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ORIGINAL CONTRIBUTION

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Rheological characterization and modeling of end-functionalized polybutadienes

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Abstract The rheological characterization and modeling of a series of polybutadienes obtained by anionic solution polymerization is presented in this work. The polybutadienes are synthesized using two different initiators: R,R′,R″-silyloxyalkyllithium (F1) and R,R′,R″-silylalkyllithium (F3). In addition, a polybutadiene obtained with a conventional alkyllithium initiator (*n*-butyllithium) is used as a reference.
The rheological characterization is carried out under small amplitude oscillatory shear in the stress-controlled mode. Microstructure, molecular weight, and molecular weight distribution are determined by FTIR and GPC. The vinyl content of the polybutadienes synthesized using the functionalized initiators is similar to that obtained with *n*-butyllithium (8–11%). Materials obtained with F1 show a relatively low polydispersity within a narrow molecular weight range (250,000–300,000 g/mol), while samples obtained with F3 cover a wider range of molecular weights (65,000–670,000 g/mol) and display higher values of polydispersity. In all cases, a parallel reaction using propylene oxide in the termination step is done to place a functional group at the chain ends. The effect of this group on the rheological behavior appears to be negligible. Three rheological models are used and their predictions of the experimental data are compared. The models include the Doi and Edwards reptation model, expressions using a discrete spectrum of relaxation times based in the rubber-like liquid constitutive equation and the fractional Maxwell equation in which a given analytical relaxation-spectrum is used. Relevant relations are obtained between the models' parameters and the molecular properties of these systems, which in turn are related to the presence of functional groups at the polymer chain ends.

Keywords Polybutadiene · Anionic polymerization · Functionalized initiators · Small amplitude oscillatory

Introduction

Anionic polymerization has the advantage that the polymer chains maintain their reactivity once the monomer has been consumed. This opens up the possibility to have specific control over the molecular architecture of the polymer through termination reactions, which among other things facilitate the synthesis of end-functionalized polymers. An interesting process to develop functionalized polymers is based on using reactive initiators with functional groups that remain at the chain end of the growing molecule once the polymerization process has been completed. In this regard, the use of alkyllithium initiators containing functional groups has been proven to be a versatile method to prepare functionalized elastomers.

In an anionic polymerization process, a functionalized initiator produces a macromolecule with its correspondent functional group at one end and an active carbanion at the other. Thus, in contrast to most functionalization processes involving termination reactions with electrophilic groups, the use of a functionalized initiator maintains intact the anionic end of the chain and enables the preparation of block copolymers, stars, or other specific molecular architectures. This in turn is a useful procedure to synthesize telechelic polymers, in which a functional group is provided by the initiator and the other is obtained through a termination reaction.

In this work, two different functional initiators are used to synthesize polybutadienes with different molecular weights and molecular weight distributions, without altering the polymer microstructure. A silyloxy-type initiator (F1) is used to synthesize polybutadienes with narrow molecular weight distributions and similar molecular weights (250,000–300,000 g/mol). In addition, a silyl-type initiator (F3) is used to produce samples within a wider range of molecular weights (65,000–670,000 g/mol), which in general turn out to be more polydisperse. The rheological behavior of these end-functionalized polybutadienes has been characterized and compared to that of a polybutadiene sample obtained using a conventional alkyllithium initiator. This rheological characterization enables one to relate the linear viscoelastic behavior of these materials to their molecular characteristics. In addition, the rheological response has been modeled to correlate the basic features of the polymeric systems with their viscoelastic response and to provide a molecular insight of the models' parameters used. The selected rheological models include the Doi and Edwards reptation model, expressions using a discrete spectrum of relaxation times based in the rubber-like constitutive equation and the fractional Maxwell model, in which existing analytical expressions for the relaxation spectrum are employed. It is found that only one sample is properly fitted with the Doi and Edwards model, using a single relaxation time behavior in the low frequency range of the spectrum. In contrast, most of the functionalized polybutadienes exhibit a more complex rheological behavior due to polydispersity, low molecular weight fractions, and additional relaxation modes in the terminal or in the plateau region of the spectrum.

