ACS Macro Letters
Letter
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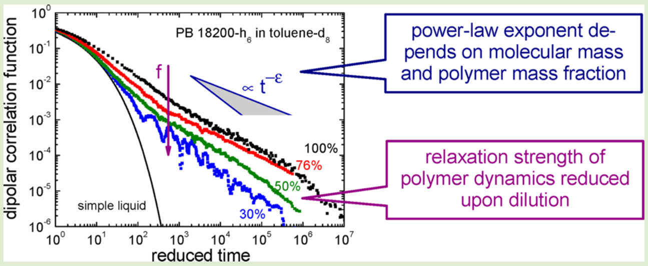
Dynamics of Linear Polybutadienes in Solution Studied by Field Cycling ^{1}H NMR

Axel Herrmann and Ernst A. Rössler*

Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany

ABSTRACT: Field cycling ^{1}H NMR relaxometry is utilized to investigate dynamics in solutions of monodisperse polybutadienes of different molecular mass (M) and deuterated toluene. Broad temperature and polymer mass fraction ranges (c = 5−100%) are studied. By applying frequency−temperature superposition, susceptibility master curves $\chi''_{\mathrm{DD}}(\omega\tau_s)$ are constructed. They cover the segmental relaxation and polymer chain dynamics, and provide the concentration dependence of the segmental time constant $\tau_s(T)$. The relaxation strength of polymer dynamics is reduced similarly for all M with decreasing c; for the lowest c, almost no polymer dynamics shows up, that is, the dipolar correlation function obtained via Fourier transform decays almost completely due to segmental dynamics. The dipolar correlation function is decomposed into contributions of segmental and polymer dynamics. Its long-time power-law exponent associated with entanglement dynamics is increased from its bulk value with reduced c. This is interpreted as a continuous increase of the effective entanglement molecular mass.



The dynamics of polymer melts is most often described by the tube-reptation model,[1] which yields predictions for the subdiffusive behavior of a chain segment. For polymers in concentrated and semidilute solution, modifications with respect to the bulk behavior have been reported, for example, by rheology[2−4] or analyses of the dielectric normal mode spectrum.[5] Expected are, for example, a concentration dependence of the monomeric friction coefficient ζ_0 and of friction-insensitive properties, for example, the plateau modulus G_N^0, a shift of the terminal relaxation time τ_d toward shorter times and an increase in the entanglement spacing M_e. Pioneering works of field cycling (FC) NMR relaxometry by Kimmich and coworkers have qualitatively disclosed a transition from entanglement dynamics for a high M melt to Rouse-like behavior for high dilution.[6,7]

FC NMR relaxometry has been established as a powerful technique to probe the microscopic dynamics of polymers.[7,8] By electronically controlling the magnetic relaxation field B, the dispersion of the spin−lattice relaxation time T_1 is measured over 3−5 decades in frequency, which is given by the Larmor frequency $\omega = \gamma B$ (γ: gyromagnetic ratio). A very helpful concept in analyzing the NMR relaxation dispersion is the construction of master curves in the susceptibility representation:[8] first, the measured relaxation rate $R_1(\omega) = 1/T_1(\omega)$ is transformed to the susceptibility representation $\chi''_{\mathrm{DD}}(\omega) = \omega/T_1(\omega)$, which at low temperatures allows to extract the time constant τ_s of segmental motion. Second, by applying frequency−temperature superposition (FTS), the susceptibility is shifted solely in frequency to finally provide a master curve as a function of the reduced frequency $\omega\tau_s$. Thereby, the frequency window of the technique is significantly extended. FTS is well-known from, for example, rheology and reflects a fundamental feature of cooperative dynamics in condensed matter.[8] The master curves $\chi''_{\mathrm{DD}}(\omega\tau_s)$ ("NMR susceptibility" in the following) exhibit a peak at $\omega\tau_s \approx 1$, which is identified with the segmental or local dynamics governed by the α-process of the glass transition. For polymers at $\omega\tau_s < 1$, an excess intensity with respect to the spectrum of a simple liquid is observed, which is due to the slower, M-dependent polymer dynamics. Its integral is a measure for the polymer relaxation strength f, that is, the residual correlation that relaxes at $t > \tau_s$ due to Rouse and entanglement dynamics.[8] It is dominated by the Rouse contribution and is an analog to G_N^0 obtained by rheology; the latter, however, is determined solely by the terminal relaxation caused by entanglement dynamics.

