-constants	A	26.9	27.6	28.3	27.6
	B	753.9	1000.5	1059.1	1077.8
	T_0	152.4	148.5	148.6	151.2

Fig. 4 Temperature dependence of the product of relaxation strength and temperature for unmodified polybutadiene (α-relaxation) and a polybutadiene carrying 4 mol% of phenylurazole (α- and α*-relaxation)



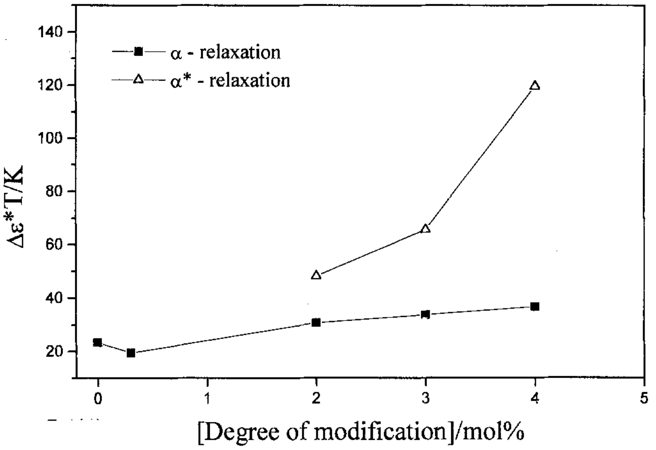


Fig. 5 Product of relaxation strength and temperature of the α-relaxation (at $T - T_g = 24$ K) and α*-relaxation (at $T - T_g = 57$ K) as a function of the degree of modification

Fig. 6 Normalized dielectric loss $\varepsilon''/\varepsilon''_{max}$ of the α-relaxation for different degrees of modification versus normalized frequency ν/ν_{max}

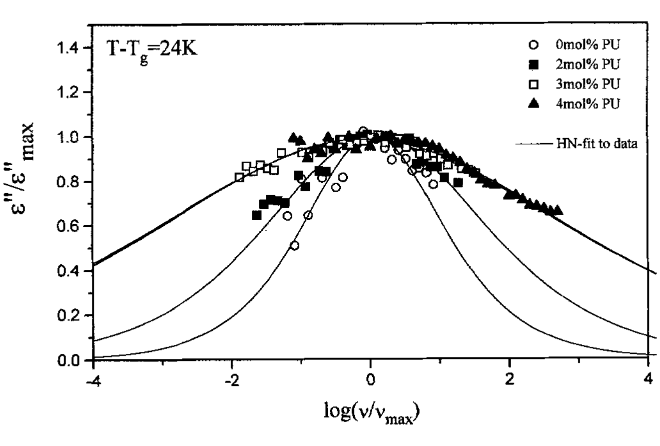


Table 2 Havriliak–Negami parameter α as a function of the degree of modification

Sample	Degree of modification [mol%]	HN-parameter α
PB-28-0	0	0.58
PB-28-PU-2	2	0.39
PB-28-PU-3	3	0.21
PB-28-PU-4	4	0.22

α*-relaxation

The α*-relaxation only appears in the dielectric spectra of functionalized polybutadienes. Whereas the analysis of the product of the relaxation strength and temperature of the α-relaxation as a function of the degree of modification (Fig. 5) and temperature (Fig. 4) shows that free urazole units contribute to the α-relaxation, an equivalent analysis of the α*-process proves that the relaxation strength of this relaxation is correlated to the number of the dimeric units:

With increasing temperature the product of relaxation strength and temperature of the α*-relaxation decreases (Fig. 4, filled squares). This indicates that the relaxation strength of the α*-relaxation is correlated to the number of dimeric association complexes, which decreases with increasing temperature. In temperature-dependent IR measurements [7], this decrease of the concentration of dimeric complexes could be analyzed quantitatively and is in qualitative agreement with the data of the dielectric measurements.

The same conclusion can be drawn from $\Delta\varepsilon \cdot T$ as a function of the degree of functionalization. This product shows a more than linear increase with increasing degree of modification (Fig. 5, open triangles). This can be explained by taking into account the enhanced probability of the formation of dimeric complexes at higher degrees of modification.