Experimental

Polybutadiene samples are prepared by anionic polymerization in solution. 1,3-Butadiene polymerization is carried out in cyclohexane, using two functionalized initiators: R,R′,R″-silyloxyalkyllithium (F1) and R,R′,R″-silylalkyllithium (F3). In both initiators, the R, R′, and R″ represent alkyl groups containing between one to four carbon atoms in their structure. Another sample is polymerized with *n*-butyllithium and used as a reference (PB-701).

The polymerization is carried out at 70 °C, using a 10/1 solvent to monomer ratio, which enables the control of the viscosity of the reacting solution. Prior to their injection to the reactor, both monomer and solvent are purified using a set of packed columns filled with molecular mesh and activated alumina. Once the system is water- and impurity-free, the initiator is injected to the solution and the polymerization is started. Both F1 and F3 initiators yield α-functionalized polybutadienes after addition of a measured amount of isopropanol, which deactivates the growing chain. In all cases, a parallel reaction using propylene oxide in the termination step is done in order to introduce a terminal hydroxyl group at the chain ends, rendering α,ω-functionalized polybutadienes. To prevent oxidation of the polymers, *tert*-butylhydroxytoluene (BHT), Irganox-1076, and trinonylphenylphosphine (TNPP) are added after termination. Polymer samples are classified according to the type of initiator (F1 or F3) and if appropriate, by the presence of the hydroxyl group included after the termination with propylene oxide (X).

Polymer samples are characterized by infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). The FTIR analysis is carried out in solution, using a KBr cell and CS_2 as solvent at a polymer concentration of 0.0115 g/ml. 1,4-trans and 1,2-vinyl double bonds are identified from their corresponding absorbance signals at 966 and 910 cm^{-1}, respectively. A reference sample with 49% of 1,4-*trans* and 10% of 1,2-vinyl double bonds, characterized independently by FTIR, carbon, and hydrogen NMR, is used for the quantitative determination of the microstructure of the functionalized polybutadienes. Average molecular weights and molecular weight distributions are determined by GPC analysis carried out in THF at 30 °C using polystyrene/divinylbenzene packed columns, with a flow rate of 1 ml/min. The GPC columns are calibrated using polystyrene standards, so that the average molecular weights reported in this study are in all cases polystyrene-equivalent molecular weights.

Finally, the rheometric characterization is performed in a Carri-med CSL 500 controlled stress rheometer equipped with a 4-cm, 2° cone and plate fixture. Small amplitude oscillatory shear flow renders the linear viscoelastic properties of the polymer systems.

Results and discussion

Microstructure and molecular weight distribution

It is well known that vinyl group content substantially influences the glass transition temperature of polybutadiene and hence its rheological behavior (Carella et al. 1984; Alcantar et al. 1995; Hsieh and Quirk 1996). A high concentration of vinyl groups modifies the glass transition to values near –5 °C, which is usually accompanied with lower relaxation times and a lower shear viscosity. Microstructure control using non-polar solvents like cyclohexane and alkyllithium initiators usually leads to materials with 8–12% vinyl content. In this work, samples within this range of vinyl content are obtained. Results of the infrared analysis are shown in Table 1 for the case of four representative samples and a polybutadiene reference, in which the F1, F3, and *n*-butyllithium initiators are used. As seen in this table, regardless of the initiator employed, low vinyl content is kept in all samples, resulting in vinyl contents that range between 9 and 10%. These

Table 1 Microstructure of samples obtained using different polymerization initiators

Sample	Initiator	Absorbance 1,4-trans 966 cm^{-1}	Absorbance 1,2-vinyl 910 cm^{-1}	1,4-trans (%)	1,2-vinyl (%)
Standard	*n*-BuLi	0.74	0.2	49	10
F3602	IF3	0.77	0.178	51.2	8.94
F3602X	IF3	0.775	0.185	51.63	9.31
F1801	IF1	0.735	0.195	49.05	9.83
F1801X	IF1	0.735	0.2	49.05	10.08
PB-701	*n*-BuLi	0.775	0.195	51.76	9.83

results suggest that any changes observed in the rheological behavior of samples synthesized with different initiators (F1 or F3) do not arise as a consequence of observed differences in their microstructure.