Our previous studies[8−11] have focused on understanding the NMR relaxation of simple liquids, nonentangled and entangled polymer melts, that is, the emergence of polymer dynamics with M. The dipolar correlation functions $C_{\mathrm{DD}}(t/\tau_s)$ have been extracted by Fourier transform of the NMR susceptibility, cover 10 decades in time, and exhibit different power-law regimes, which have been compared to the predictions of the tube-reptation model.

The aim of this Letter is to investigate how the addition of a low-M diluent to a linear polymer melt (polybutadiene with $M > M_e$) is probed by ^{1}H FC NMR. As a reference for the behavior of bulk melts the previous results[10] are used. A comprehensive picture is rendered by employing the above approach for the first time to polymers in solution, because the susceptibility master curves $\chi''_{\mathrm{DD}}(\omega\tau_s)$ reflect the spectral

Received: October 9, 2012
Accepted: October 26, 2012
Published: November 1, 2012

changes upon dilution in a similar way as those of rheology. A large temperature range is studied and FTS is applied in order to include both the (fast) segmental and the (slow) chain dynamics in the master curves.

The monodisperse 1,4-polybutadienes (PB, PDI $\leq$ 1.04) were purchased from PSS, Mainz, Germany, and $M = M_w$ in g/mol denotes their mass average molecular mass. Solutions of PB-h_6 and deuterated toluene (Sigma-Aldrich, degree of deuteration above 99.96%, used without further purification) were prepared by degassing both components, dissolving different mass ratios, and flame sealing the glass tube with the frozen compound under vacuum. The given concentration c is the mass fraction of the polymer, which is very similar to the volume fraction, because the mass densities are rather equal. The volume fraction associated with the critical concentration at the overlap limit can be estimated by $c^* < N_m^{-4/5}$, where N_m is the number of monomers per chain.[13] For the PB samples, this yields values $c^* < 0.02$ (for $M = 9470$), thus, the regimes of concentrated and semidilute solutions are covered. The samples were measured with a commercial Stelar FC spectrometer in the frequency range $\nu = \omega/(2\pi) = 10$ kHz to 20 MHz and T_1 was determined by an exponential fit of the magnetization curve. Note that by applying ^{1}H FC NMR only the dynamics of the protonated PB is probed.

In Figure 1a–c, the master curves $\chi''_{DD}(\omega\tau_s)$ in the susceptibility representation are compiled by applying FTS for PB with $M = 9470$, 18200, and 47000, respectively, and different polymer mass fractions c. A temperature range of $T = 168$–393 K has been covered depending on c in order to create the master curves. The relaxation regimes of glassy (0), free Rouse (I), and constrained Rouse (II) dynamics are indicated as obtained for the undiluted melts (black curves).[10] Regime 0, in fact, contains an interplay of segmental (glassy) and Rouse dynamics. Note that the master curves are an isofrictional representation, as changes in the time scale due to a concentration-dependent friction coefficient are scaled out by plotting the data as a function of the reduced frequency $\omega\tau_s$. This allows of monitoring the concentration dependence of the spectral shape of $\chi''_{DD}(\omega\tau_s)$: The segmental dynamics is represented by the α-peak at $\omega\tau_s \approx 1$. At $\omega\tau_s < 1$ the excess intensity reflecting the polymer relaxation contribution with respect to the simple liquid (PB 466) is diminished for all M with decreasing concentration c. For the lowest concentration of PB 9470, the susceptibility almost approaches that of the simple liquid, that is, the polymer character as probed by ^{1}H relaxation gets lost as the dipolar correlations are relaxed almost completely by the segmental dynamics.