The experimental data show that the α^*-relaxation is related to a dynamical process associated with dimeric complexes. In principle, two different molecular explanations could account for the α^*-relaxation:
i) an orientation fluctuation of the complexes
ii) the dissociation dynamics of the complexes
As a result of the centrosymmetric structure, the dipole moment of the dimeric complexes is zero. Thus, the fluctuation of dimeric complexes cannot be observed by dielectric spectroscopy. The second molecular explanation of the α^*-process is based on the local complex dynamics (decomplexation ⇔complexation) as characterized by Eq. (3). From the Onsager equation, we have

$$\mu^2 = \frac{9kT}{4\pi\rho}\varepsilon_0 \frac{(\varepsilon_S - \varepsilon_\infty)(2\varepsilon_S + \varepsilon_\infty)}{\varepsilon_S(\varepsilon_\infty + 2)^2} \tag{4}$$

(where ε_S and ε_∞ are the plateau-values of the real part of the complex dielectric function at the low and high frequency side of the relaxation process, k is the Boltzmann constant and $\rho = N/V$ is the number density of the fluctuating units) and it is possible to calculate the effective dipole moment μ of the fluctuating units. Under the assumption that in the dynamic equilibrium between uncomplexed and dimeric urazoles (Eq. (3)) both the number of dimeric and free urazoles is constant at a given temperature, the number of uncomplexed urazoles (known from IR measurements) [2] represents an upper limit $N_{\max}$ for the number of dissociating dimers. With this maximum value $N_{\max}$ the calculation according to Eq. (4) leads to a minimum value of the effective dipole moment of 2.3 D. Thus, dimeric association complexes $U_2(|\vec{\mu} = 0)$ are in dynamic equilibrium with free uncomplexed stickers (with $|\vec{\mu}| > 0$). On decomplexation the absolute value of the dipole moment changes from zero to a finite value $|\mu|$. Under the assumption that cross-correlations between different polymer chains can be neglected the microscopic correlation function $\gamma(t)$ can be expressed by the (macroscopic) dielectric function

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon - \varepsilon_\infty} = L(-\dot{\gamma}(t)), \tag{5}$$

where $\gamma(t)$ is expressed in terms of the orientational autocorrelation function according to

$$\gamma(t) = \frac{\langle \vec{\mu}_i(0) \cdot \vec{\mu}_i(t) \rangle}{\langle \vec{\mu}_i(0) \cdot \vec{\mu}_i(0) \rangle}. \tag{6}$$

In this equation $\bar{\mu}_i$ describes the dipole moment of a monomer unit.

In the present situation the variation of the dipole moment with time is not a consequence of a reorientation, but rather a consequence of the time-dependent variation in the absolute value of the dipole moment $|\vec{\mu}(t)|$ as discussed in detail in the work of Schwarz [17] and Williams [18].

$$\gamma(t) = \frac{\langle |\vec{\mu}_i(0)| \cdot |\vec{\mu}_i(t)| \rangle}{\langle |\vec{\mu}_i(0)| \cdot |\vec{\mu}_i(t)| \rangle}. \tag{7}$$

By this mechanism the dissociation of the dimeric complexes results in a relaxation process (α^*) which is detectable by dielectric spectroscopy.

The relaxation time of the α^*-process is about five decades slower than the α-relaxation. Describing the experimental data by a WLF equation gives the parameters summarized in Table 3.

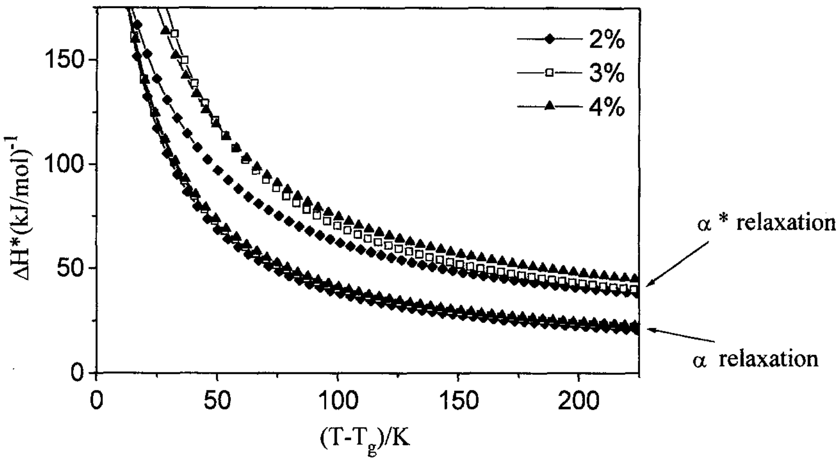
Both the reference temperature T_{ref} and C_2 are at higher values than is the case for the α-relaxation. The apparent activation enthalpy $E_A^{\alpha*}$, as obtained from the VFT constants, is considerably higher than the corresponding data of the α-process (Fig. 7).