The rheological behavior is also strongly influenced by molecular weight and molecular weight distribution. For instance, the equilibrium shear compliance has been shown to be strongly altered by polydispersity (Choi et al. 1988; Struglinski and Graessley 1985; Meister 1989; Montfort et al. 1986; Ngai and Plazek 1986) and very sensitive to the elasticity of the material, and hence to the proportion of long chains in the polymeric matrix (Montfort et al. 1986; Watanabe and Tirrell 1989). Table 2 shows results of the synthesized structures with respect to number-average molecular weight, polydispersity, and type of distribution. As shown in this table, nearly monodisperse materials are obtained with F1 and higher polydispersity is generally observed in the F3 series. Also, to analyze further the effect of polydispersity on the rheological response, two samples were synthesized with a bimodal distribution of molecular weights (F3703 and F3703X) using the F3 initiator.

Polydispersity influence can be quantitatively analyzed by considering the variation of the imaginary part of the complex viscosity (η'') with frequency. The height of the observed peaks is proportional to the concentration of species in the sample, such that a peak observed at low frequencies would increase with higher long chain fractions, and in the same manner, a peak located at high frequencies would increase with the fraction of short chains. This is based on the fact that the peak at high frequencies, which describes the dynamic response of the short chains, would shift to lower frequencies due to an increase in the elastic component of the modulus brought about by the long chains. In Fig. 1, the normalized imaginary part of the complex viscosity is plotted as a function of frequency for the F3703 and F3703X bimodal samples. Only one peak is observed at high frequencies and corresponds to the response of the short chains within these samples. This might be related to the small high molecular weight content in these samples (14%), which is probably negligible for the case of the modulus spectrum. As observed, the increase in the long chain fraction promotes both a decrease in the height of the peak in the viscosity function and also a shift towards lower frequencies of the maximum in the viscosity function. These results suggest that, even in these samples in which a bimodal distribution of molecular weights is observed, the rheological response is dominated by the predominant component in the sample, which in these particular cases correspond to the short chains. A highly cooperative type of relaxation process is expected to occur in samples in which the two characteristic species show significant differences in

Table 2 Average molecular weights, polydispersity and type of molecular weight distribution for the samples synthesized in this study

Sample	Mn×10^{-3}	Mp (Peak)×10^{-3}	Mw×10^{-3}	Mw/Mn	Distribution
F1602	255.4	276.6	274.1	1.073	Monomodal
F1602X	257.5	275.7	270.8	1.051	Monomodal
F1703	266.2	275.7	281.7	1.058	Monomodal
F1703X	277.7	303.6	297.0	1.069	Monomodal
F1801	239.8	248.5	254.3	1.060	Monomodal
F1801X	239.7	253.5	256.4	1.070	Monomodal
F3602	51.1	76.8	65.7	1.286	Monomodal
F3602X	51.5	80.0	68.0	1.320	Monomodal
F3701	568.7	681.4	667.2	1.173	Monomodal
F3701X	549.1	694.3	657.6	1.198	Monomodal
F3703	89.6	115.0 (85%) 270.9 (15%)	124.2	1.386	Bimodal
F3703X	98.8	124.6 (87%) 279.8 (13%)	131.6	1.331	Bimodal
F3801	173.0	244.6	225.1	1.300	Monomodal
F3801X	147.0	242.6	207.8	1.413	Monomodal
PB-701	160.9	183.4	182.1	1.131	Monomodal

relaxation times as described by Kasehagen et al. (1996) for the case of branched polymers.