Upon addition of a deuterated diluent it is expected on the one hand that the polymer dynamics is modified; on the other hand for ^{1}H NMR the dipolar coupling of the protons which comprises intramolecular and intermolecular contributions is reduced due to the latter. Isotope dilution experiments by ^{1}H FC NMR, that is, blending protonated and deuterated polymers with similar M, allow attaining both relaxation contributions. Thereby, it has been demonstrated[11,12] that, while the intermolecular part dominates at low reduced frequencies ($\omega\tau_s \ll 1$), also in the frequency range of the α-peak ($\omega\tau_s \approx 1$) the amplitude is reduced. However, this is surprisingly not observed in the present case (cf. Figure 1).

The segmental time constants $\tau_s(T)$ are displayed in Figure 2 for the dilution series of PB 9470 with different c as yielded from the construction of the susceptibility master curves. The curves can be interpolated with a Vogel–Fulcher–Tammann (VFT) function[8] and are shifted toward lower temperatures with decreasing c. This indicates the well-known plasticizer effect, that is, the segmental dynamics of the polymer gets faster by addition of the solvent. The glass transition temperature is usually defined as $T_g = T(\tau_s = 100\text{ s})$. Because FC NMR detects

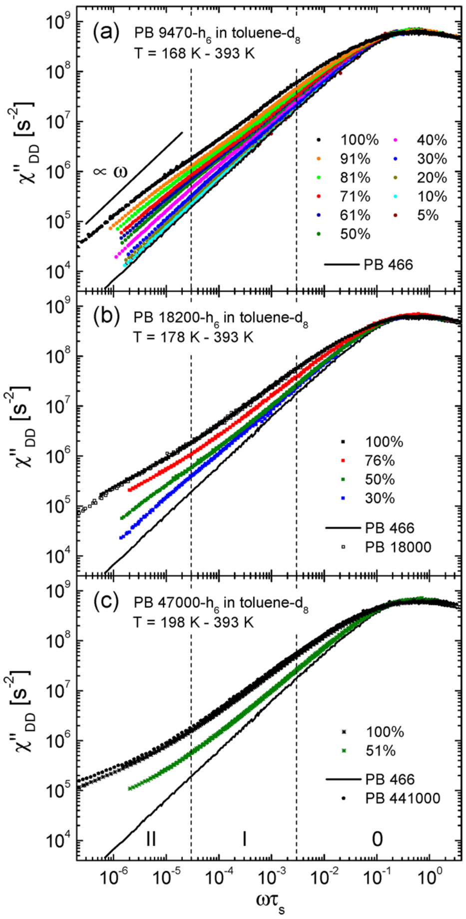


Figure 1. Susceptibility master curves $\chi''_{DD}(\omega\tau_s)$ of PB-h_6 with $M = 9470$ (a), 18200 (b), and 47000 (c) diluted in toluene-d_8 for the polymer mass fractions and in the temperature range as indicated. PB 466 and PB 441000: reference for the simple liquid and undiluted high-M limit, respectively.[10] Dashed lines: regimes of glassy (0), free Rouse (I), and constrained Rouse (II) dynamics. The undiluted PB samples have been measured also toward lower frequencies,[10] where the susceptibility of PB 18000 perfectly extends that of PB 18200.

