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An Improved Method To Obtain Direct Rheological Evidence of Monomer Density Reequilibration for Entangled Polymer Melts

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Introduction

The concept of monomer density reequilibration along an entanglement segment as well as the concept of relaxation of this segment has been introduced in polymer physics since its beginnings,[1−3] but it has remained a theoretical concept for a long time because it was not possible to detect it experimentally. Recently, Liu et al.[4] were able to show that, for highly entangled linear polymers, the monomer density reequilibration can be obtained by deducting a Rouse model[5] (a line with slope 0.7) from its linear viscoelastic curves. However, although the corresponding signal had the strength of ~30% of the reptation process, its importance stays relatively weak in comparison to the much stronger glass transition process, with which it overlaps and which makes its detection difficult.

Spectra are the material function behind all experiments in the linear viscoelastic regime.[6] For describing rheological data, two types of spectra are commonly used: relaxation time and retardation time spectra. Both of them describe the importance of a process at a specific time. As the determination of a relaxation spectrum is an ill-posed problem, i.e., that different spectra can lead to the same dynamical response, a direct relationship between a frequency or a time and a specific relaxation time cannot be found.[7] Since the spectrum cannot be measured directly, it must be determined from the experimental dynamic data by approximating the real spectrum. To this end, several different approaches have been proposed in the past 20 years, able to deal with this ill-posed problem and which have been compared in refs 3 and 7. The continuous relaxation spectrum and the complex modulus are linked such as

$$G^*(\omega) = G'(\omega) + jG''(\omega) \tag{1}$$

with

$$G'(\omega) = G_\infty + \int_0^\infty H(\tau)\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right) \mathrm{d}\ln\tau \tag{2}$$

$$G''(\omega) = \int_0^\infty H(\tau)\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) \mathrm{d}\ln\tau \tag{3}$$

where $H(\tau)$ is the continuous relaxation spectrum, G_∞ is the modulus at infinitely low frequencies and is equal to 0 for thermoplastics, and τ are the different characteristic times.

Despite their ill-posed behavior, relaxation and retardation spectra are a viable tool in order to detect and characterize specific mechanisms. Indeed, while the influence of a relaxation process described by a characteristic time τ will be observed in the relaxation spectrum at time $t = \tau$, its influence in the frequency domain will be observed not only at the frequency ω equivalent to the inverse relaxation time $(1/\tau)$ but also on a much broader frequencies range (for details see ref 8). This leads to an attenuation of the signal, which can become difficult to detect. Therefore, using the spectrum method is comparable to using an antiblur filter in digital imaging: it enhances the importance of the signal corresponding to a specific relaxation time, which becomes detectable even at low intensity. In a spectrum, relaxation processes are more clearly separated than dynamic-mechanical such as the storage and loss moduli or the transient data such as the relaxation modulus $G(t)$. This makes it an extremely useful tool for finding weak processes next to stronger ones and thus a very good candidate for improving the method of characterizing the monomer density reequilibration.

However, they can also enhance artifacts and, thus, need to be analyzed cautiously, based on carefully selected experimental data. To avoid misinterpretation, different data sets of either the same or similar materials should be used.

Experimental Section

The data in this paper are mostly taken from papers by Liu et al.[4,9] and from Kapnistos et al.[10,11] All polymers except PS-275K are 1,4-polybutadienes with a very high stereoregularity, given by the low T_g around −99 °C. PS-275K is an atactic polystyrene. PBd-430K was purchased from Polymer Source and used as is. It was characterized using a TA Instruments ARES with 8 mm parallel plate geometries. By using a liquid nitrogen evaporating unit, the temperature was controlled between −95 and +100 °C. Frequency sweeps were carried out to ensure a shift factor around 100 between the individual temperatures. The data were manually shifted using thermal expansion, density correction, and a compliance correction. Further experimental details can be found elsewhere.[12]

The relaxation spectra of all samples were calculated using a self-programmed spectrum calculation routine based on determining the spectrum as a spline instead of individual relaxation modes like most other calculation routines.[7,8] This method ensures a very precise calculation of the relaxation spectrum, which is demonstrated in the Supporting Information.

