From a Simple Liquid to a Polymer Melt: NMR Relaxometry Study of Polybutadiene

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We utilize NMR field cycling relaxometry to study the crossover from glassy dynamics ($t \gtrsim \tau_\alpha$) through Rouse to reptation behavior in a series of monodisperse polybutadienes with molecular weights $M = 355$ to $817\,000$ g/mol. We separate characteristic polymer dynamics from the total spectrum dominated by glassy dynamics. The polymer dynamics show typical Rouse relaxation features that grow with M and saturate at high M. Comparing to Rouse theory, we determine the Rouse unit size $M_R \simeq 500$ and entanglement weight $M_e \simeq 2000$; the Rouse spectrum saturates at $M_{\max} \simeq 4000$. The local order parameter $S \approx 0.11$ is relatively large, indicating noticeable local packing already in the Rouse regime. The M dependence of the glass transition temperature T_g, obtained from dielectric relaxation spectra, shows distinctive kinks at M_R and M_e.

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Dynamics of simple monomeric liquids at temperatures about and below the melting point are determined by the glass transition phenomenon. Connecting monomers into linear polymer chains leads to further relaxation processes [1] that are slow with respect to the glass transition time scale τ_α, determined by the local segmental dynamics with $\tau_s \approx \tau_\alpha$. Depending on the molecular weight M relative to the entanglement weight M_e, the dynamics are described either by the Rouse ($M < M_e$) or reptation model ($M > M_e$). Many studies cover the crossover from Rouse to reptation dynamics, while the transition from a simple liquid to polymer melt received less attention [2–6]. In particular, the nature of $T_g(M)$ dependence is still debated. It was, e.g., argued that M_e and the Rouse unit size M_R are not relevant for $T_g(M)$ [4], or that T_g is governed by the concentration of polymer ends [7].

Nuclear magnetic resonance (NMR) field cycling (FC) relaxometry is well suited to study slow polymer dynamics by detecting the dispersion of the related spin-lattice relaxation time $T_1(\omega)$ [8]. Compared to other methods, it is unique in that it predominantly detects segmental reorientation dynamics (incoherent, local response) in a wide range up to 10^3–10^8 Hz. Routine FC studies became recently possible with the availability of a commercial spectrometer, which allowed Kimmich and co-workers to thoroughly investigate Rouse and reptation dynamics [8]. However, a relaxometric study down to the limit of simple liquid is still missing. We present such ^{1}H NMR study of 1,4-polybutadiene (PB), covering $355 \le M_w \le 817\,000$ g/mol and using polymer standards (Polymer Standards Service GmbH, $M_w/M_n \lesssim 1.05$) with noninteracting butyl and H termination to exclude polydispersity- and end-group effects. Characteristic polymer dynamics emerge on top of the glassy spectrum above certain M. Separated from the total spectrum, the polymer spectra exhibit growing Rouse dynamics, their saturation at $M \sim M_e$, and entanglement effects at higher M. From the related dielectric-spectroscopic results of PB we conclude that both M_R and M_e indeed are sensitively reflected in $T_g(M)$.

Differing from previous approaches, we separate the weak polymer dynamics $\chi_{\rm pol}(\omega)$ by carefully measuring, extrapolating, and subtracting out the much stronger glassy spectrum $\chi_{\rm gl}(\omega)$. We thus assume that, since these dynamics are statistically independent and well separated in time, their contributions are approximately additive. In terms of the normalized susceptibility $\tilde{\chi}''(\omega)$,

$$\tilde{\chi}''(\omega) = (1 - S)\tilde{\chi}''_{\rm gl}(\omega) + S\tilde{\chi}''_{\rm pol}(\omega), \tag{1}$$

where S, the relative magnitude of polymer dynamics, has the meaning of local order parameter in the case of NMR data [see Eq. (5a)]. From Eq. (1) it is obvious that a separation is necessary unless $(1 - S)\tilde{\chi}''_{\rm gl}(\omega) \ll S\tilde{\chi}''_{\rm pol}(\omega)$. Since S turns out to be small, $S \lesssim 0.1$, the condition generally does not hold. Consequently, interpreting polymer-related effects without accounting for the underlying glassy spectrum may be misleading.