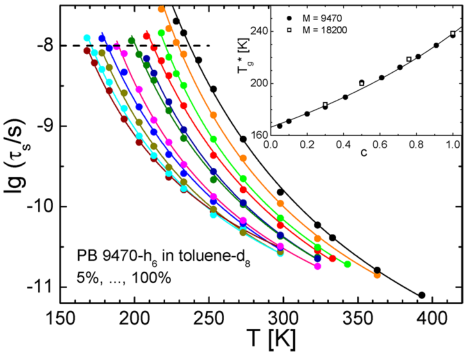


Figure 2. Time constants $\tau_s(T)$ of segmental motion for PB 9470 with different concentrations. Lines: VFT interpolations. Inset: glass transition temperature T_g* as a function of concentration; line: fit with Fox eq ($1/T_g^* = c/T_{g,\text{polymer}} + (1 - c)/T_{g,\text{solvent}}$).

dynamics on much faster time scales, we define $T_g* = T(\lg(\tau_s/s = -8))$. The corresponding dependence $T_g*(c)$ is shown in the inset of Figure 2 for PB with M = 9470 and 18200. A continuous decrease of about 70 K with reduced c is observed that follows the Fox equation.[2]

In Figure 3a the relaxation strength f of polymer dynamics is plotted as a function of c. It is given by the difference between the integrated susceptibilities of the polymer and the simple liquid (e.g., PB 466). With decreasing concentration, f is reduced similarly for all M. This demonstrates that for lower c less correlation survives beyond glassy dynamics, that is, on time scales $t > \tau_s$. Obviously due to the enhanced segmental mobility at lower c, the α-process is more efficient at the expense of the relaxation contribution of polymer dynamics. As noted, in FC NMR f is dominated by Rouse dynamics (regime I, cf. Figure 1). The plateau modulus $G_N{}^0$ of rheology is expected[3,4] to be decreased upon dilution along $G_N{}^0(c) = G_N{}^0(c = 1)c^{2.3}$, which is included in Figure 3a (dashed line). A similar trend is observed at high c for f and $G_N{}^0$. However, the latter is determined solely by the integral of the terminal relaxation spectrum associated with entanglement dynamics.

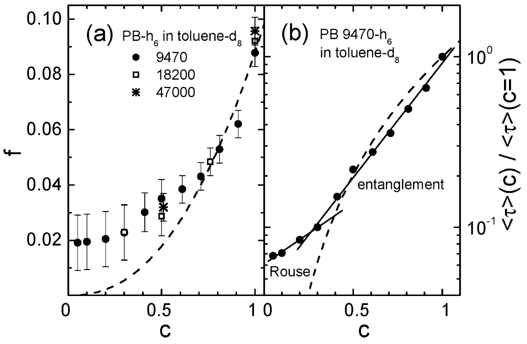


Figure 3. (a) Relaxation strength f of polymer dynamics as a function of polymer mass fraction c for PB with different M. Dashed line: expectation for $G_N{}^0(c)$. (b) Ratio $\langle\tau\rangle(c)/\langle\tau\rangle(c = 1)$ of PB 9470 obtained from the susceptibility at lowest frequencies. Dashed line: expectation for $\tau_d(c)$ from rheology.

For PB 9470 the NMR susceptibility $\chi''_{DD}(\omega\tau_s)$ exhibits a behavior close to $\propto \omega$ at lowest reduced frequencies (Figure 1a), that is, the slowest or terminal relaxation process is detected. This is equivalent to an essentially constant dipolar spectral density $J_{DD}(\omega)$, as $\chi''_{DD}(\omega) = \omega J_{DD}(\omega)$ holds.[8] Therefore, at lowest frequencies, the mean correlation time $\langle\tau\rangle$ of polymer dynamics is provided, that is, $\langle\tau\rangle = J_{DD}(0) \propto \chi''_{DD}(\omega\tau_s = 2 \times 10^{-6})$. The mean correlation time comprises a weighted sum of the individual correlation times of the different Rouse and entanglement modes and, for $M > M_e$, its slowest contribution is given by the terminal relaxation time τ_d. In Figure 3b the ratio $\langle\tau\rangle(c)/\langle\tau\rangle(c = 1)$ is depicted. It decreases with lower c, as expected[4] by rheology for the terminal relaxation time $\tau_d(c) \propto c^{2.3}$ (dashed line). A crossover (solid lines) to a weaker c-dependence can be anticipated below c = 40%, which we interpret as a transition from Rouse and entanglement dynamics to solely Rouse-like relaxation (see also below).

