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Universal Polymer Dynamics Revealed by Field Cycling ^{1}H NMR

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ABSTRACT: We apply fast field cycling ^{1}H NMR to study segmental reorientation dynamics in melts of linear polybutadiene, polyisoprene, and polydimethylsiloxane in the high molecular weight limit. Measuring fully protonated as well as partially deuterated polymers, we show that in contrast to previous reports the relaxation behavior at low frequencies, for which polymer-specific contributions show up, is not universal but depends on the particular internuclear vectors of the ^{1}H spin pairs in the monomer unit. Only after extracting the polymer specific contributions from the overall susceptibility spectra by accounting for the glassy contribution, the "polymer spectra" reveal universal behavior which can be described by two power law regimes: one attributed to free Rouse dynamics and one, at lower frequencies, to entanglement effects. Yet the predictions of the tube-reptation model are not observed.

I. Introduction

The dynamics of melts of linear polymers comprises both polymer specific dynamics and glassy dynamics. Whereas polymer dynamics originate from collective dynamics of Rouse and reptation type,[1,2] glassy dynamics[3−5] are attributed to "segmental" or "local" relaxation of the polymer chain. Here, one has to keep in mind that the glass transition phenomenon itself includes cooperative motion, and the segmental correlation time τ_s may be identified with that of the α-process, τ_α, characterizing glassy dynamics. The latter drives the polymer dynamics via determining the monomeric friction coefficient and is responsible for the non-Arrhenius temperature dependence of the relaxation times in polymer melts.

From an experimental point of view it is of interest whether one can separate polymer dynamics from glassy dynamics in order to test predictions by respective theories. For example, it may be possible that polymer dynamics modify glassy dynamics.[6] In many cases one chooses experimental conditions which suggest that separation of time scales holds, and one assumes that solely polymer dynamics or solely glassy dynamics are probed as the contribution from the other relaxation is believed to be ignorable. Such an approach has also been taken in the case of fast field cycling (FFC) NMR experiments, a technique well suited to investigate the low-frequency motion in polymers.[2] FFC NMR monitors the dispersion of the spin−lattice relaxation time $T_1(\omega)$. To a fair approximation, the dispersion of ^{1}H T_1 reflects the spectrum of reorientational dynamics of a polymer segment in terms of the dipolar or second Legendre polynomial correlation function $F_2(t)$ of the spin pairs within a monomer unit. By converting the dispersion data into the time domain, the bond vector correlation function becomes accessible.[7]

Measuring at frequencies $\omega\tau_s \ll 1$, experimental results on several polymers have been reviewed by Kimmich and Fatkullin[2] which appear to indicate universal dispersion behavior of the spin−lattice relaxation in linear polymers. The T_1 dispersion manifests itself in characteristic power-law regimes which have been interpreted within Rouse theory (nonentangled polymers) and renormalized Rouse theory (entangled polymers).[2] Thus, the experiments seem not to disclose the power laws expected for the Doi−Edwards tube-reptation model; the latter have only been observed by FFC NMR for polymers confined to tubelike pores formed by a solid matrix.[8] However, there are reports in the literature that do not confirm such universal relaxation behavior, e.g., for the case of polyisoprene.[2,9] Here, the question is whether these deviations from the presumably universal relaxation behavior at $\omega\tau_s \ll 1$ are significant and may cast doubt on the previous approach[2] taken to interpret the FFC NMR data. The present publication attempts to answer this question.

In a series of papers,[7,10−12] we recently have reinvestigated the ^{1}H T_1 dispersion behavior of polybutadiene (PB) covering a broad range of molecular weight (M) including the low M limit; i.e., we have studied the crossover from simple liquid, to Rouse, and to entanglement dynamics. Experiments have been performed with a commercial spectrometer STELAR FFC 2000.[13] Applying frequency−temperature superposition (FTS), we have obtained master curves covering 6 decades in frequency at $\omega\tau_s \ll 1$, and the T_1 dispersion data have been interpreted in a new fashion. The results relevant for the present context can be summarized as follows. (i) In the frequency regime attributed to Rouse dynamics the influence of the spectral contribution of the glassy dynamics cannot be ignored. (ii) The entanglement regime ($M > M_e$) manifests itself at lower frequencies or longer times than Rouse dynamics, and here the contributions from glassy dynamics can be ignored. This is the case for PB, which exhibits a comparatively strong relaxation strength of the polymer dynamics, but it may not be necessarily the case for other polymers. (iii) The bond vector correlation function shows striking similarity with those obtained from simulations;[14] however, up to $Z = M/M_e \cong 9$ no indication of the power laws of the tube-reptation model can be identified, and also the renormalized Rouse theory does not fully apply. One possibility to explain these findings is to assume that the crossover to full entanglement dynamics occurs only at higher M; i.e., the crossover is "very protracted".[7,14]

Investigating now different polymers by FFC ^{1}H NMR, the present contribution aims at demonstrating that in contrast to previous reports[2,13] the T_1 dispersion at low frequencies in polymer melts is not universal but rather depends on the

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orientation of the internuclear vectors with respect to the contour of the chain in the particular monomer, a fact also discussed by Spiess and co-workers in the context of their high-resolution double-quantum NMR experiments.[15−17] Only by taking into account the spectral contribution from the glassy dynamics, indeed universal polymer relaxation behavior is revealed for all the polymers investigated. These results are further substantiated by examining partially deuterated polymer samples. In particular, we will discuss results for polybutadiene (PB), polyisoprene (PI), and polydimethylsiloxane (PDMS) in the high M limit for which entanglement effects are well established and the T_1 dispersion has become M independent ($M \gg M_e$). We will show once again that the universal relaxation behavior revealed after isolating the polymer contribution is not described by current polymer theories, at least in the frequency range accessible by FFC NMR at the present time.

