Viscoelastic Behavior of Polybutadienes with High 1,4-Microstructure and Narrow Molecular Weight Distribution

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ABSTRACT: Polybutadienes (PBs) of narrow molecular weight distributions with high 1,4-microstructure were synthesized by *sec*-butyllithium-initiated, living polymerization. The shoulder-like anomalous behavior of the storage modulus $G'(\omega)$ in the terminal zone for PBs was studied using size exclusion chromatography (SEC) and rheometric mechanical spectrometry (RMS). It was found that a high-molecular-weight fraction in the PBs was the main reason for the occurrence of the shoulders. The linear viscoelastic spectra were successfully obtained by the Pade–Laplace method from experimental dynamic data, using either the dynamic storage, $G'(\omega)$, or loss, $G''(\omega)$, modulus. Both the dynamic moduli and stress relaxation in the linear regime were then calculated with reasonable precision. The feasibility of time–temperature–molecular weight superposition for PBs using this method was demonstrated. The dependencies of relaxation spectra on temperature and molecular weight were obtained by a fitting procedure. Thus, with a known reference state, the relaxation spectrum for a given molecular weight PB at a given temperature can be predicted. The predicted dynamic moduli are in good agreement with experimental data. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1315–1324, 1999

Key words: Polybutadiene; viscoelastic; master curve; prediction; dynamic moduli

INTRODUCTION

Polymers with narrow molecular weight distributions and long flexible chains display very distinct rheological behavior in the linear viscoelastic regime. This can be observed experimentally through the dynamic storage and loss moduli. Since the 1950s, many theoretical attempts have been made to describe the linear viscoelasticity for these polymers, based on simplified models of macromolecular motion.[1–5] The bead-and-spring model proposed first by Rouse[1] for dilute polymer solutions was then extended for polymer melts and has reached a high level of sophistication today (for a review, see, for example, Bird et al.[2]). Additionally, some types of topological constraints imposed on the motion of a single macromolecule by the surrounding ones were taken into account by the reptation models.[3] Alternative stochastic models for the motion of a single macromolecule in a macromolecular environment were developed based on the idea of relaxation interactions (for example, see Volkov et al.[4]), and, more strictly, using the mode–mode coupling approach (for example, see Schweizer[5]). Unfortunately, the theoretical predictions are still unreliable.

It is well known that for any viscoelastic liquid, the log–log plots of $G'(\omega)$ and $G''(\omega)$ should exhibit in the terminal zone ($\omega \rightarrow 0$) slopes equal to

2 and 1, respectively. However for monodispersed linear flexible polymers, some publications[6–9] have revealed discrepancies between the experimentally observed and the expected slopes. This is especially true for $G'(\omega)$ data for such popular well-defined polymers as polybutadiene (PB) and polystyrene (PS) with narrow molecular weight distributions. It was noticed that $G'(\omega)$ displays a shoulder-like trend at low frequencies. This anomaly might be simply explained by some material defects or instrument limitations. Also, a hypothetical super-slow relaxation mechanism was introduced in articles[10,11] to theoretically explain this shoulder-like behavior. One of our objectives in this article is to clarify the situation.

The linear viscoelastic relaxation spectrum is the basic building block for all rheological studies of polymers. However, the straightforward regression procedure for obtaining the spectrum from the dynamic data was found to be ill-posed.[12] One possible way to obtain the spectrum is the Pade–Laplace (PL) method.[13] This method is well posed since it works on the analytic continuation of the dynamic data in the complex frequency domain. The extension of this method, along with some applications, was given in a recent article.[14] We will use this method below to study the relaxation behavior of our samples.

The time–temperature superposition principle requires that all relaxation modes have the same temperature dependencies. Therefore, the master curves for dynamic moduli can be constructed by a shifting procedure on the logarithmic plots at a reference temperature to predict the behavior at other temperatures. However, it was reported[8,15,16] that this principle is applicable for amorphous polymers only within a certain time–temperature range. It is also of interest to verify the feasibility of the time–temperature–molecular weight superposition principle. Up to date, this principle has only been applied to the Newtonian viscosity of long chain flexible polymers[17] and is known as the rule of logarithmic additivity.