Replotting $\log(1/\tau_{\max})$ versus the inverse temperature for fixed differences to the glass temperature of the α-relaxation of each system shows that, independent from this glass temperature, the α^*-relaxation slows down with increasing degree of modification. This is most obvious when comparing the degree of modification of 2 mol% and 3 mol% (Fig. 8).

Table 3 WLF and VFT constants of the α^*-relaxation of polybutadienes of different degrees of functionalization. T_{ref} is the temperature where the relaxation has a relaxation time of 100s

Sample		PB-28-PU-2	PB-28-PU-3	PB-28-PU-4
Degree of modification [mol%]		2%	3%	4%
WLF-constants	C_1	15.3	15.1	15.6
$2\pi\nu_{\mathrm{ref}} \approx 0.01\ \mathrm{s}^{-1}$	C_2	59.8	57.6	65.9
	T_{ref}	190.9	201.0	203.7
VFT-constants	A	28.3	27.4	29.0
	B	2104.5	2000.5	2364.4
	T_0	131,1	143,4	137.8

Fig. 7 Apparent activation enthalpy of the α- and α*-relaxation for different degrees of modification at fixed difference to the glass temperature $T_g(\alpha)$ of each system



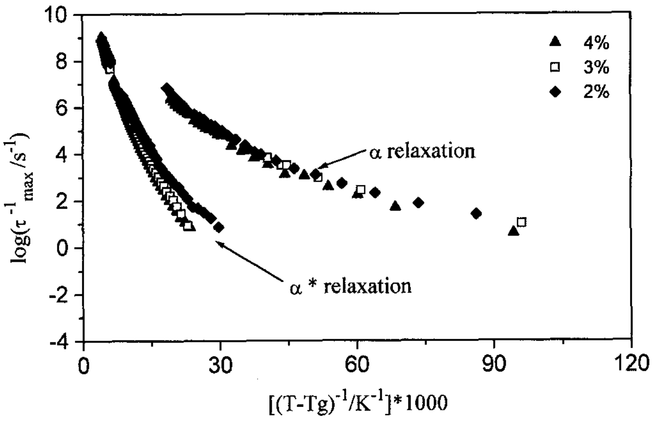
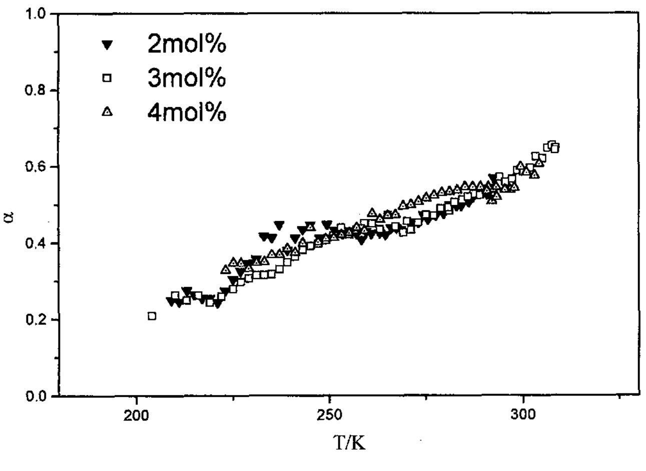


Fig. 8 Activation plot at fixed difference to the glass transition temperature $T_g(\alpha)$ of polybutadienes functionalized by different amounts of phenylurazole

Fig. 9 Havriliak-Negami parameter α of the α*-relaxation as a function of temperature for polybutadiene functionalized by an amount of 4 mol% of phenylurazole



The Havriliak–Negami parameter α only shows a small increase in the relaxation time distribution with increasing substitution. With increasing temperature the Havriliak–Negami parameter increases from values around 0.2 at 200 K to values of about 0.6 at 300 K (Fig. 9) for all degrees of functionalization (2, 3, and 4 mol%). This reflects a considerable broadening of the relaxation time distribution at temperatures near the glass temperature of polybutadiene and corresponds to a strong increase in the cooperativity of the α*-relaxation with decreasing temperature and prooves that the α*-relaxation does not obey time-temperature superposition.