Zero shear-rate viscosity

From the rheometrical data in oscillatory simple shear, the viscosity at vanishing shear rates η_o is obtained using the following expressions:

$$\eta_0 = \frac{\pi^2}{12} G_0 \lambda \tag{1}$$

$$\eta_0 = 2.21 \left[\frac{G'(\omega)}{\omega} \right]_{\max} \tag{2}$$

where G_o is the plateau modulus, λ ($\lambda = 1/\omega_c$) is a reference relaxation time, ω_c is the corresponding frequency at the crossing of the dynamic moduli $G'(\omega)$ and $G''(\omega)$, and ω is the frequency of the oscillations. Equation (1) was proposed in the Doi and Edwards reptation model (Doi and Edwards 1979) and has been tested in polybutadiene samples with polydispersity values less than 1.7 with fairly good results (Rahalkar 1990). Equation (2) was proposed by Colby et al. (1987), and it considers the maximum of the imaginary part of the complex viscosity $\eta''(\omega) = G'(\omega)/\omega$ as a description of the zero shear-rate viscosity. This equation is valid for polybutadiene samples with a narrow molecular weight distribution.

The complete set of results of the experimentally determined zero shear-rate viscosity at 50 °C for all the samples in this study as compared with the calculated values from Eqs. (1) and (2) can be found in the Electronic Supplementary Material of this paper. In general, both equations give reasonable predictions of the zero shear-rate viscosity. The largest difference corresponds to sample F3703 (14%), which presents a bimodal distribution of molecular weights. Evidently these observations suggest that the effect of high polydispersity effects is not considered in any of these equations.

It is well known that the viscosity at zero shear-rate follows a power-law relation with molecular weight, i.e.,

$$\eta_0 = \mathrm{K} \cdot M_w^n \tag{3}$$

in which K and n are constants (Colby et al. 1987; Struglinski and Graessley 1985; Rahalkar 1990; Rahalkar and Tang 1987). Figure 2 shows the variation of the experimentally obtained zero shear-rate viscosity with molecular weight for the functionalized samples of both the F1 and F3 series. Data analysis reveals that the estimated value of K (2.76×10^{-13}) differs slightly from typical results for polybutadienes obtained with alkyllithium compounds, where representative values lie in the range 3.4–3.7×10^{-13}. In addition, the value of n found is equal to 3.15, which differs from the prediction of the pure reptation model (Colby et al. 1987; Monfort et al. 1986; Rahalkar 1990; Graessley 1980, 1986; Doi and Edwards 1979), suggesting that for these systems there is an important contribution of polydispersity to their viscoelastic response, something that is not captured by the pure reptation model.

Comparison between the viscosities of the F1 and F3 series reveals interesting differences. This should be done only by comparing samples with similar molecular weights obtained with different initiators. For example, sample F1801 with a molecular weight of 254,000 g/mol has a zero shear-rate viscosity of 43.75 kPa s, whereas the viscosity of sample F3801 with a similar molecular weight (225,000 g/mol) is 24.57 kPa s. This result apparently reveals a specific influence of the initiator

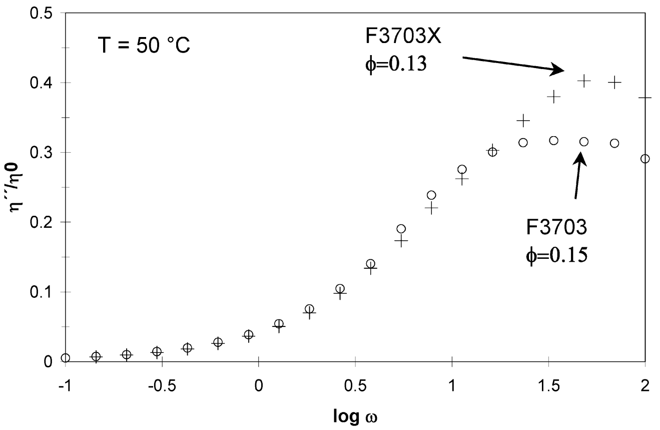

Fig. 1 Normalized imaginary part of the complex viscosity (η''/η_0) as a function of the frequency of oscillations. Shown are two bimodal samples with different high molecular weight content (ϕ)