EXPERIMENTS

Sample Preparation and Characterization

Benzene[18] and butadiene[19] were purified as described previously.[18] *sec*-Butyllitium (Foote Mineral Corp., 12 wt % in cyclohexane) was used as received and titrated using the Gilman double titration method with 1,2-dibromethane.[20] All poly-

merizations were carried out in all-glass, sealed reactors using breakseals and standard high-vacuum techniques.[21] Butadiene polymerizations using *sec*-butyllithium as the initiator were carried out in benzene (5–10 vol % butadiene) at room temperature for a period of 12 h and terminated by addition of several milliliters of degassed methanol via a breakseal. Polymers were isolated by precipitation of the benzene solutions into excess methanol and then dried at room temperature under vacuum. Molecular weights and molecular weight distributions of PBs were determined by size exclusion chromatography (SEC) analyses at a flow rate of 1.0 mL/min in tetrahydrofuran at 30°C using a Waters high-pressure liquid chromatography (HPLC) component system [refractive index (RI) detector] equipped with four ultra-μ-styragel columns (1×10^3, 1×10^4, 1×10^5, and 1×10^6 Å) after calibration with PB standards from American Polymer Standards Corp. ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Varian Gemini-200 spectrometer using deuterated chloroform (Aldrich, 99.8% CDCl$_3$) as solvent and polymer concentrations of 15 wt %. Spectra for quantitative microstructure analyses were recorded using a 5.0 s delay time and a total of 65,536 transients. The microstructure of PB was determined by ^{13}C-NMR by integration using the peak assignments described by Frankland et al.[22] The molecular characterization data for these PB samples are listed in Table I.

Rheological Measurements

Linear viscoelastic measurements were performed using the Rheometrics Mechanical Spectrometer (RMS-800) with a 2000 g-cm transducer. The geometry of the testing fixture was parallel plates with a diameter of 25 mm. Small strain oscillation and stress relaxation experiments were carried out at 30, 60, and 90°C under 5% strain amplitude in a nitrogen environment. Four runs were performed for each test, with the mean data shown below.

RESULTS AND DISCUSSIONS

Terminal Shoulder-Like Anomalous Behavior

In accordance with the literature observations,[6–9] the storage modulus $G'(\omega)$ for our PB samples also displayed a shoulder-like trend at low fre-

Table I   Molecular Characterization of Polybutadienes

| Sample | $M_w(\times 10^{-3})$ (g/mol)[a] | M_w/M_n | Microstructure (mol %)[b] | | |
			cis-1,4	trans-1,4	Vinyl
B97	97	1.04	43	51	6
PB225	220	1.06	50	46	4
PB361	360	1.03	52	40	8

[a] Determined by SEC using polybutadiene standards obtained from American Polymer Standard Corp.

[b] Determined by ^{13}C-NMR spectroscopy using the assignments of Edwards et al.[22]

quencies. A typical anomaly for PB361 at 30°C is seen in Figure 1, where, at lower frequencies, $G'(\omega)$ deviates from the reference dashed line with the slope of 2.

We suspected that the existence of a high molecular fraction was responsible for this anomalous behavior. To verify this assumption, both SEC and the rheological methods were used. Fresh samples (PB361 and PB225) were heat-treated in a vacuum oven for 5 and 30 h at 90°C, respectively. Then the samples were characterized with SEC. The results are shown in Figure 2. Here, a small higher-molecular-weight shoulder peak appears at a shorter retention volume for samples with 30 h of treatment. No shoulders can be distinguished for samples after the 5-h treatment. It was obvious that a high molecular frac-

tion was formed due to oxidation,[23] and its amount in some cases might be too small to be detected by SEC. Since the storage modulus G' is very sensitive to the high molecular fraction in the terminal zone, sample PB361 was consecu-

Figure 1   Description of G' and G'' for PB361 with 6 refined relaxation modes at 30°C.

Figure 2   SEC results for PB361: (a) fresh sample (without treatment); (b) 5-h treatment in vacuum at 90°C; (c) 30-h treatment in vacuum at 90°C.

Figure 3 G' and G'' data for the sample PB361 at 90°C with different thermal histories.