In ^{1}H (proton) NMR, the spin-lattice relaxation rate $1/T_1(\omega)$ is related to the spectral density $J(\omega)$ of the monomer orientational dynamics [8]. In terms of the susceptibility $\chi''(\omega) = \omega J(\omega)$, this so-called Bloembergen, Purcell, Pound relation reads:

$$\omega/T_1(\omega) = C[\chi''(\omega) + 2\chi''(2\omega)] \equiv C\chi''_{\rm NMR}(\omega), \tag{2}$$

where C is the NMR coupling constant. Analyzing NMR susceptibility $\propto \omega/T_1(\omega)$ rather than the relaxation rate $1/T_1(\omega)$, as is usually done, facilitates comparisons with dielectric and mechanical spectra and spectral decompositions. As an example, Fig. 1(a) shows ^{1}H NMR susceptibility spectra of 4600 g/mol PB sample in the temperature range $203\ \mathrm{K} \le T \le 389$ K ($T_g = 174$ K) that we measured with STELAR FFC 2000 spectrometer [8]. At low temperatures, a relaxation maximum is observed that shifts to higher frequencies with increasing the temperature. It reflects the segmental motion of the polymer, controlled by the glass transition (α process) with a time constant τ_α. At high temperatures, one explores the $\omega\tau_\alpha \ll 1$ range of polymer dynamics. This is recognized when the PB data are compared to those of o-terphenyl (OTP), a low mo-

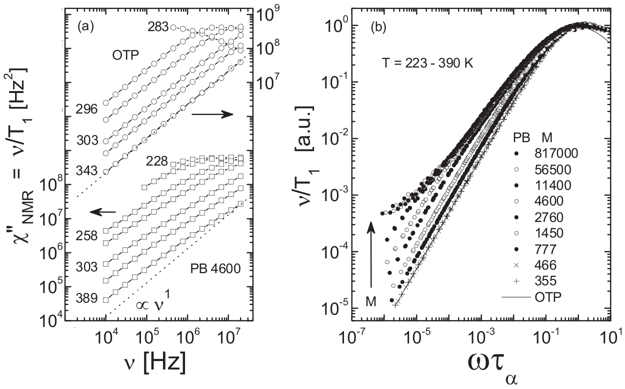

FIG. 1. (a) NMR susceptibility $\chi''_{NMR}(\nu) \propto \nu/T_1(\nu)$ [see Eq. (2)] at indicated temperatures, plotted vs frequency ν for polybutadiene (PB) with molecular weight $M = 4600$ g/mol and for o-terphenyl (OTP). Note the different behavior at low frequencies with respect to $\propto \nu^1$. (b) Master curves for the polybutadienes with different M as indicated, obtained by applying frequency temperature superposition.

lecular glass former [see Fig. 1(a)]. In the latter case, $\chi''(\nu) \propto \nu$ at $2\pi\nu\tau_\alpha \ll 1$, which is typical of a simple liquid. In contrast, the PB data show a weaker increase, i.e., monomer connectivity and tube confinement lead to retarded reorientation at $\omega\tau_\alpha \ll 1$.

The spectra in Fig. 1(a) can be approximated around the peak by a suitable function. We based our interpolations on the generalized gamma distribution of relaxation times that results in relaxation functions similar to that of Kohlrausch [9]. In each data set (each M) we pick a reference spectrum at T_{ref}, where the peak is best pronounced, and determine its $\tau_\alpha(T_{\mathrm{ref}})$. We then plot these spectra as functions of the reduced frequency $\omega\tau_\alpha$. For all other temperatures, we assume the validity of frequency temperature superposition (FTS) and shift the spectra horizontally, without altering their amplitude, until they join up with each other and with the corresponding reference spectrum at T_{ref}. This results in a master curve for each PB with a given M. Figure 1(b) shows the resulting master curves for all investigated M's, rescaled vertically so that their peaks overlap.

Applying FTS is a crucial point of our analysis. It is identical with assuming that different relaxation processes in a polymer show the same temperature dependence, i.e., they follow $\tau_\alpha(T)$ without changing their spectral shapes. Though often applied in polymer science, FTS may break down, especially close to T_g [10,11]. In the present case, polymer dynamics are investigated at temperatures well above T_g, while partial data at different temperatures overlap well on the master curves. Thus, FTS is well justified, so that shifting a spectrum onto the master curve, its relaxation time is obtained by dividing the shift factor into the known τ_α of the reference spectrum at T_{ref}. Thus, $\tau_\alpha(T, M)$ for all temperatures is obtained and can be compared with the corresponding dielectric results. As shown later in Fig. 4, the NMR and dielectric time constants agree well. We also note that the relaxation peak, which reflects the α relaxation, is similarly manifested in all polymers.