The molecular data of the linear samples used in this study are given in Table 1.

The samples by Kapnistos et al.[11] are combs with starlike backbones, synthesized by the group of Hadjichistridis, University of Athens (Table 2). They are characterized by a 4-arm star

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Table 1. Molecular Data of the Linear Polybutadienes and Polystyrenes[a]

	M_w [kg/mol]	M_w/M_n	T_g [°C]
PBd-1.2M	1240	1.13	−99.5
PBd-430K	450	1.03	−98.0
PBd-100K	98.8	1.03	−97.5
PBd-39K	38.6	1.03	−98.0
PS-275K	275	n.a.	n.a.

[a] n.a. = data not available, M_w/M_n probably around 1.1, T_g ca. +95 °C.

Table 2. Molecular Data of the Star-Comb Polybutadienes

	f	M_b [kg/mol]	M_a kg/mol]	q
65-*g*-252-PBd	4	65	23.2	1.7
4sc1t2-PBd	4	28.5	11.5	13/4
4sc2-PBd	4	28.5	25	15/4

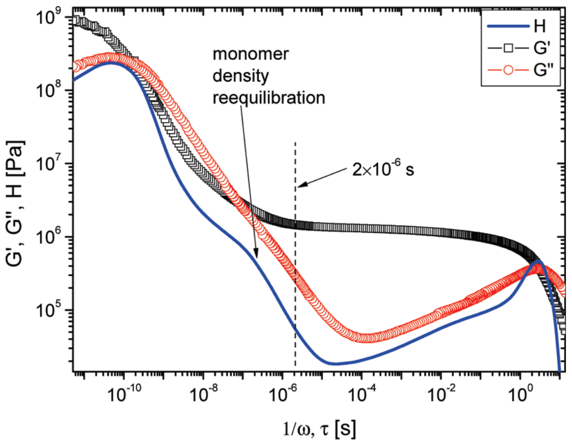

Figure 1. Relaxation spectrum $H(\tau)$, $G'(1/\omega)$, and $G''(1/\omega)$ for PBd-430K.

(f = 4) with 65 and 28.5 kg/mol backbone arm molar mass M_b. On each backbone arm are fixed several branches with a molar mass M_a of 12 or 23 kg/mol. For the sample with the longer star arms (65-*g*-252-PBd), 1.7 branches reside on each star arm (q); for the other star combs, between 3 and 4 branches per star arm are present. For further details about these polymers, see the original publication.[11]

Results

Figure 1 shows the relaxation spectrum H as a function of the relaxation time τ of PBd-430K, spanning from the glass transition to the terminal regime. The real and imaginary part of the complex modulus G' and G'' as a function of inverse angular frequency $1/\omega$ are also plotted in Figure 1.

As stated by Liu et al.,[4] pointing out the monomer density equilibration is not easy. The monomer density equilibration cannot be seen from $G''(\omega)$. In order to detect it from dynamical response, a tangent (see Figure 2) is necessary to find the small shoulder around 2×10^{-6} s. When looking at the spectrum (continuous curve in Figure 1), however, it is obvious that a small but clearly separated process exists around 10^{-7} s.

Using the method of Liu et al.,[4] i.e., subtracting a linear relation with a slope of around −0.7 (in this case −0.71) from $G''(1/\omega)$ (see Figure 2a), a weak shoulder is obtained at around 2.5×10^7 s, pointing out the monomeric density reequilibration. Its corresponding time is significantly below the time mentioned in Figure 1. However, this is not surprising when considering the different y-scaling. Here, we test a similar approach[4] on the relaxation spectrum (see Figure 2b). When taking the location of the shoulder, approximately the same time τ is obtained, which is coincidental considering that the methods differ distinctly in scaling and quantity.