II. Theoretical Background

The spin−lattice relaxation time T_1 describes the evolution of the nuclear magnetization toward its equilibrium value. Its frequency dependence (or dispersion) can be studied by applying the FFC technique where the external magnetic field is switched between a variable relaxation field B and a constant detection field. The angular frequency is defined by the Larmor frequency $\omega = \gamma B$, where γ denotes the gyromagnetic ratio of the nucleus. In the case of ^{1}H nuclei, the spin−lattice relaxation is determined by fluctuations of the dipolar interaction of the proton spins. Usually it is argued that T_1 is dominated by intramolecular contributions.[2,13] Accordingly, ^{1}H FFC NMR relaxation data are expected to reflect mainly reorientation dynamics. However, the role of intermolecular or intersegmental contributions in the case of polymers must not be ignored.[2]

As introduced before, we rewrite the Bloembergen−Purcell−Pound (BPP) expression[18] for the relaxation rate $1/T_1$ in the susceptibility form[7,10−12]

$$\omega/T_1 = C[\chi''(\omega) + 2\chi''(2\omega)] \equiv 3C\tilde{\chi}''(\omega) \qquad (1)$$

where C is the NMR coupling constant and $\chi''(\omega) = \omega J(\omega)$ the susceptibility representation of the fluctuation spectrum, with the spectral density $J(\omega)$ being given in first approximation by the Fourier transform of the second rank orientational correlation function $F_2(t)$ of a polymer segment, more precisely of the internuclear vectors of the spin pairs in the monomer.[2,11] The factor 3 appears in order to keep the integral over the susceptibility" $\tilde{\chi}''(\omega)$ normalized to $\pi/2$ as usual.

As we cover a large temperature range, glassy dynamics as well as polymer dynamics are probed, and one is able to construct master curves $\tilde{\chi}''(\omega\tau_s)$ for the NMR susceptibility extending over many decades in time, assuming frequency−temperature superposition (FTS). For details about obtaining the master curves, the reader may consult our previous publications.[7,10−12] The master curves $\tilde{\chi}''(\omega\tau_s)$ combine the results from a broad temperature range (say $\Delta T \cong 180$ K) and present "isofrictional" spectra which allow comparing the results for different M. For simple liquids and oligomers with low molecular weight $M < M_R$ (M_R denoting the molecular weight of the Rouse unit[12]), no spectral contribution at $\omega\tau_s < 1$ in excess to the Debye behavior $\tilde{\chi}''(\omega) \propto \omega^1$ is observable, and their susceptibility master curves solely represent glassy dynamics ("glassy spectrum"). For samples with higher M, i.e., $M > M_R$, additional intensity on the low-frequency side of the α-peak reflects polymer specific dynamics that involve time scales longer than τ_s.

As a guideline for a phenomenological decomposition of the spectral contributions from polymer and glassy dynamics, one assumes that both are statistically independent, so that their contributions to $F_2(t)$ are multiplicative:[2,7,10−12]

$$F_2(t) = F_{\mathrm{glass}}(t)F_{\mathrm{polymer}}(t) \qquad (2)$$

Depending on molecular weight M, the polymer part $F_{\mathrm{polymer}}(t)$ may contain contributions from Rouse as well as entanglement dynamics. Introducing the relative magnitude f of polymer dynamics, we write

$$F_2(t) = [(1-f)\phi_{\mathrm{glass}}(t) + f]F_{\mathrm{polymer}}(t) \qquad (3)$$

where $\phi_{\mathrm{glass}}(t)$ denotes the normalized correlation function describing the glassy dynamics alone.

Assuming time scale separation (cf. also ref 19), the contributions to the total susceptibility are approximately additive

$$\tilde{\chi}''(\omega\tau_s) \cong (1-f)\tilde{\chi}''_{\mathrm{glass}}(\omega\tau_s) + f\tilde{\chi}''_{\mathrm{polymer}}(\omega\tau_s) \qquad (4)$$

Under such conditions the "polymer spectrum" $\tilde{\chi}''_{\mathrm{polymer}}(\omega\tau_s)$ containing only the spectral contributions attributed to polymer dynamics can be extracted from the master curve $\tilde{\chi}''(\omega\tau_s)$ of each sample by subtracting the glassy spectrum $\tilde{\chi}''_{\mathrm{glass}}(\omega\tau_s)$. Thereupon the relaxation strength $f(M)$ of polymer dynamics is obtained, which is the relative correlation loss due to polymer dynamics on time scales $t \gg \tau_s$. As found for PB, its dependence on M reflects three dynamic regimes, namely simple liquid, Rouse, and entanglement regime. Specifically, $f(M)$ strongly increases in the Rouse regime ($M_R < M < M_e$) but saturates beyond the entanglement molecular weight M_e[12] or at $M_c \cong 2M_e$. In other words, the glassy dynamics are more and more impeded by the emerging polymer dynamics. The relaxation strength f is connected to what has been called the local order parameter $S = \sqrt{f}$.[11,12,15,16,20] Though the applicability of eq 4 may be questioned as time scale separation may not always apply in a strict sense the results appear physically reasonable and allow a comparison of the polymer contribution for different polymers what is needed when searching for presumably universal polymer relaxation. In the Appendix we compare the results from applying eq 4 with those from eq 3. In the latter case a full deconvolution is applied, and the differences can essentially be ignored in the case of the PB data.

As discussed, for example, by Spiess and co-workers[15,16] considering the entanglement regime, the particular value of the relaxation strength f or the order parameter S depends on the direction of the internuclear vector between a spin pair with respect to the contour of the chain. Given the order parameter of the chain S_{chain}, the order parameter S_{ij} (or f_{ij}) of a particular spin pair ij oriented with an angle ϑ_{ij} toward the contour direction is found[16] by tensor calculus

$$S_{ij} = \sqrt{f_{ij}} = 1/2(3\cos^2\vartheta_{ij} - 1)S_{\mathrm{chain}} \qquad (5)$$

Thus, the measured order parameter S_{ij} is smaller than that of the chain. Moreover, the magnitude of spectral contribution attributed to polymer dynamics depends on the structure of the particular monomer. In other words, no universal dispersion for the overall spin−lattice relaxation time is expected. Only if the susceptibility spectra are decomposed along eq 4 the so-extracted "polymer spectra" will be expected to show universal features. As will be demonstrated, these considerations do not only hold for the entanglement regime but also for the Rouse regime. Here we add that, in contrast to double-quantum (DQ) NMR, FFC NMR usually provides only average values for f as the method cannot discriminate the contributions from different spin pairs in the monomer. However, by measuring partially deuterated polymers, the situation becomes more favorable, and this is