The master curves of the two lowest molecular weights $M = 355$ and 466 of PB in Fig. 1(b) agree with each other and with the OTP curve at $\omega\tau_\alpha \ll 1$, and exhibit $\chi''(\omega) \propto \omega$, as is typical of simple liquids. For the analysis of polymer dynamics, we are only interested in the frequency range $\omega\tau_\alpha < 1$, where additional intensity in excess of $\chi''(\omega) \propto \omega$ that signals the emergence of polymer dynamics is first recognized at $M = 777$, see Fig. 1(b). We thus tentatively conclude that the smallest possible Rouse chain is in the range $466 < 2M_R < 777$ (a chain has to contain at least two units, thus the factor 2). For $M < 2M_R$, the spectra only reflect glassy dynamics, which at $\omega\tau_\alpha \ll 1$ are identical with those of OTP. For $M > 2M_R$, the excess intensity progressively grows with M, until at $M \geq 56\,500$ the spectra become independent of M, indicating that the entanglement is fully established. (We note that the data leading to these master spectra are similar to those reported in Ref. [8].)

Next, we separate $\chi''_{\mathrm{NMR}}(\omega)$ according to Eq. (1) into polymer and glassy contributions,

$$\chi''_{\mathrm{NMR}}(\omega\tau_\alpha) = \chi''_{\mathrm{pol}}(\omega\tau_\alpha) + \chi''_{\mathrm{gl}}(\omega\tau_\alpha). \tag{3}$$

In Fig. 2(a), we show the "polymer spectra" $\chi''_{\mathrm{pol}}(\omega)$ after subtracting from the total the "glass spectrum" $\chi''_{\mathrm{gl}}(\omega)$, given by the data of $M = 466$. For $M \leq 4600$, the spectra exhibit a maximum, increasing in height with M. At $M > 4600$, the amplitude of the spectra saturates, though there remain small differences at the lowest reduced frequencies. The corresponding intensities are by a factor of 10–100 smaller than the total intensities in Fig. 1(b).

Qualitatively, we interpret the spectra in Fig. 2(a) as fingerprints of emerging Rouse dynamics with growing chain length, which saturate at high M due to entanglement effects. For $777 \leq M \leq 11\,400$, a crossover to a $\chi''(\omega) \propto \omega$ behavior is recognized at the lowest reduced frequencies. This indicates that the Rouse τ_R and terminal τ_t times are reached. For a quantitative analysis we calculated the Rouse susceptibility for a series of Rouse chain lengths $N = M/M_R$. The NMR susceptibility is approximately given by [12,13]

$$\chi''_R(\omega) = \omega J_R(\omega) \propto \omega \int_0^\infty F_R^2(t)\cos(\omega t)dt, \tag{4}$$

where $F_R(t) = \langle \boldsymbol{b}(0) \cdot \boldsymbol{b}(t) \rangle$ is the autocorrelation function of the Rouse segment vector $\boldsymbol{b}$, which is related to the p's Rouse mode correlation function $C_p(t)$ via $F_R(t) \propto \sum_{p=1}^{N-1} p^2 C_p(t)$ [8]. The result is shown in Fig. 2(b). The similarity between the experimental and theoretical polymer spectra is striking. Dashed line in Fig. 2(b) shows the limiting behavior $\propto \omega \ln\omega$, which is usually compared with experimental NMR relaxation data in the Rouse regime [8]. We find, however, that the limiting behavior is only reached in the model at $N \gg 100$, i.e., for long nonentangled chains that cannot exist in an equilibrium polymer melt. The limiting behavior is therefore hardly reached experimentally.

Since our NMR data reveal complete Rouse spectra, we further test the integral $I_{\mathrm{pol}} = I_{\mathrm{pol}}(N)$ over the Rouse spectrum and the spectral density at the lowest frequencies $J_R^0(N) = J_R(0) \approx J_R(\omega\tau_\alpha \ll 1)$ as a function of $N \propto M$ against the model predictions. One expects [8,12,13] that

$$I_{\mathrm{pol}} \propto S \propto (1 - 1/N)^2, \tag{5a}$$

$$J_R^0(N) \propto \ln N, \quad N \gg 1, \tag{5b}$$

where S is the local order parameter that measures the amount of segmental orientational correlation with respect to the local chain direction, which is left unrelaxed by the α process. Figure 3 presents the order parameter $S = S(M) = I_{\mathrm{pol}}(M)/[I_{\mathrm{pol}}(M) + I_{\mathrm{gl}}]$, which in good approximation is proportional to $I_{\mathrm{pol}}(M)$. At low M, the integral $I_{\mathrm{pol}}(M)$ grows as predicted, but it saturates around $M_{\max} \simeq 4000$. Here the entanglement is fully established, in the sense that the number of Rouse modes does not grow any more. Dashed line is the theoretical result of Eq. (5a), assuming $M_R = 500$ and adjusting the amplitude to match the data points below $M_{\max}$. We find that $N_{\max} = M_{\max}/M_R \simeq 8$. Regarding the parameter S, its value rises from zero to about 0.11. We emphasize that S is much higher than a value of 0.001–0.01, usually expected on general grounds [8]. It appears that S is essentially given by the Rouse dynamics. At $M > 4000$, a weak increase of χ''_{pol} with M is still apparent, though the effect is too small to be reflected in $S(M)$.