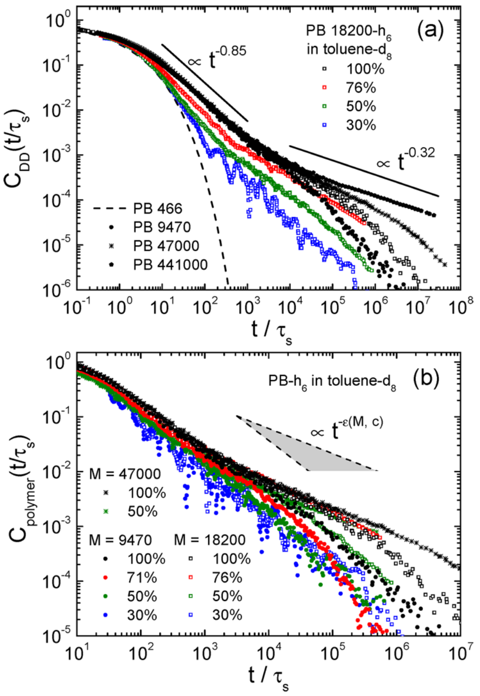


Figure 4. (a) Dipolar correlation functions $C_{DD}(t/\tau_s)$ of PB 18200 with different c and undiluted PB with different M, as indicated. Lines: power laws observed for the free Rouse (I) and constrained Rouse (II) regime of the tube-reptation model for high M = 441000.[10] (b) Correlation function $C_{polymer}(t/\tau_s)$ of the polymer relaxation contribution of PB with M = 9470, 18200, and 47000 at some c. $\varepsilon(M,c)$ denotes the power-law exponent of regime II.

The dipolar correlation function $C_{DD}(t/\tau_s)$ obtained by Fourier transform of the susceptibility master curves (Figure 1) is presented in Figure 4a for PB 18200 with different c. As a reference for the bulk melt behavior, which is discussed first, $C_{DD}(t/\tau_s)$ of undiluted PB with different M (black symbols) including PB 466[10] as the low-M system and PB 441000[10] for $M \gg M_e$ = 2000 is presented. Analogously to the susceptibility representation, $C_{DD}(t/\tau_s)$ reflects segmental, free Rouse, and entanglement dynamics.[10] The latter two can be described by power-laws $\propto t^{-\varepsilon}$, which exhibit the exponents ε = 0.85 and ε = 0.32 ($M \gg M_e$) for the regimes I and II, respectively. In regime II, ε depends on M, and only for very high M the prediction ε = 0.25 of the tube-reptation model is almost approached, which indicates a highly protracted transition to reptation dynamics.[10] For the decay of $C_{DD}(t/\tau_s)$ of PB 18200 with different c, a similar effect is observed: the exponents ε depend on c. Its origin cannot be unambiguously clarified due to the interplay of segmental and polymer relaxation contributions which is difficult to interpret.

To eliminate the influence of the segmental dynamics, Figure 4b shows the correlation functions $C_{polymer}(t/\tau_s)$, which contain only the polymer relaxation contribution of PB with different M and comparable c. Statistical independence between segmental and polymer dynamics, that is, a multiplicative approach $C_{DD}(t) = C_{segmental}(t)\cdot C_{polymer}(t)$, is assumed and the polymer relaxation strength f (cf. Figure 3a) is introduced. Finally, $C_{polymer}(t/\tau_s)$ is obtained by dividing each $C_{DD}(t/\tau_s)$ by the contribution $C_{segmental}(t/\tau_s)$ of the segmental dynamics, as given by PB 466, explicity: $C_{polymer}(t/\tau_s) = C_{DD}(t/\tau_s)/[(1 - f)\phi_{segmental}(t/\tau_s) + f]$, where $\phi_{segmental}(t/\tau_s)$ denotes the normalized segmental correlation function. While ε remains essentially unchanged in the Rouse regime (I), effects on dilution are observed for the entanglement dynamics at long times; in regime II, ε is increasing with lower c for M = 9470 and 18200. The values $\varepsilon(c)$ obtained by a power-law fit are displayed in Figure 5 together with $\varepsilon(c = 1)$ of the undiluted PB melts with different