Table 1. Details on the Samples

sample	M_w [g/mol]	M_w/M_n	reference
propylene glycol (PG)	76		this work
PB466-h_6	466	1.06	10
PB2020-h_6	2020	1.07	10
PB18000-h_4	18000	1.02	this work
PB20000-h_2	20000	1.02	this work
PB35300-h_6	35300	1.02	7
PI111000-h_5	111000	1.03	9
PI127000-h_3	127000	1.03	9
PI157000-h_8	157000	1.01	this work
PDMS860-h_6	860	1.41	this work
PDMS5940-h_6	5940	1.15	this work
PDMS128000-h_6	128000	1.13	this work

exploited in the present contribution. Still, the particular f_{ij} may depend on the configuration of the monomer unit. For example, in the case of PB samples an average over cis and trans isomers is measured. Finally, we mention that although assumed to be negligible, intermolecular coupling may still play a role. Thus, a quantitative analysis of the relaxation strength f measured by FFC ^{1}H NMR appears to be not straightforward.

III. Experimental Section

We investigated samples of differently deuterated as well as fully protonated 1,4-polybutadiene (PB) and 1,4-polyisoprene (PI) with $M > M_e$. The T_1 dispersion data of partially deuterated 1,4-polyisoprene (PI) from ref 9 were transformed to the susceptibility representation. Moreover, we measured samples of polydimethylsiloxane (PDMS) with different M (see Table 1). Note that the sample name of the polymers reflect the weight-average M_w and the number of proton nuclei in the monomer unit. The fully protonated samples (PB-h_6, PI-h_8, PDMS-h_6) were purchased from Polymer Standards Service PSS, Mainz, Germany, while the partially deuterated samples (PB-h_2, PB-h_4, PI-h_3, PI-h_5) were kindly provided by D. Richter and L. Willner, Institut für Festkörperforschung, Forschungszentrum Jülich, Germany. The concentration of cis, trans, and vinyl units is 51%, 42%, and 7%, respectively, for the deuterated PB samples. Propylene glycol (PG, purity $\geq$99.5%) was purchased from Sigma-Aldrich.

The spin−lattice relaxation time $T_1(\omega)$ was determined with a STELAR FFC 2000 relaxometer which allows measurements in the temperature range of 160−400 K and ^{1}H Larmor frequency range ν = 10 kHz−20 MHz. For temperature control at the sample position we used a thermocouple in a test tube and inserted it into the probe. The accuracy of temperature measurements was better than ±1 K, and temperature stability was better than ±0.3 K. T_1 was obtained by a monoexponential fit of the magnetization curve.

IV. Results

^{1}H T_1 Dispersion. Figure 1 displays the dispersion of the spin−lattice relaxation time $T_1(\nu)$ for the investigated polymers PB, PI, and PDMS measured at a single temperature. The respective temperature is selected to allow the best comparison among the different polymers. As the glass transition temperature T_g increases in the order of PDMS, PB, and PI,[6] similar temperatures with respect to T_g are chosen. In the low-M system (PB466-h_6) the dispersion profile for low frequencies ($\nu < 500$ kHz) is virtually constant, and it has been shown that the relaxation behavior (i.e., its master curve) is indistinguishable from that of a simple liquid such as *o*-terphenyl.[11] Thus, still no polymer specific dynamics are found for PB at $M = 466$. In contrast, the dispersion data of the polymers in the high M limit ($M \gg M_e$) can be approximated at low frequencies by a power law ν^a with $a > 0$ (as indicated in Figure 1). For the fully protonated PB (PB35300-h_6) an exponent $a = 0.23$ is observed. However, this power law is not found for the fully protonated PI (PI157000-h_8); instead, here $a = 0.17$. In the case of PDMS128000-h_6 a quite large exponent $a = 0.29$ is found. Moreover, for the partially deuterated PB samples (PB18000-h_4 and PB20000-h_2) power laws with $a = 0.21$ and $a = 0.27$, respectively, are obtained as shown in Figure 1. Clearly, the three differently protonated PB samples show significant variation in the exponent a. In the case of PI, partial protonation only weakly changes the exponent of the corresponding power law. Here, we emphasize that interpolation by power laws is only an approximation for specifying the differences in the relaxation behavior of the investigated polymers. Because of a different ^{1}H NMR coupling constant C the level of the $T_1(\nu)$ curves of the samples varies.

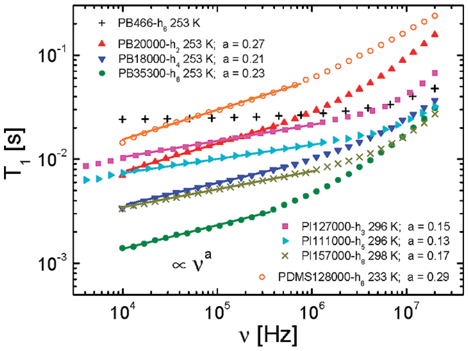

Figure 1. Dispersion of spin−lattice relaxation time $T_1(\nu)$ measured for polybutadiene (PB) at $T = 253$ K, for polyisoprene (PI) at $T = 296$ K,[9] and $T = 298$ K and for polydimethylsiloxane (PDMS) at $T = 233$ K. Power laws ν^a with a between 0.13 and 0.29 (straight lines) at low frequencies can be observed for the polymers with $M > M_e$. The $T_1(\nu)$ curve of PB466-h_6 does not exhibit dispersion toward low frequencies (simple liquid limit).

Since the apparent exponent a differs by a factor of about 2 among the differently protonated polymers PB, PI, and PDMS, it can be concluded that no universal dispersion is observed. Here, we note that Kimmich and co-workers[2,13] introduced three presumably universal power law regimes (I, II, III, starting from high frequencies) for the T_1 dispersion behavior of linear polymers, and the frequency range considered in Figure 1 is that which has been called regime II with an universal exponent $a = 0.25 \pm 0.05$.[2] Clearly, the variation of a found in the present contribution exceeds this margin. Concerning the power laws for PI the deviations have already been recognized in refs 9 and 13. It is the goal of our contribution to understand the variation of the exponent a in the light of interplaying spectral contributions from glassy and polymer dynamics.