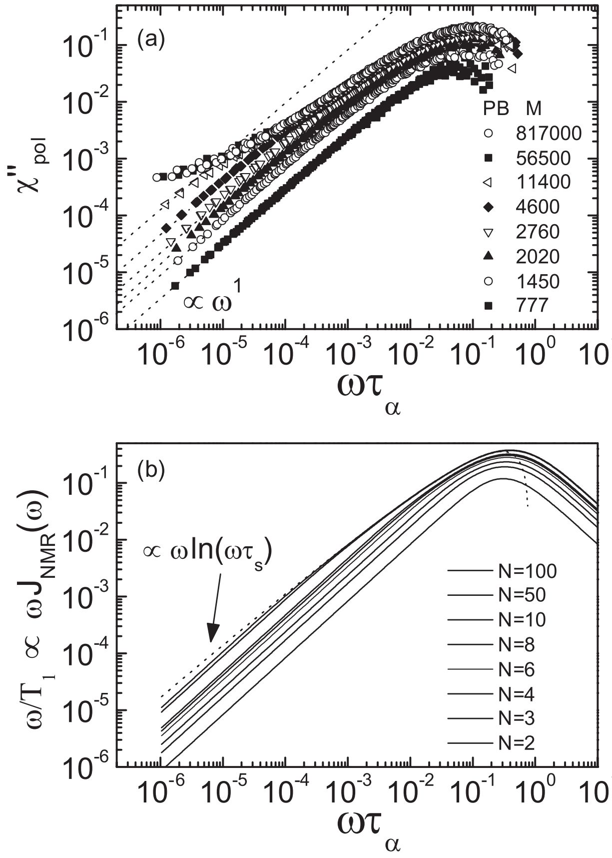

FIG. 2. (a) Spectra attributed to polymer dynamics as obtained from the data in Fig. 1(b) after subtracting the glass dynamics spectra. At the lowest frequencies, a linear behavior $\propto \omega^1$ is observed. (b) NMR susceptibility $\chi''_{\mathrm{NMR}} = \omega[J_R(\omega) + 4J_R(2\omega)]/3$ calculated from Rouse theory for several numbers of Rouse units N as indicated. The low-frequency interpolation for the high molecular weight limit is shown (dotted line).

For an estimate of $J_R^0(N)$ at $\omega = 0$, we take the experimental $J_{\mathrm{NMR}}(\omega\tau_\alpha)$ at the lowest reduced frequency, see inset in Fig. 3. Crosses and the dashed line through them are obtained from the theoretical spectra of Fig. 2(b), assuming again $M_R = 500$ and adjusting the amplitude to match the experimental data at $M \lesssim 2000$. The theoretical curve shows a behavior $\propto \ln M$ [see Eq. (5b)] at $M > 2000$, while the experimental values exhibit a much stronger increase. We take this as an indication that at low reduced frequencies the Rouse spectra are truncated by entanglement effects leading to a further retardation of the relaxation, and that this happens already at a somewhat lower $M_e \simeq 2000$ than $M_{\max}$.

Figure 4 shows the time constants $\tau_\alpha(T)$ obtained from the shift factors when building the master curves in Fig. 1(b), as explained above, together with dielectric results obtained at lower temperatures. Dielectric and NMR relaxation times agree well, though do not match exactly. Taken together, the data sets cover about 12 decades in $\tau_\alpha(T)$. With increasing M, the curves shift to higher temperatures and saturate at $M > 2000$. Defining T_g as the temperature at which the dielectric relaxation time $\tau_\alpha = 100$ s, we plot the function $T_g(M)$ in the inset of Fig. 4.