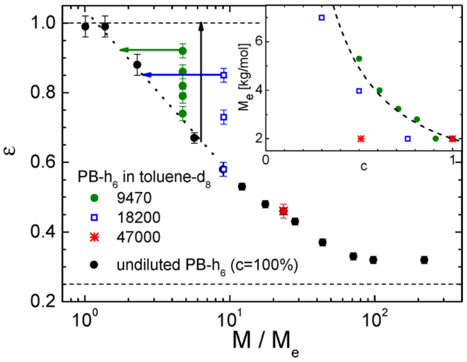


Figure 5. Exponent ε as a function of reduced molecular mass M/M_e (black symbols) and polymer mass fraction c (colored symbols). The black arrow indicates lower c. Dashed lines: predictions for the free Rouse and constrained Rouse regime of the tube-reptation model. Data of undiluted PB from ref 10. Inset: Dependence of the entanglement molecular mass M_e on c. Dashed line: $M_e(c) = M_e(c = 1)\ c^{-1.3}$.

M.[10] While decreasing c, the exponent is increased with respect to its bulk value (black symbols). We interpret this as an effect due to a changed entanglement molecular mass M_e upon dilution. As a result, the exponent is increased toward $\varepsilon = 1$ of the free Rouse regime. The entanglement molecular mass M_e as a function of c is estimated by mapping (cf. green and blue arrows in Figure 5) $\varepsilon(M,c)$ on the curve $\varepsilon(M,c = 1)$. This reveals that M_e is continuously enlarged upon dilution (inset of Figure 5) as expected[3,4] from rheology by $M_e(c) = M_e(c = 1)\ c^{-1.3}$ (dashed line). It appears that for higher M much lower concentrations c are needed to cause an increase of ε (or M_e), because ε remains unchanged with respect to the bulk in the case of PB 47000 with c = 50%.

In conclusion, the feature of entanglement dynamics, that is, the "shoulder" at long times in $C_{\text{polymer}}(t/\tau_s)$ (Figure 4b) continuously disappears and a transition from entanglement to Rouse behavior is observed for decreasing c, similar to that for decreasing M in neat PB (Figure 4a).[10] This conclusion is also supported by prior reports[7] of FC NMR relaxometry by Kimmich and co-workers. At longest times, the faster decay upon dilution may reflect the shortening of the terminal relaxation time τ_d, as displayed in Figure 3b. We note that, at longest times, effects of a reduced intermolecular relaxation for lower c may contribute.[11]

In summary, we have demonstrated that FC NMR relaxometry is well suited to investigate and quantitatively characterize the dynamics of polymers also in solution. The NMR susceptibility representation, the application of FTS, and the transformation to the dipolar correlation function allows of analyses of relaxation features, depending on temperature, molecular mass, and polymer mass fraction. Explicitly, we observe the disappearance of the entanglement dynamics upon dilution as it is indicated by the increase of the power-law exponent of the constrained Rouse regime of the tube-reptation model. The well established results of rheology are reflected by the master curves of NMR relaxation; this representation goes significantly beyond literature reports[7] and may render FC NMR as "molecular rheology".

AUTHOR INFORMATION

Corresponding Author

*E-mail: ernst.roessler@uni-bayreuth.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The financial support of Deutsche Forschungsgemeinschaft (DFG) through priority program SPP 1369 "Polymer-Solid Contacts: Interfaces and Interphases" (RO 907/16) and Grant FU 308/14 are acknowledged.

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