Susceptibility Master Curves. Measuring the T_1 dispersion in the temperature range of 223−393 K enables us to construct susceptibility master curves $\tilde{\chi}''(\omega\tau_s)$ for the samples of PB and PI assuming FTS. The corresponding master spectra are plotted in Figure 2 as a function of the reduced frequency $\omega\tau_s$ and are scaled by the corresponding amplitude of α-relaxation peak to account for the individual NMR coupling constant of the different polymer samples; i.e., they agree in the frequency range $\omega\tau_s \geq 1$. The susceptibility representation of the relaxation data allows to clearly distinguish between glassy and polymer specific dynamics. Whereas around the relaxation peak with $\omega\tau_s \cong 1$ contributions of glassy dynamics dominate, the excess intensity on the low-frequency side of the peak ($\omega\tau_s \ll 1$) compared to the spectrum of the simple liquid limit (PB466-h_6 or *o*-terphenyl) represents the spectral contribution for which polymer dynamics more and more dominate. The corresponding

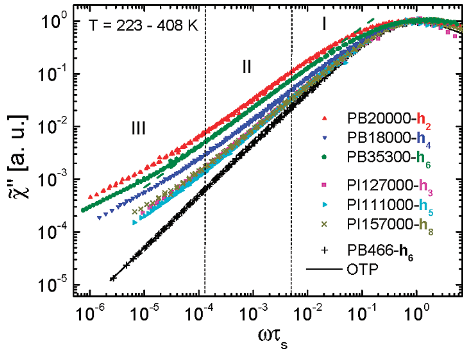

Figure 2. Master curves of the susceptibility $\chi'' = \omega/T_1$ as a function of the reduced frequency $\omega\tau_s$ for polybutadiene (PB) and polyisoprene (PI) in temperature range as indicated. Curves of PB with $M = 466$ (PB466-h$_6$) and *o*-terphenyl (OTP) are included as a reference for a "glassy spectrum". Green dashed line: $\tilde{\chi}''(\omega) \propto \omega^{1-a}$ with $a = 0.23$ as obtained for PB35300-h$_6$ in regime II. Numbers and vertical dashed lines mark the different relaxation regimes according to refs 2 and 13.

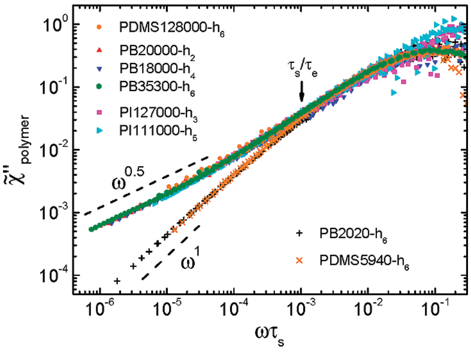

Figure 3. Normalized polymer spectra $\tilde{\chi}''_{\text{polymer}}(\omega\tau_s)$ obtained by subtracting the contribution of glassy dynamics (PB466-h$_6$ for PB and PI; PDMS860-h$_6$ for PDMS) from the total susceptibility spectra of Figures 2 and 4 coincide for the high-M limit. Dashed lines: power laws at low frequencies ω^1 representing terminal relaxation and $\omega^{0.5}$ for high-M polymers. Note that the polymer spectra of PDMS are shifted by a single factor in frequency (see text).

amplitude is different in the entire range $\omega\tau_s < 1$ for each of the samples. In particular, the master curve of PB20000-h$_2$ with protons at the double bond exhibits a higher intensity than that for the fully protonated PB35300-h$_6$, whereas the situation is vice versa for the spectrum of PB18000-h$_4$ in which only the protons of the methylene groups are present. Obviously the spectra depend on the particular proton spin pair probed in the ^{1}H relaxation experiment. In the case of PI, however, this effect is quite small; i.e., the excess intensity does not change strongly when partially deuterated PI is considered. We note that the different spectral intensity is not related to M since saturation is well established at $M \gg M_e$,[9] i.e., in the high-M limit which is considered within the experimentally accessible frequency range.

The power law behavior discussed for the $T_1(\nu)$ data in Figure 1 transforms into a susceptibility behavior $\tilde{\chi}''(\omega) \propto \omega^{1-a}$, and the power law for regime II (discussed in Figure 1) with the corresponding exponent for PB-h$_6$ is included in Figure 2 (green dashed line). From this it becomes obvious that at lowest frequencies the susceptibility bends over to a weaker frequency dependence, and a second power law regime may be identified: Here, apparent exponents $a = 0.43-0.48$ and $a = 0.28-0.35$ are found for PB and PI, respectively; the values vary less than those found at higher frequencies for regime II (cf. Figure 1). Nevertheless, they again do not appear to be universal in contrast to the value $a = 0.45 \pm 0.05$ reported by Kimmich and Fatkullin for this frequency range called regime III.[2] For convenience, we indicate in Figure 2 the corresponding regimes according to the Kimmich and Fatkullin classification. At high frequencies close to the susceptibility maximum, it is obvious that in addition to polymer dynamics glassy dynamics contribute significantly to the relaxation. This regime has been called regime I by Kimmich and co-workers, and a power law exponent $a = 0.5 \pm 0.05$ has been claimed to be found.[2,13] However, such an exponent cannot be clearly recognized, and as said the corresponding relaxation contributions cannot be attributed to polymer dynamics alone.

Polymer Spectra. Separating glassy and polymer spectral contributions along eq 4 by subtracting the "glassy spectrum" of PB466-h$_6$ from each of the total susceptibility curves $\tilde{\chi}''(\omega)$ of Figure 2 yields spectra reflecting only polymer dynamics ("polymer spectra", cf. Figure 3). This allows extracting the relaxation strength f of polymer dynamics by calculating the relative integrated intensities of the individual polymer spectra (see Table 2). For PB the highest value $f = 0.16$ is obtained for the sample PB20000-h$_2$. As discussed before, for PB18000-h$_4$ f is smaller ($f = 0.06$); the fully protonated sample PB35300-h$_6$ is somewhat in between ($f = 0.11$). For the differently deuterated PI samples we find similarly small values ($f = 0.03$).