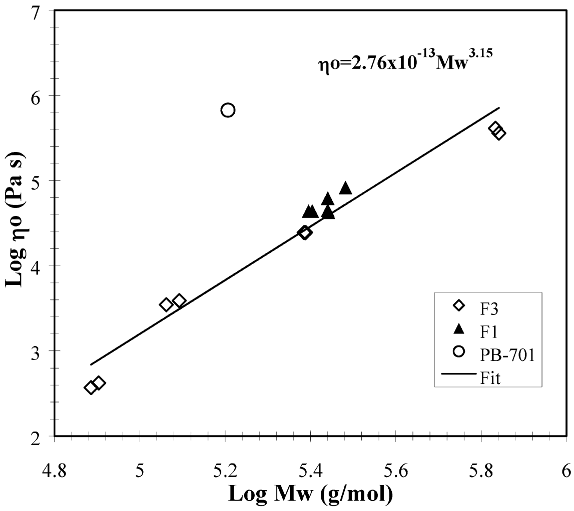

Fig. 2 Variation of the zero shear-rate viscosity with molecular weight for the polybutadienes analyzed in this study (T = 50 °C)

molecular structure upon the resulting dynamic behavior of the system. Since this clear difference in viscosity cannot be explained in terms of a molecular weight difference, this can be an indication of a specific effect of the structure and size of the larger silyloxy group in the F1 initiator. However, according to their molecular weights, highly entangled systems are expected in these samples, and so significant influences due to the presence of the end groups brought about by the different initiators are not expected. The differences between these two samples are probably related to their clear differences in polydispersity, promoting additional relaxations in the polydisperse sample F3801 that overall decrease its viscosity.

On the other hand, it is evident that the presence of a hydroxyl group at the chain ends does not promote significant differences in the viscosity of these systems. In fact, only the F1703X displays significant changes in viscosity, with respect to the α-functionalized sample (F1703). In the case of the F3 series, some differences are observed between samples F3703 and F3703X that can also be related to their high molecular weight and polydispersity.

As shown in Fig. 2, the polybutadiene sample obtained with *n*-butyllithium (PB-701) exhibits larger viscosity than those of the functionalized structures, despite the fact that its molecular weight is relatively low (182,000 g/mol). Remaining solvent in the functionalized samples is likely to account for the reduction in the viscoelastic properties, as is also observed in the modulus data. This precludes any further comparison with pure polybutadiene, and in the following, comparative analysis is made only between the functionalized samples themselves.

Plateau modulus

The relationship between polymer molecular structure and the resulting elastic behavior under shear has been extensively studied for polybutadienes and linear polymers (Colby et al. 1987; Doi and Edwards 1978a, 1978b, 1978c; Macosko 1994; Mark et al. 1993; Aharoni 1986). However, the influence of a functional group in the viscoelastic response of a polymer has not been widely analyzed and understood yet. Table 3 shows results for the plateau modulus (G_o), molecular weight (M_w), molecular weight between entanglements (M_e), and other molecular parameters of some of the samples analyzed here. Again the complete set of results can be obtained in the Electronic Supplementary Material of this paper. Molecular weight between entanglement points is calculated according to the expression derived from rubber elasticity:

$$G_0 = \frac{\rho RT}{M_e} \tag{4}$$

where ρ is the density, R is the gas constant, and T is the temperature. G_o has been calculated either from the variation of the elastic modulus ($G'(\omega)$) at large frequencies or from the following expression valid for monodisperse systems of linear chains:

$$G_0 = 3.56 \cdot G''(\omega)_{\max} \tag{5}$$

where $G''(\omega)_{\max}$ is the maximum of $G''(\omega)$ in the frequency range (Kraus and Gruver 1965). This expression has been checked by Carri and Winter (1997) for polystyrene and polybutadiene samples, obtaining a $G_o/G''(\omega)_{\max}$ ratio of 4.8 for all the molecular weights of both samples, which has been considered to be in reasonable agreement with Eq. (5). The parameter L_c/A is defined in terms of the number of atoms in the main chain (N_c) of a critical molecular weight (M_c) and bond length (l_o), according to

$$L_c = l_0 N_c \tag{6}$$

A is the Kuhn length, a length scale representative of the statistical subunits making up the chain. In flexible polymers, A is given by (Aharoni 1986)

$$A^2 = 0.44N_c - 10.55 \tag{7}$$

In Eqs. (6) and (7) a value of $l_o = 1.47$ Å for polybutadiene has been used.