Discussion

According to [13] the β-relaxation is associated with the local motion of the main chain or side groups. 1,4-Butadiene units are not expected to have any dipole moment. A possible explanation for the occurrence of a β-relaxation is the presence of 1,2-units which make up a fraction of 10% of the repeating units. The functionalization of the polybutadiene by phenylurazole has no effect on the β-relaxation.

The α-relaxation can be attributed to a cooperative main-chain motion of polybutadiene which corresponds to the dynamic glass transition. In the case of the unmodified polybutadiene the results are in agreement with literature data [13]. As a consequence of the functionalization with polar stickers, the glass temperature and the WLF-constant C_2 increase. A second consequence of the functionalization is the increased effective dipole moment by increasing the concentration of free urazole units. This can be achieved either by increasing the degree of functionalization or increasing the temperature. The formation of reversible contacts also enhances the cooperativity of the α-relaxation as reflected by a broadening of the relaxation time distribution.

The experimental data reported so far give strong evidence that the α*-relaxation monitors the local complex dynamics of the hydrogen bonded dimers. This process plays an important role in the sticky reptation model (Leibler, Rubinstein, Colby) [7]. As already mentioned, dynamic mechanical measurements also show the existence of a relaxation process which was attributed to the complex dynamics. In experiments carried out by Stadler et al. [2] on a sample with 2 mol% of polar stickers, the dynamic mechanical master curve showed this relaxation at a frequency of about 10^4 $^{rad}/s$ at 273 K. Colby et al. [8] examined a sample with 4 mol% polar units and found in the same way a relaxation maximum at $6 \cdot 10^3$ rad/s at 273.6 K. In the dielectric measurements the α*-relaxations of comparable samples appear at 1.6 10^6 Hz in case of 2 mol% and $1 \cdot 10^5$ Hz in the case of 4 mol% polar stickers at 273 K. Though the results of the two methods differ by more than one decade, the most important point of the hindered reptation model- the existence of a relaxation below the dynamic glass transition-holds for both experiments. The construction of an isothermal master curve in the case of the dynamic mechanical measurements implies thermorheologically simple behavior which does not exist according to dielectric data in the case of functionalized polybutadienes. The analysis of the dynamic mechanical data thus bear some uncertainties. Furthermore, it must be considered that both methods monitor different types of molecular dynamics. While in dielectric spectroscopy the comparably fast local dissociation dynamics of hydrogen bonded association complexes is detected, the viscoelastic response results from the diffusion of the center of mass of chain segments adjacent to the opened stickers after complex dissociation. The breaking and forming of dimeric association complexes (according to Eq. (3)), which is combined with a change in the absolute value of the dipole moment from zero in the case of the dimeric complexes to a finite value for the free units, can only lead to a signal in dielectric spectroscopy if one assumes that the microscopic correlation function can also be expressed in terms of the absolute values instead of the vectors of the dipole moments of the fluctuating units. Equation (3), which describes the local complex dynamics, can be written as two equilibria, the first describing the dissociation of the hydrogen bonds and the second related to the reorientation of the free units which are generated after dissociation.