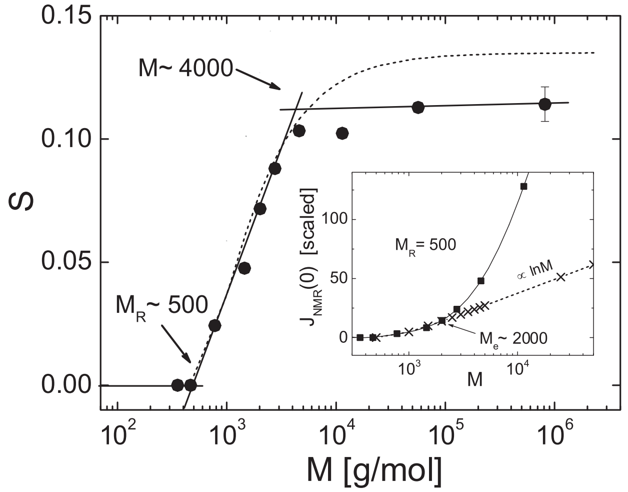

FIG. 3. Order parameter $S(M)$ as function of molecular weight M; dashed line: Rouse theory. Inset: $J_R^0(N)$ as function of M; crosses and dashed line: Rouse theory.

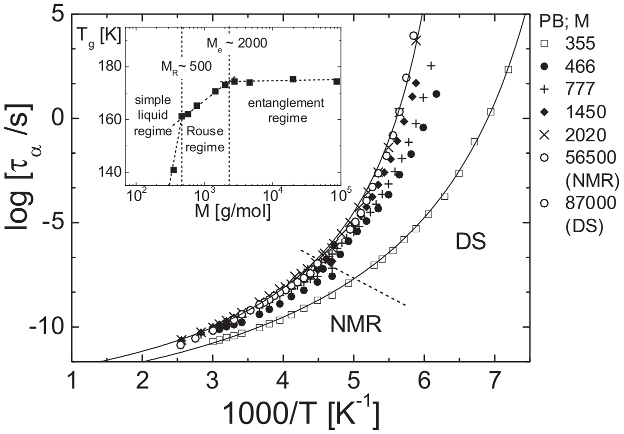

FIG. 4. Time constant τ_α of the glass transition as function of the reciprocal temperature for the polybutadiene samples investigated by NMR relaxometry and dielectric spectroscopy (DS). Full lines: Vogel-Fulcher-Tammann fits. Dashed line separates NMR and DS data sets. Inset: molecular weight dependence of the glass transition temperature as obtained through the condition $\tau_\alpha(T_g) = 100$ s from the DS data.

Clearly, three regimes, separated by M_R and M_e, are identified in the figure. A strong M dependence at $M < M_R$, typical of low molecular weight glass forming liquids, becomes weaker in the Rouse regime at higher $M > M_R$, and eventually saturates once the entanglement sets in at $M \simeq M_e$. We emphasize that this result originates solely from the analysis of the dielectric time constants, as the NMR time constants are only accessible if they are shorter than roughly 10^{-6} s.

Concluding, we have demonstrated that NMR FC relaxometry provides a detailed picture of Rouse dynamics developing with growing chain lengths, until truncated by entanglements. Our approach of subtracting out the glassy spectra differs from what has been reported so far, so that we are able to extract more detailed information of the polymer dynamics.

Our results of PB agree well with those obtained by other methods [14–16], including other NMR techniques [3], where the Rouse model was found to work well for $M < M_e \simeq 2000$ and the critical molecular weight $M_c \simeq 5000$ was reported from the M dependence of viscosity. We find the Rouse unit weight $M_R \simeq 500$, which is somewhat larger than the value of 240 reported in Ref. [3]. Comparing with the Kuhn segment size $M_K \simeq 115$ [17], we conclude that the Rouse unit contains several Kuhn segments, as it should, since the Rouse unit is in a sense the smallest Gaussian subchain, while the Kuhn segment the largest "rigid" one, so that the former has to contain several of the latter.

Approximately, a factor 2 appears between $M_{\max}$ and M_e, which is similar to the ratio of M_c and M_e [1]. Thus, we tentatively identify $M_{\max}$ with M_c. Though the Rouse model appears well applicable, we find two quantitative disagreements. (i) At the lowest N, the Rouse spectrum is supposed to be Debye-like, while we observe, consistent with other studies, a much broader spectrum. (ii) The segmental time τ_s is usually identified with τ_α, while we find $\tau_s \simeq 4\tau_\alpha$; cf. Figs. 1(b) and 2(a).

A recent NMR study [18] reported an unexpectedly high order parameter $S = 0.13$, indicating high residual orientational order of the chain, and attributed it to constraints introduced by entanglement. From our study, we find that S reaches a comparable value $S = 0.11$ already in the Rouse regime, without any significant increase at higher M. Thus, high local packing is already achieved for short chains. Finally, the different regimes of polymer dynamics, defined by M_R and M_e, are directly reflected in the $T_g(M)$ dependence. To our knowledge, such relationship was not reported before; usually, a smooth $T_g(M)$ is assumed. Clearly, this finding merits further investigation.

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