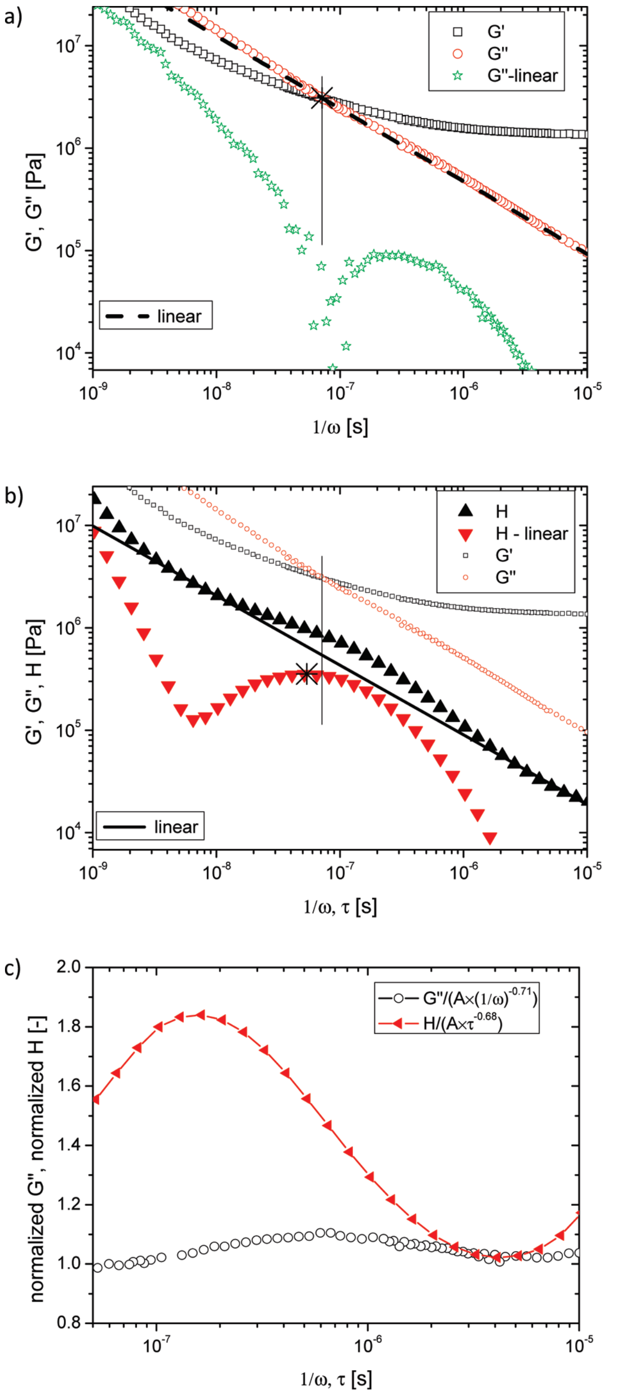

Figure 2. Zoom into the regime of the entanglement motion and monomer density reequilibration of PBd-430K: (a) $G'(1/\omega)$ and $G''(1/\omega)$, (b) $H(\tau)$ for PBd-430K including the subtracted straight lines, and (c) normalized $H(\tau)$ and $G''(1/\omega)$ using the same lines. Open symbols: data obtained from dynamic-mechanical tests; filled symbols: data from the relaxation spectrum.

In comparison to the subtraction of a linear relation from $G''(1/\omega)$, the subtraction of the linear relation from the relaxation spectrum—in this case with a slope of −0.68—leads to a much clearer peak, which, however, is located at a shorter relaxation time $\tau \approx 5 \times 10^{-8}$ s than the inverse frequency $1/\omega$ of the G'' subtraction (see the asterisk in Figure 2a). This clear peak is a very clear proof that the spectrum reveals the information more easily accessible than $G'(\omega)$ and $G''(\omega)$, although the spectrum is