Table II   Relaxation Modes Obtained by PL Method for PB361 at 30°C

θ_k (s)	G_k (Pa)
0.009	1.49×10^5
0.070	7.20×10^4
0.141	5.10×10^4
0.770	2.40×10^5
7.27	5.37×10^5
398	2.30×10^2

experimental window has covered the relaxation time regime. Table II gives an example of the set of relaxation modes for PB361 at 30°C, obtained by the PL method using only $G'(\omega)$. Good agreement between the calculated dynamic moduli, $G'(\omega)$ and $G''(\omega)$, based on the set of modes and experimental data is shown in Figure 1. With the same relaxation modes, the stress relaxation process was predicted. The comparison with experimental data is presented in Figure 4.

The relaxation spectra were then used to calculate the Newtonian (zero shear) viscosity, η_0, for PBs, using the following well-known expression:

$$\eta_0 = \sum_{i=1}^{n} G_i \theta_i \tag{1}$$

tively tested under frequency sweep mode 4 times at 90°C during 13 h on the RMS. The results shown in Figure 3 indicate that the plot $G'(\omega)$ in the low frequency region changes dramatically with the thermal history of the sample. It is seen that the samples with longer heat treatment at 90°C display a higher anomalous shoulder in $G'(\omega)$ due to the higher degree of oxidation. Based on the demonstration of the SEC and RMS results, it is also highly possible that a small amount of high-molecular-weight fraction exists in the fresh samples, which leads to the shoulder in the terminal zone. The existence of this fraction can be detected by low frequency $G'(\omega)$ measurements, but not by SEC, since SEC with a refractive index detector is not sensitive enough. Similar anomalous behavior was also observed for blends of narrowly distributed polymers with small amounts of a high-molecular-weight fraction.[24–28]

Relaxation Spectra

Discrete relaxation spectra for PB samples were obtained using the Pade–Laplace method. The basic procedure includes obtaining primary data for relaxation modes from Pade tables using $G'(\omega)$ or $G''(\omega)$ data, followed by refinement of the set of relaxation parameters.[14] It should be mentioned that the relaxation processes for our PB samples required < 60 s. Hence, the oscillatory

Figure 4 Comparisons of calculated stress relaxation and experimental data for PB361 at different temperatures.

Figure 5 Relaxation times versus molecular weight for PBs at 30°C.

The value of η_0 was also independently obtained from the loss modulus data as

$$\eta_0 = \lim_{\omega \to 0} G''/\omega \qquad (2)$$

It was confirmed that the values of η_0 obtained by both methods are almost the same. It was also

Figure 6 G' time–temperature master curves for PBs reduced to the reference temperature of 30°C.

Figure 7 G' and G'' master–master curve for PBs reduced to the reference temperature of 30°C and the reference molecular weight of PB361.

found that the dependence of η_0 on molecular weight follows the familiar power law (for example, see Vinogradov and Malkin[17]) with the values of the exponents ranging from 3.22 to 3.46.

Figure 8 Comparison of G' and G'' for sample PB225 at 60°C between experimental data and the predictions with 6 relaxation modes shifted from the reference state (PB361 at 30°C).

Figure 9 G' and G'' master–master curve for our PBs and literature data[30] reduced to the reference temperature of 30°C and the reference molecular weight of PB361.

The plots of the three longest relaxation times (in decreasing order, 1–3) versus molecular weight are shown in Figure 5. It is seen that the sample PB361 exhibits an unusual high modulus mode, which significantly departs from the reference dashed line with the slope of 3.4. This mode, which was found by the PL method, seemingly corresponds to the high-molecular-weight fraction in the sample. Since those high-modulus modes are more involved in the terminal relaxation behavior, our results in Figure 5 indicate that the first and second longest relaxation times might have power law dependence on molecular weight, similar to that found for the zero shear viscosity. The same observation was reported by Baumgaertel et al.[7] for narrow molecular weight distribution PBs with high molecular weight.

Time–Temperature–Molecular Weight Superposition

In spite of the doubts expressed in some articles,[8,15,16] we found that the principle of time–temperature superposition is valid in our experi-

ments. Thus the dynamic moduli at 60 and 90°C could be successfully shifted for our three PBs to the reference temperature of 30°C. The corresponding master curves are shown in Figure 6. The temperature shift factor can also be expressed according to the following WLF relation

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0}. \qquad (3)$$

The values of C_1 and C_2 obtained from our experiments were found to be equal to 3.507 and 171.2, respectively. These agree well with the reported values, $C_1 = 3.64$, $C_2 = 186.5$, for PBs with similar microstructure.[29] As in Rochefort et al.,[30] the temperature shift factors were found to be independent of molecular weight. A slight temperature dependent shift in the vertical direction was also required.