It is interesting to point out that the ratio M_w/M_e, which defines the number of entanglements per molecule, is smaller in the case of more polydisperse samples

Table 3 Molecular parameters of some of the samples analyzed in this study. G_0 from $G'(\omega)$ at high frequencies and from Eq. (5). M_e from Eq. (4) and L_c/A from Eqs. (6) and (7)

Sample	G_0 (MPa)	G_0 from Eq. (5) (MPa)	M_w (g/mol)	M_e (g/mol)	M_c (g/mol)	M_w/M_e	L_c/A
PB-701	1.05	1.25	160,956	2289	4,577	70.33	42
F1801	0.42	0.598	248,526	5721	11,443	43.44	65
F3602	0.3	0.441	76,822	8010	16,020	9.59	77
F3701	0.2	0.268	681,369	12015	24,030	56.71	94
F3703	0.33	0.356	115,401[a]	7282	14,564	15.85	74
F3801	0.33	0.445	244,592	7282	14,564	33.59	74

[a] Bimodal distribution

(F3602 and F3703). The highest ratio corresponds to the sample with the largest molecular weight but with the smallest plateau modulus (F3701). By comparing samples with similar molecular weights (F1801 and F3801), these results suggest that a smaller molecular weight between entanglements (i.e., a more entangled system) is found in the polybutadiene sample synthesized by the F1 initiator (silyloxyalkyllithium initiator). According to the degree of flexibility given by the value of L_c/A, this latter sample is also apparently less flexible than that synthesized with the smaller silyl initiator F3. Apparently, the presence of the larger silyloxyalkyl group in the F1 initiator promotes differences in the entangled structure of a polybutadiene sample that might also create differences in its rheological behavior.

Polybutadiene (PB-701) modulus compare well to the value reported in the literature (Colby et al. 1987; Aharoni 1986), which ranges from 1.10 to 1.31 MPa. Again, the lower magnitudes obtained in the functionalized samples are due to a small solvent content, which is difficult to extract, due to the polarity of the systems. However, it is still possible to make a comparison and achieve general conclusions when analysis between the functionalized structures is made. Previous investigations have shown that the presence of different end groups in a molecule affects its relaxation process in a considerable manner (Tassin et al. 1990; Doi and Edwards 1978a, 1978b, 1978c, 1979). This is also suggested here when comparing the overall relaxation time of samples obtained with different initiators. Once again, for samples with similar molecular weights, the relaxation time in a polybutadiene obtained with the silyloxy initiator (F1801) is larger than that observed in a sample synthesized using the silyl initiator (F3801), 0.13 s and 0.08 s respectively. Therefore, the relaxation of the system with the smaller silyl end-group is faster. This observation correlates with the obtained values for the plateau modulus, where the slow relaxation is also related to a more entangled network in the F1801 sample. This suggests the presence of short length interactions among the functionalized molecular segments and the polymeric network, the so-called orientational coupling (Tassin et al. 1990), which states that a more rigid or nematic-like conformation exists in the final segments of the chain. These interactions are of larger magnitude in the more polar silyloxy end-group. In this case, orientational coupling induces a reduced relaxation time in samples synthesized by F1 with respect to those obtained using F3. Once again, the differences in polydispersity between these samples may also be related to the observed differences in their relaxation process. The presence of low molecular weight fractions due to the increased polydispersity in the F3 sample may promote a faster relaxation process, decreasing the modulus and the viscosity in a significant manner.