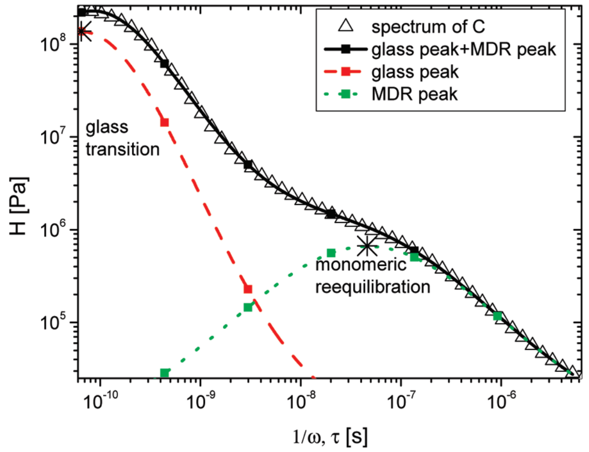

Figure 3. Fit of the glassy and MDR regime with two Gaussian functions.

calculated from these two quantities. The reason for this is clearly that the processes are smeared out in the frequency domain. This is comparable to the improved ability of the $\delta(|G^*|)$ plot or the plot of tan $\delta(\omega)$ for detecting thermorheological complexity in comparison to plots of $G'(\omega)$ and $G''(\omega)$.[13−16] In both cases, using a different way of plotting filters the information to highlight the effect of interest.

Figure 2c shows the normalization of $G''(1/\omega)$ and $H(\tau)$ by the fitted straight line, around the monomeric density reequilibration process. In this way, the reequilibration process is even better highlighted. The normalization of $G''(1/\omega)$ leads to a broad maximum around $\tau \approx 7 \times 10^{-7}$ s with a height of 1.1; i.e., the data only deviated by about 10% from the classically assumed behavior. On the other hand, the spectrum normalization leads to a clear peak around $\tau \approx 1.63 \times 10^{-7}$ s, i.e., around 4 times faster than the G'' maximum. The peak has a height of 1.8, which makes its deviation by about 80% from the assumed behavior, i.e., much more important than the deviation obtained from G''.

Furthermore, the peak of the spectrum appears at shorter times than the G'' peak. This is due to the fact that for the loss modulus the separation between the glass transition peak and this weak monomer density reequilibration process is much smaller due to the smearing out of the processes in the frequency domain and to the subsequent overlap by the glass transition. For the spectrum, the overlap in the relaxation time domain is much smaller and, thus, the processes can be separated much better. Because of this better separation, a clearer signal is found, which leads to a small difference between the monomeric density reequilibration time determined from the subtraction method (linear scaling) and from the normalization method (logarithmic scaling) (Figure 2c).

A close look at Figure 1 reveals that the relaxation times spectrum ranging between $\tau = 10^{-10}$ and 10^{-5} s shows two relaxation processes, which can be fitted by two Gaussian functions (for numerical reasons log H (log τ) was fitted). As shown in Figure 3, the result is an almost perfect fit of the two processes with characteristic relaxation times of 6.47×10^{-11} s (glass transition) and 4.65×10^{-8} s ($*$ in Figure 3), obtained by best fitting of the data. The relaxation time of 4.65×10^{-8} s for the MDR process almost perfectly agrees with the value obtained from the G'' subtraction method and is in very good agreement with the high-frequency crossover relaxation time usually attributed to τ_e.[4]

Using this fitting procedure on the relaxation spectrum, the admittedly weak MDR/τ_e process is, thus, determined without any ambiguity, offering a powerful and physically sounded approach to define these values.