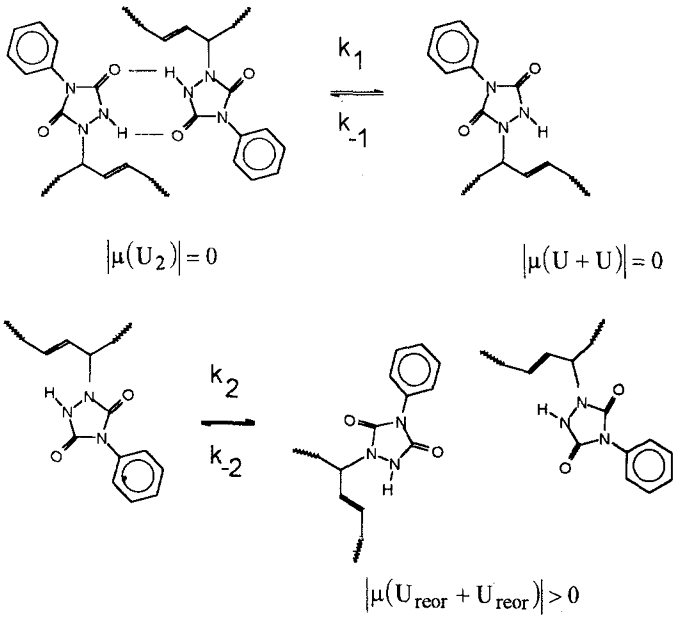


Fig. 10 Local complex dynamics formally written in two equilibriums. The first describes the mere breaking of the hydrogen bonds so the resulting units as a whole still do not possess any dipole moment. The second "reaction step" consists of the reorientation of free urazole units (connected to polybutadiene chains) which result after the breaking of the hydrogen bonds giving rise to a finite value of the dipole moment

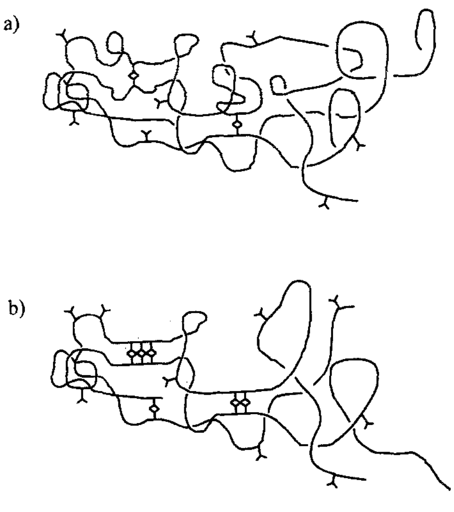


Fig. 11 Schematic representation of functionalized polybutadiene chains with low (a) and high (b) degree of modification. In the case of the high degree of modification double and triple dimers are formed with a higher stability than simple dimeric complexes

This second process corresponds to a reorientation of free urazole units connected to the polybutadiene chain. This is identical with the "α-relaxation". As the α-relaxation is much faster than the α*-relaxation the "reaction rate" of the overall complex dynamics is governed by the slow bond dissociation. The lower the temperature the closer the relaxation times of the α- and α*-relaxation (Fig. 3). The overall reaction rate is becoming more influenced by the second "reaction step": The localized dissociation of a dimeric contact is superimposed by the cooperative chain motion. This explains the WLF behavior of the α*-relaxation. The slowing down of the α*-relaxation (increasing apparent activation enthalpy) with increasing degree of modification is stronger than expected from the shift of the glass transition temperature. This may be interpreted as a higher stability of dimeric association complexes at higher degrees of modification. Such a behavior could be explained on the basis of a theoretical prediction made by Nyrkova, et al. [19]. They gave a theoretical description of the formation of dipole-dipole clusters in ionomers showing that the stability of clusters which form if the units are closely neighbored (Fig. 10b) is enhanced in comparison to isolated binary contacts (Fig. 10a). With increasing substitution the probability increases that two functional units are directly neighbored. As a consequence, double or triple clusters of dimers are formed which would have a higher stability. Recent simultaneous measurements of infrared dichroism and birefringence on bidisperse functionalized polybutadiene samples lead to the same conclusion [9].

Conclusions

Dielectric measurements on polybutadiene reveal two relaxation processes, the α-relaxation which corresponds to the dynamic glass transition, and a β-relaxation which is correlated to local segmental motions of polybutadiene segments. In polybutadienes functionalized statistically by small amounts of 4-phenyl-1,2,4-triazoline-3,5-dione a third additional relaxation process (α*-relaxation) with a considerably higher relaxation strength than the α- and β- relaxations is observed. This relaxation is assigned to the dissociation dynamics of complexed urazoles. While the relaxation strength of the α*-relaxation is correlated to the number of dimeric units the uncomplexed urazoles contribute to the α-relaxation. As a further consequence of the functionalization the cooperativity of the α-relaxation is increased and the relaxation slows down considerably with increasing amount of polar stickers. Contrary to the α- process the β-relaxation is not affected by the polar stickers. With dielectric spectroscopy thus the local complex dynamics of hydrogen bonded binary contacts in thermoreversible networks can be monitored. The results are in agreement with the LCR model [7] and are confirmed by recent simultaneous measurements of infrared dichroism and birefringence [9].

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