Table 2. Relaxation Strength *f* of Polymer Dynamics in Fully and Partially Protonated Samples of Polybutadiene (PB) and Polyisoprene (PI) as Well as Polydimethylsiloxane (PDMS) with *M* > *M*$_e$, As Obtained by Subtractive Decomposition and by Comparing Amplitudes in Figure 5

sample	*f* (from spectra decomposition)	*f* (from Figure 5)
PB20000-h$_2$	0.16 ± 0.02	($\equiv$0.16)
PB18000-h$_4$	0.06 ± 0.006	0.064 ± 0.003
PB35300-h$_6$	0.11 ± 0.01	0.109 ± 0.003
PI127000-h$_3$	0.03 ± 0.01	0.031 ± 0.002
PI111000-h$_5$	0.02 ± 0.01	0.025 ± 0.001
PI157000-h$_8$	0.03 ± 0.01	0.036 ± 0.001
PDMS128000-h$_6$	0.02 ± 0.002	

In Figure 3 we show the polymer spectra $\tilde{\chi}''_{\text{polymer}}(\omega\tau_s)$ which have been obtained by normalizing the polymer spectrum to provide an integral which equals $\pi/2$ (cf. ref 12). In this representation it is clearly seen that the high-M polymer spectra for the differently deuterated and the fully protonated PB and PI are virtually identical. In particular, power laws with the same exponents are revealed, and therefore the spectra reflect the same dynamic process, which was not evident from inspecting the total relaxation spectra. Only by accounting for the contribution of glassy dynamics universal polymer spectra are revealed. Such spectra may now be compared to predictions of polymer theories which usually exclude fast segmental dynamics. We note that at $\omega\tau_s \geq 10^{-1}$ a maximum appears in Figure 3 which signals the cutoff of the polymer spectra at high reduced frequencies.

Special Case PDMS. The susceptibility master curve of PDMS is not included in Figure 2 as particularities show up which we want to discuss separately. In Figure 4a the master curve for PDMS128000-h$_6$ (full circles) is displayed together with that for $M = 5940 \cong M_e = 8100$[21] (open circles) and for the lowest M measured (PDMS860-h$_6$; crosses). For comparison, again the low M data for PB (PB466-h$_6$; pluses) are included. When comparing the data also with those in Figure 2 for PB or PI significant differences show up. For example, the data for PDMS860-h$_6$ show a different behavior to that of the low M limit for PB (PB466-h$_6$); specifically, the relaxation peak for PDMS860-h$_6$ has a shoulder at low frequencies ($\omega\tau_s \leq 1$), i.e., significant excess intensity with

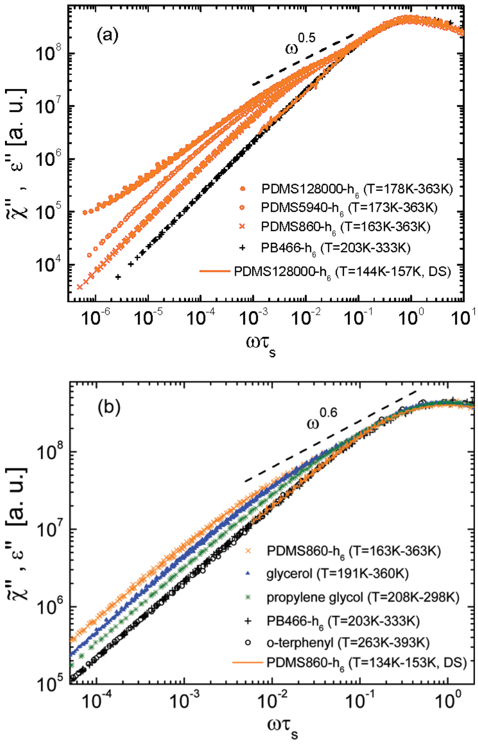

Figure 4. Master curves of the susceptibility $\chi'' = \omega/T$ as a function of the reduced frequency $\omega\tau_s$ for (a) different polydimethylsiloxanes (PDMS) as well as a master curve from dielectric studies (orange line).[6] (b) Master curves for low-*M* polydimethylsiloxane (PDMS860-h_6), glycerol,[22] and propylene glycol for temperature ranges as indicated: each spectra exhibits an anomaly for $\omega\tau_s \leq 1$ compared to the master curve of polybutadiene (PB466-h_6) or *o*-terphenyl as reference systems of simple liquids. Orange line: master curve for PDMS860-h_6 from dielectric spectroscopy (DS).

respect to the spectrum of PB466-h_6. Presumably, the susceptibility data of PDMS860-h_6 show very weak contributions from polymer relaxation, if any. We have not been able to measure PDMS samples with lower *M* to fully check this assumption as crystallization always interferes. Inspecting all the three curves for PDMS (high and low *M* limit as well as M_e), this shoulder appears in all cases leading to a virtually common relaxation behavior at $10^{-2} < \omega\tau_s \leq 1$, i.e., in a frequency range for which *M* depending spectral contributions from polymer dynamics are already found in PB as well as in PI. This common relaxation regime is found for all investigated PDMS samples independent of *M*; *M*-dependent contributions only appear at $\omega\tau_s < 10^{-2}$. Thus, the shoulder cannot originate from some polymer specific relaxation. We will attribute it to a particular relaxation feature already observed in the low-*M* limit, for which only glassy dynamics control the relaxation (cf. below).