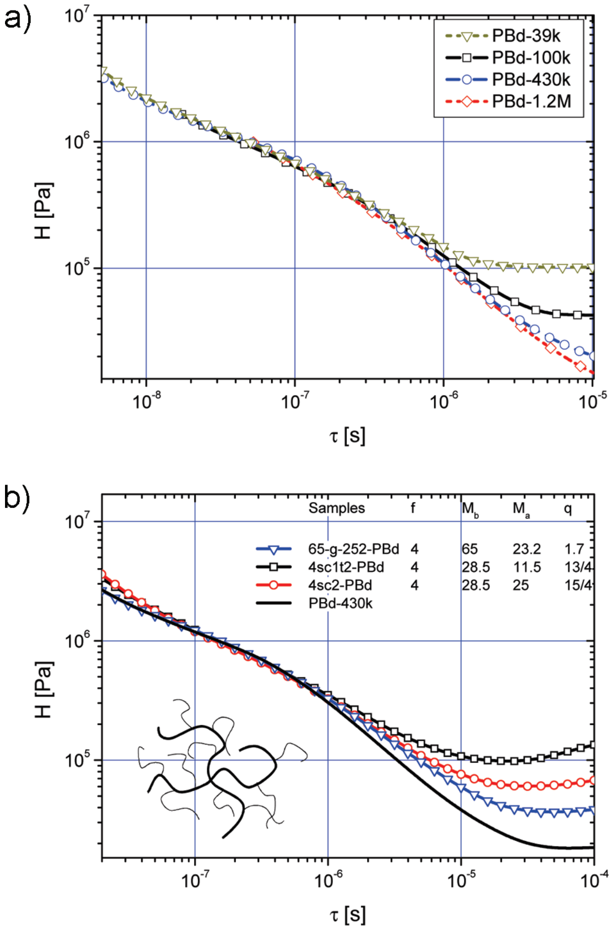

Figure 4. Comparison of the relaxation spectra $H(\tau)$ of the monomer density reequilibration regime of (a) linear monodisperse PBd and (b) comb samples with starlike backbones.

This interesting finding raises the question of its generality, which can be tested by analyzing the LVE data of other monodisperse polybutadienes with different molar masses. Liu et al.[4] found that they could only do the subtraction for highly entangled polymers (number of entanglements $Z > 200$). Their lowest entangled sample was a polybutadiene with $M = 410$ kg/mol, about the same molar mass as PBd-430K used in this article.

Figure 4a shows the relevant area for four polybutadienes with molar masses M of 39, 100, 430, and 1200 kg/mol.[9] In all cases, a clear shoulder is obvious in the spectrum. In fact, the spectra are almost undistinguishable below $\tau \approx 7 \times 10^{-7}$ s, which is slightly slower than the monomer density reequilibration (cf. Figure 3). This confirms the quality of the spectra (and, thus, the chosen input data) as well as the molecular models, according to which before the monomer reequilibration time, only motions below one entanglement are possible and, thus, no molar mass dependence should be present.[3,6]

In Figure 4b, the spectra of linear polymers are compared to the one of branched architectures. In this last case, the molar mass is quite high in total, but the individual molecular segments of the star with comblike backbones are relatively short. Please note that the data of PBd-430K in Figure 4b were shifted along the time axis by a factor $a_T = 3$ to compensate for the differences in reference temperature T_0. Comparing the spectra of all well-entangled linear and model branched polymers described in Tables 1 and 2, one can conclude that this shoulder in the glass transition peak always appears and is independent from the molar mass and the architecture of the polymer. This universality indicates that the process indeed is a process which is related

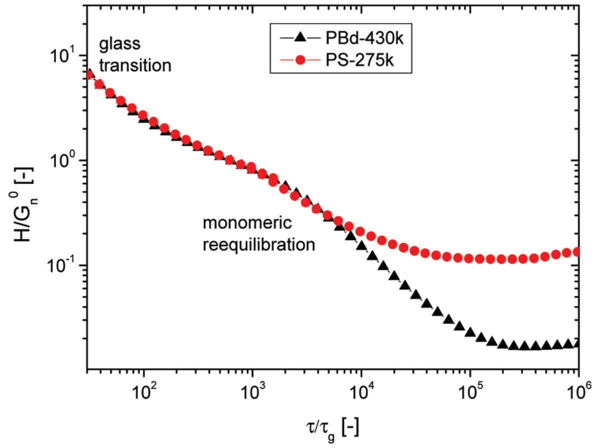

Figure 5. Comparison of the relaxation spectra $H(\tau)$ of the monomer density reequilibration regime of PBd-430K and PS-275K, normalized to G_n^0 and glass transition relaxation time.