It is of interest to reduce time–temperature master curves of different molecular weights to the reference state, PB361 at 30°C. Figure 7 indicates that such a master–master curve is feasi-

Figure 10 The relaxation time shift factor versus molecular weight for narrowly distributed PBs. The filled circles are from our samples and the open ones are from Rochefort et al.[30]

ble. Slight deviations at the highest and lowest frequency regions are due to frequency cut-off and presumably the existence of a high-molecular-weight fraction. Besides the time–molecular weight shift applied horizontally, a slight vertical shift was also needed.

In both shifting procedures, we have used the following logarithmic additive formulae for temperature and molecular weight dependencies of relaxation spectra:

$$\theta_i(T, M_w) = \theta_{ir} \cdot a(T) \cdot c(M_w); \qquad (4a)$$

$$G_i(T, M_w) = G_{ir}/[b(T) \cdot d(M_w)]. \qquad (4b)$$

Here θ_{ir} and G_{ir} are the relaxation times and moduli of the reference sample PB361 at the reference temperature 30°C. The shift factors were found by a fitting procedure as

$$a(T) = 3.27 \times 10^{-6} \cdot \exp(3820/T) \qquad (5a)$$

$$b(T) = 0.173 \cdot \exp(529/T) \qquad (5b)$$

$$c(M_w) = 3.00 \times 10^{-9} \cdot M_w^{3.3} \qquad (5c)$$

$$d(M_w) = 0.57 \cdot M_w^{0.095} \qquad (5d)$$

Using the above formulas, the viscoelastic spectrum for a given molecular weight PB at a given temperature can be predicted. The example shown in Figure 8 demonstrates the agreement between the dynamic experimental data and the calculations based on the predicted spectrum for PB225 at 60°C.

To confirm the feasibility of the time–temperature–molecular weight superposition, we also employed the available literature dynamic data for polybutadiene.[28] Figure 9 shows the master–master curve that consists of 8 time–temperature master curves[28] and three of ours. They were shifted horizontally and slightly vertically to the reference state (PB361 at 30°C). The plot of time–

Figure 11 The relaxation modulus shift factor vs molecular weight for narrowly distributed PBs. The filled circles are from our samples and the open ones from Ref. [30].

molecular weight shift factors versus molecular weight is shown in Figure 10. These are well fit to a power law relation. The regression result is similar to eq. (5c), as follows:

$$c(M_w) = 1.50 \times 10^{-9} \cdot M_w^{3.426} \qquad (6)$$

However, unlike our data related to $d(M_w)$, modulus–molecular weight shift factors seem not to follow any rule, as shown in Figure 11. It will be difficult to accurately predict the PBs' spectra without a good regression of $d(M_w)$. Yet, an attempt to predict the dynamic data for the sample 347L using eq. (4a and b), (5a, b, and d), and (6) is shown in Figure 12. It is seen that the predicted dynamic moduli are in good agreement at lower frequencies. In the plateau zone, moduli are underpredicted due to eq. (5d). It is not clear what is the cause of the failure with vertical shifts for PBs[25] of different molecular weights. Some possible reasons might be related to problems with calibration of the instrument or differences in the structures of the polymers.

CONCLUSIONS

Our SEC and RMS results demonstrate that narrow molecular weight distribution PBs can be oxidized to cause branching and crosslinking when exposed to oxygen at elevated temperatures. The anomalous shoulder-like $G'(\omega)$ data in the terminal zone is likely due to the existence of very small amounts of a high-molecular-weight fraction. Therefore, the explanation of such anomaly by the physical super-slow relaxation mechanism,[10,11] if based only on such shoulder-like observations, seems questionable. Relaxation spectra can be successfully obtained from dynamic data by the Pade–Laplace method. Time–temperature–molecular weight master–master curves can be constructed in most cases. Therefore, with

Figure 12 The experimental data and predictions of G' and G'' with 6 relaxation modes shifted from the reference state (PB361 at 30°C) for sample 146L[30] at 24.5°C.

the relaxation spectrum for the reference PB at the reference temperature, one can predict the linear viscoelastic behavior of narrow-molecular-weight distribution PBs with different molecular weights and at different temperatures, at least within our experimental window.

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