It is worthwhile to note that a similar anomaly as for PDMS860-h_6 is also observed in the low molecular weight glass formers glycerol[22] and propylene glycol (PG). In order to show this effect more clearly, we display the corresponding master curves together with those for PDMS860-h_6, PB466-h_6, and *o*-terphenyl (OTP) in Figure 4b. Indeed, the curves for glycerol, PG, and PDMS860-h_6 are very similar, showing in all the cases a low-frequency shoulder with respect to the data of PB466-h_6 or OTP; the latter may be taken as reference systems for FFC spectra of simple liquids.[10,11] Interestingly, this low-frequency anomaly is only observed in the NMR data but not in the dielectric data of PDMS860-h_6,[6] which is also displayed in Figure 4b (a similar behavior is observed for glycerol[22]). Converting our dielectric results for PDMS128000-h_6[6] into a master curve (line), it is seen that this curve coincides very well with the dispersion data of PB466-h_6 or *o*-terphenyl (also included in Figure 4b). We emphasize that PDMS is a type B polymer;[23] thus, dielectric spectroscopy only probes glassy dynamics. Up to now this relaxation feature is not understood. We conclude that in PDMS contributions from polymer dynamics are only found at reduced frequencies lower than say $\omega\tau_s < 10^{-2}$.

In order to obtain the polymer spectrum in the case of PDMS, we have subtracted the master curve of PDMS860-h_6 from the susceptibility data of the higher *M*. For comparing the data with the polymer spectra of PB and PI in Figure 3, however, the polymer spectra for both PDMS128000-h_6 and PDMS5940-h_6 have been shifted in frequency by a factor of 17. This is understood by the fact that as discussed polymer dynamics set in for PDMS only at significantly lower frequencies as compared to those in PB or PI. Again, a good agreement is found. Essentially, all the polymer spectra agree after correcting for the contribution of glassy dynamics.

We note that for the high-*M* limit of PDMS an apparent power law behavior, $\tilde{\chi}''(\omega) \propto \omega^{1-a}$, with $a = 0.5$ can be observed over a quite extended frequency range $10^{-3} < \omega\tau_s < 5 \times 10^{-2}$ (dashed line in Figure 4a). Thus, in the case of PDMS indeed a clear-cut power law regime is recognized as expected for regime I of the Kimmich–Fatkullin classification scheme. However, it does not reflect solely polymer dynamics; instead, it has its origin in interplay of the contributions from (anomalous) glassy and polymer dynamics. In the case of the data for the low-molecular-weight systems displayed in Figure 4b a similar power law with an exponent $a = 0.60 \pm 0.03$ is observed (dashed line in Figure 4b). We emphasize that the experimental data for PDMS (as well as for PB) agree with those compiled by Kimmich and co-workers.[24,25]

Comparison of Rouse and Entanglement Contribution. In order to understand the relaxation behavior of linear polymers in the limit of high *M*, i.e., with fully established entanglement dynamics, it is of interest to compare the polymer spectra (after subtracting the glassy spectrum from the overall relaxation spectra) with the corresponding spectrum from a sample with $M \cong M_e$ for which solely Rouse dynamics are expected and entanglement dynamics are not established yet. Therefore, we include in Figure 3 the polymer spectrum of PB2020-h_6[10] and PDMS5940-h_6. Clearly, a quite different behavior is observed at $\omega\tau_s \leq 10^{-3}$ between the master curves of high *M* and $M \cong M_e$ whereas for $\omega\tau_s > 10^{-3}$ they coincide. We attribute the much stronger amplitude below $\omega\tau_s < 10^{-3}$ of the high-*M* samples to contributions specific to entanglement effects; i.e., as expected, entanglement results in a significant retardation of the correlation loss which leads to a kind of bimodal relaxation. We find a power law behavior, $\tilde{\chi}''_{\text{polymer}}(\omega) \propto \omega^{1-a}$, with an exponent $a = 0.50 \pm 0.05$ as already concluded from discussing Figure 2 for which the contribution from glassy dynamics have not yet been accounted for. In other words, at lowest frequencies the glassy contribution in $\chi''(\omega)$ can be ignored indeed.[7]

Regarding the frequency range $\omega\tau_s > 10^{-3}$ the susceptibility curves for the sample with $M = M_e$ and for the high *M* limit are virtually the same (cf. Figure 3). This means that the polymer dynamics of entangled polymers at such comparatively high frequencies are essentially the same as those of nonentangled polymers with $M = M_e$. As previously shown for PB,[12] the spectra of the latter can be semiquantitatively reproduced by the discrete Rouse model assuming a few Rouse modes being activated (note $M_e/M_R = 4-5$ for PB and 9−10 for PDMS). Within the tube-reptation model we can identify the crossover at the $\omega\tau_s \cong 10^{-3}$ reflecting the ratio τ_s/τ_e. At the entanglement time $\tau_e \cong 10^3\tau_s$ the polymer chain "feels" first entanglement effects. We note that for PB2020-h$_6$ and PDMS5940-h$_6$ the crossover to the Debye limit $\chi''(\omega) \propto \omega^1$ is observed at lowest frequencies, indicating that contributions up to the slowest (Rouse) relaxation mode are detected.[7,12] We take the fact that the shapes of the polymer spectra of PB and PDMS for $M \cong M_e$ agree so well even at intermediate frequencies ($\omega\tau_s < 10^{-1}$) as an additional argument that indeed the additive separation of contributions from polymer and glassy dynamics is appropriate.

V. Discussion and Conclusions

Extending our previous FFC ^{1}H NMR measurements and analysis on PB[7,9−12] to different polymers including partially deuterated systems and concentrating on the entanglement regime ($M \gg M_e$), it turns out that the low-frequency behavior ($\omega\tau_s < 1$) of the T_1 dispersion does not show universal power law characteristics, in contrast to what was claimed before.[2,13] If at all power law regimes can be identified, their apparent exponents differ (cf. Figure 1). Comparing the dispersion behavior in form of the susceptibility (cf. Figure 2) to that of the low-M systems ($M < M_R$) with no polymer specific contribution but only glassy contribution, the extent of excess intensity at $\omega\tau_s < 1$ with respect to the simple liquid limit $\chi''(\omega) \propto \omega^1$ ($\omega\tau_s < 1$) is very different for the investigated polymers. It may even depend on the extent of protonation of a given monomer, i.e., on the particular spin pairs probed by ^{1}H NMR. In other words, the relaxation strength f in terms of eq 3 is different in the polymers. We recall that within the present definition f is a measure of the spatial restriction of glassy dynamics for a given spin pair (or groups of spin pairs) imposed by Rouse as well as entanglement dynamics. Referring in particular to the case of PDMS with its M-independent anomalous glassy dynamics in order to understand the polymer specific contribution in the T_1 dispersion data of polymers, our results emphasize the importance of including a study of the low-M limit for each polymer. However, this may not always be possible as crystallization may occur.