to the molecular structure on a level which is not sensitive to molecular topography (as branches, molar mass, etc.). The conclusion of Liu et al.[4] to identify this process as the entanglement relaxation time is the logical consequence. The fact that it occurs on the same time scale as the entanglement relaxation processes identified previously in the literature[4] confirms this conclusion. Of course, the time scale of this process depends on reference temperature (of the master curve of the input data) and the chemical composition of the polymer chosen.

The dependence on chemistry and reference temperature can be eliminated by normalizing the data on the time scale of a well-defined molar mass and architecture independent process. The glass transition is destined for this normalization, as it is the quite strong and molar mass independent. Figure 5 shows data for samples with a different chemical composition (PS and PBd). The *x*-axis was normalized by the glass transition time, determined from the spectrum around the glassy peak, while the *y*-axis was normalized by the plateau modulus G_N^0.[17] It is obvious from this comparison that, for times shorter than the MDR time, the shape of the relaxation spectrum is identical within the experimental error and, thus, a constant factor between relaxation time of the glass transition and the monomer density reequilibration exists. The experimental confirmation of this by spectra gives raise to the assumption of mesoscopic molecular models that the exact chemical composition of a sample is not important. The dependence of the chemical composition is covered by the three polymer and temperature specific parameters: the entanglement molar mass M_e, the plateau modulus G_N^0, and the entanglement relaxation time τ_e.

The finding that relaxation spectra of the glassy and MDR processes are identical confirms these assumptions, which have been used for a long time.

Summary

The detection of the monomer density reequilibration mechanism can be achieved with a good signal-to-noise ratio by using the relaxation spectrum instead of the loss modulus. When normalizing both functions, the signal detected by the spectrum is 8−9 times larger than that of the loss modulus. This shows clearly that spectra are a very powerful tool to highlight molecular processes, albeit the fact that spectra are only recalculated linear viscoelastic data.

Table 3 shows the comparison between the different values of the monomeric density equilibration time τ_{MDR} for PBd-430K, introduced in the discussions around Figures 2 and 3. It is obvious that the spread is relatively large. The location of the peak is at slightly shorter relaxation times than for the loss modulus, but that is an artifact of the broader glass transition peak in the loss modulus than in the spectrum.

Table 3. Comparison of the Different Methods for Determining the Monomeric Density Equilibration Time τ_{MDR}

method	relaxation time [s]
normalization method $G''(1/\omega)$	7×10^{-7}
subtraction method $G''(1/\omega)$	2.5×10^{-7}
normalization method $H(\tau)$	1.63×10^{-7}
subtraction method $H(\tau)$	5.4×10^{-8}
fit of $H(\tau)$	4.65×10^{-8}
inverse crossover frequency $(1/\omega_c)$	7.14×10^{-8}

The determination from the spectrum leads to values which lie about 0.2 decades away from the inverse crossover frequency $1/\omega_c$, which, considering the large time scales of rheological tests and the still weak signal, is quite good. The fact that the subtraction method leads to higher relaxation times than the normalization and the fit method is logical considering that the subtraction method determines the difference in absolute numbers, the other two methods determine ratios and, thus, tend to find the lower one of two adjacent peaks of distinctly different height closer to the higher peak.

Several other architectures were also tested with this method and were found to also fulfill the relations. The monomer density reequilibration mechanism's time regime is chemistry and molecular architecture independent relative to the glass transition and thus identified to be identical with the entanglement motion time τ_e.

This indicates that spectra offer a universal approach for the proper detection of weak processes such as the monomer density reequilibration.

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Supporting Information Available: Reproducibility of the spectrum calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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