As discussed in section II, in the high-M limit ($M \gg M_e$) the transient entanglement network points are believed to introduce topological constraints impeding the reorientation involved in the glassy dynamics at short times ($t \leq \tau_s$), and f or the dynamic order parameter S is expected to depend on the direction of the internuclear vector between a spin pair with respect to the contour of the chain (cf. angle ϑ_{ij} in eq 5). For example, in their DQ NMR study on PB melts, Spiess and co-workers determined quite different values f_{ij} for the different spectrally resolvable spin pairs of the monomeric segment.[15,16] Although their values of f_{ij} are significantly higher than those estimated from our FFC experiments (for a discussion of this discrepancy cf. ref 11), the same trend is observed in the present study (cf. Table 2): $f_{\mathrm{CH=CH}}$ determining the dispersion behavior of PB-h$_2$ is significantly larger than $f_{\mathrm{CH_2}}$, the latter essentially fixing the dispersion of PB-h$_4$. Qualitatively, this difference may be understood by recalling that in PB-h$_2$ with its protons attached to the carbon atoms at the double bond (in cis and trans configuration) the angle ϑ_{ij} with respect to the contour direction, the latter presumably fixed by the direction of the double bond, is rather small and thus leading to a small reduction of the order parameter with respect to that of the chain itself, S_{chain}. In contrast, a much stronger reduction is expected for the methylene group in PB-h$_4$. In the case of PI with its absence of a spin pair along the double bond, different protonation only slightly changes f (cf. Table 2).

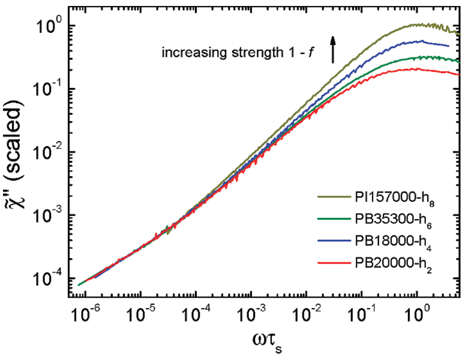

Figure 5. Susceptibility spectra for the different polymers plotted to agree at lowest frequencies.

Refraining to explain the behavior of f in detail, we rather conclude the following. (i) It appears that the considerations regarding the relative values of f hold for both the entanglement regime and the Rouse regime ($M_R < M < M_e$), and they can qualitatively explain the nonuniversal dispersion behavior of $T_1(\omega)$ in the different polymers and in selectively deuterated samples of a given polymer. (ii) Subtracting the corresponding contribution of glassy dynamics from the total dispersion via eq 4 yields universal polymer spectra (cf. Figure 3). Searching in $T_1(\omega)$ for generic polymer effects without accounting for the glass process is misleading as the latter is always a large contribution with $1 - f \gg f$. This holds especially for small M in the Rouse regime in which f decreases with decreasing M.[12]

Here two comments are worthwhile. First, subtracting the "glassy spectrum" from the total susceptibility spectrum of polymers assumes that the first does not change with M, a fact well-known from dielectric spectroscopy on type B polymers for which only the glassy transition is probed.[23] It has also been specifically tested for PB.[6] Second, although the spectral contribution of the glassy dynamics and of Rouse dynamics are not fully separated, a simple additive separation yields universal polymer spectra. Thus, we think this separation procedure is essentially a good approximation although some distortion of the polymer spectra may be expected at $\omega\tau_s \leq 1$. In the Appendix we demonstrate that indeed the results will remain essentially unchanged if one performs a decomposition of the correlation function in the time domain instead of applying the subtraction approach of the susceptibility in the frequency domain.

As an alternative approach to the additive decomposition, one can estimate the contribution from glassy and polymer dynamics, that is f, by a simple scaling procedure. In Figure 2 the susceptibility master curves are normalized to agree in the frequency range of the glass transition. Hence, the amplitude of the susceptibility at lowest frequencies for which influence of contributions from glassy dynamics can be ignored may be taken as measure of f. Vice versa, we may plot the data in a way that they agree at lowest frequencies (cf. Figure 5). Assuming universal polymer spectra, this is nothing else than plotting $\tilde{\chi}''(\omega)/fC$ except for an unknown factor. Then, the different heights of the relaxation maximum reflect the different strength $1 - f$ of the contribution from glassy dynamics assuming similar shape of $\tilde{\chi}''_{\mathrm{glassy}}(\omega)$. Explicitly, the maximum height in Figure 5 is a measure for $(1 - f)/f$. In order to get absolute values for f, we choose that of PB20000-h$_2$ obtained by the subtraction method as reference. In Table 2 we compare the results of this estimate to that of the additive separation. Very similar values are obtained, again demonstrating that the additive decomposition of the spectra yields reliable values of f. The spectra in Figure 5 agree at lowest frequencies as expected for a universal entanglement contribution (note that PDMS is excluded from this analysis due to its low-frequency anomaly of the α-process). First, deviations from the common spectrum appear at $\omega\tau_s > 5 \times 10^{-5}$ for PI which exhibits the strongest contribution $\tilde{\chi}''_{\mathrm{glassy}}(\omega)$. Thus, this plot directly shows the non-negligible influence from spectral contributions associated with glassy dynamics. The latter is smallest in PB-h$_2$, and the corresponding spectrum reflects polymer specific contributions over the largest frequency range. This again reveals an advantage of the susceptibility representation, and it becomes obvious that extracting power law exponents in the frequency range of Rouse dynamics $\omega\tau_s > 10^{-4}$ (cf. below) without taking into account the contribution from glassy dynamics yields erroneous results.

The universal polymer spectra of entangled polymers (after separating glassy and polymer specific contributions) show two power law regimes in addition to a cutoff regime at highest frequencies (cf. Figure 3). This is in contrast to previous statements by Kimmich and co-workers, who have reported three power law regimes (I−III)[2,13] although deviations were discussed, too.[9,13] Their interpretation, however, suffers from the fact that glassy dynamics have not been taken explicitly into account. From the present analysis as well as from our previous works,[7,11,12] we conclude that only two power law regimes exist for entangled polymers (at least in the currently accessible frequency range), and the crossover between them may be associated with the entanglement time τ_e. Whereas the first power law regime at high frequencies is attributed to free Rouse dynamics since it is identical with the relaxation behavior in a nonentangled polymer with $M \cong M_e$, the second one at lowest frequencies reflects contributions specific for entanglement dynamics. It is identical with regime III of the Kimmich−Fatkullin classification scheme. Since here the influence of spectral contributions from glassy dynamics can be neglected in the total dispersion spectra, the result agrees in both interpretations, i.e., a power law $\tilde{\chi}''_{\mathrm{polymer}}(\omega) \propto \omega^{1-a}$ with $a \cong 0.5$ is recognized at lowest frequencies. Kimmich and Fatkullin attributed this dispersion regime to intersegmental relaxation.[2,27] This has become possible by comparing ^{1}H and ^{2}H FFC NMR results for PB.[25] ^{2}H NMR does not probe intersegmental relaxation, and they have not observed regime III in this case. As the fraction of intermolecular or intersegmental relaxation is expected to depend on structural details of the monomer, it is surprising that taking this interpretation for granted this regime is found to be universal. More experimental data are needed to settle this point.

In Figure 3, at higher frequencies, the free Rouse regime is characterized by an apparent power law $\tilde{\chi}''_{\mathrm{polymer}}(\omega) \propto \omega^{1-a}$ with $a = 0.30 \pm 0.05$, which is similar but not identical to that observed in the total dispersion for PB-h$_6$[7] and PDMS-h$_6$ (cf. Figures 2 and 4a), and it corresponds to regime II of the Kimmich−Fatkullin classification scheme. Both polymers show a quite large excess intensity compared to their low-M system, and consequently the difference between the total relaxation spectra and the "polymer spectra" is small. However, this is not the case for PI and PB-h$_4$ with their small relaxation strength (cf. Table 2). Here, the spectral contributions of the glassy dynamics cannot be ignored. Regarding the investigated polymers, regime I of the Kimmich−Fatkullin classification observed at highest frequencies in the total spectra $\chi''(\omega)$ (cf. Figure 2 or 4) clearly is dominated by spectral contribution from glassy dynamics and thus cannot be attributed to polymer specific relaxation alone.

Finally, we note that as discussed thoroughly in ref 7, the polymer specific relaxation regimes can be explained neither by the tube reptation nor by the once renormalized Rouse model. On the one hand, assuming that the spectra at lowest frequencies (regime III) are indeed dominated by intersegmental relaxation, then the twice renormalized Rouse model predicts an exponent $a = 0.5$ as experimentally observed.[27] On the other hand, very similar results are reported by Monte Carlo (MC) simulations,[14] and as mentioned already before, it has been concluded that the crossover from nonentangled to entangled dynamics with tube-reptation dynamics is "very protracted"; i.e., it may be observed at $M \gg M_e$ (for a comparison of FFC NMR and MC simulation results cf. ref 7). This is also supported by very recent results from DQ NMR.[28] The intriguing agreement of results from FFC NMR and simulations, again, may cast doubts on the interpretation that regime III can be attributed to intersegmental correlation effects as MC simulations do not include such correlations. In any case, FFC NMR provides a unique opportunity for elucidating dynamics in polymer systems and even lower frequencies may be accessible in the near future. The program of the Kimmich group to unravel universal polymer relaxation in chemically quite different polymers by FFC NMR appears to be indeed possible provided that the spectral contribution of the glassy dynamics is well accounted for.

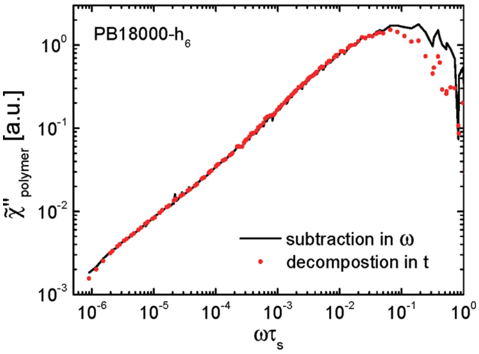

Figure 6. Polymer spectrum $\tilde{\chi}''_{\mathrm{polymer}}(\omega\tau_s)$ of polybutadiene with $M = 18\,000$ (PB18000-h$_6$) obtained by subtracting the glassy spectrum from the total susceptibility spectrum[7] (black line) and by decomposition of the correlation function along eq 3 (red dots).

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Appendix

Subtraction versus Deconvolution. Figure 6 displays the polymer spectrum $\tilde{\chi}''_{\mathrm{polymer}}(\omega\tau_s)$ of PB18000-h$_6$ (data from ref 7) as obtained on the one hand (black solid line) by subtracting the glassy spectrum of PB466-h$_6$ from the total susceptibility master curve $\tilde{\chi}''(\omega\tau_s)$ and on the other hand (red dots) by decomposing the orientational correlation function $F_2(t)$ along eq 3. In the latter case, decomposing $F_2(t)$ by dividing out $\phi_{\mathrm{glass}}(t)$ consisting of a Kohlrausch function with a stretching parameter $\beta_K = 0.4$ and a relaxation strength $f = 0.16$ (cf. Table 2) yields $F_{\mathrm{polymer}}(t)$. Fourier transform back to the frequency domain again gives $\tilde{\chi}''_{\mathrm{polymer}}(\omega\tau_s)$. As it can be concluded from Figure 6, the two approaches lead to a very similar result, in particular the shape of spectrum and consequently the apparent power laws coincide for both methods provided that $M \gg M_e$ and $\omega\tau_s < 10^{-2}$. Therefore, the additive decomposition leading to the polymer spectra reflecting a universal behavior in Figure 3 is well justified in the present context.

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