Shear compliance results

As described before, the equilibrium shear compliance J_o is sensitive to changes in the molecular weight and molecular weight distribution of a polymer. In this work, J_o values are calculated from the linear viscoelastic data using the following expressions (Macosko 1994; Colby et al. 1987; Choi et al. 1988; Struglinski and Graessley 1985):

$$J_0 = \frac{1}{\eta_0^2} \lim_{\omega \to 0} \left(\frac{G'(\omega)}{\omega^2} \right) \tag{8}$$

$$J_0 = \lim_{\omega \to 0} \left(\frac{G'(\omega)}{G''(\omega)^2} \right) \tag{9}$$

The Doi and Edwards reptation model predicts the following relation for monodisperse flexible molecules:

$$J_0 \cdot G_0 = 1.2 \tag{10}$$

As expected the equilibrium shear compliance is highly dependent on molecular weight and higher moments of the molecular weight distribution. J_oG_o values range from 1.75 to 4.77 using Eq. (8) and a shorter range is obtained when using Eq. (9). Reported values in the literature for polybutadiene range between 1.79 and 3.92 (Rahalkar 1990). In the case of a bimodal distribution, as in sample F3703, polydispersity effects increase and as expected, deviations from the theoretical J_oG_o value of 1.2 are observed. These results suggest again that polydispersity appears to be the predominant factor in controlling the rheological response of these systems.

The influence of molecular weight on the equilibrium shear compliance can be observed in the F3 series, which cover a relative wide range of molecular weights. Figure 3 shows the variation of the equilibrium shear compliance with molecular weight for the moderate polydisperse samples (i.e., excluding F3703 samples).

The shear compliance of the hydroxyl-functionalized samples barely change with respect to that of samples with no hydroxyl groups. Some exceptions are observed in samples with small proportions of high molecular weight components, as in the case of F1703 and F3703. The latter is a bimodal sample and the former has additional relaxations in the plateau region, as discussed later.

Time-temperature superposition

Thermorheological simplicity in the terminal and plateau regions of the viscoelastic spectrum is not expected

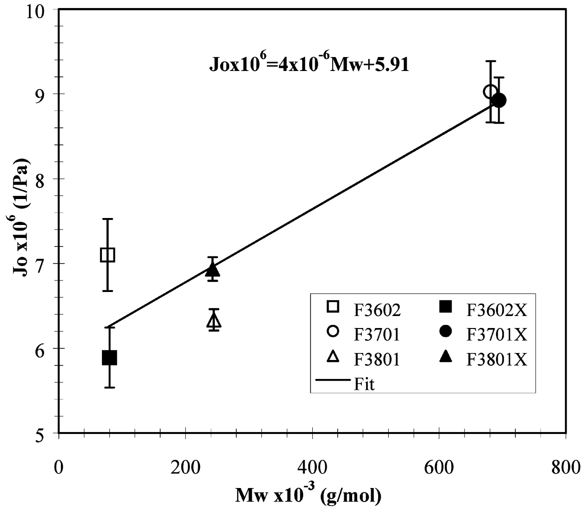

Fig. 3 Equilibrium shear compliance vs molecular weight of polybutadienes obtained with F3 (T = 50 °C)

in functionalized materials in general. However, in a relatively small temperature range and when the proportion of functionalized groups is small, it is possible to obtain time-temperature superposition. Failure to obtain superposition under a small temperature range implies larger deviations from the thermorheologically simple behavior in a wider temperature range. Data from the samples treated in this study are worked out using two shift factors defined as

$$a_T = \frac{\lambda(T)}{\lambda(T_r)} \tag{11}$$

$$b_T = \frac{T_r}{T} \frac{\rho(T_r)}{\rho(T)} \tag{12}$$

where T_r is the reference temperature and λ is the relaxation time. Values of b_T ranged from 0.941 to 1.183, within 0–70 °C. The variation of a_T with temperature is shown in Fig. 4 for $T_r = 50$ °C. In general, data follow the WLF equation with expected deviations due to polydispersity, using $C_1 = 2.21$ and $C_2 = 159$ for the F3 series and $C_1 = 2.05$ and $C_2 = 135$ for the F1 series.

In general, over the temperature range analyzed, few deviations from time-temperature superposition are observed. Figure 5a,b shows the type of superposition obtained, for the F1703 and F1801 samples, respectively. In these cases, superposition is observed in the terminal region only, and deviations are present at higher frequencies in the plateau region. These deviations are also observed in the corresponding hydroxyl functionalized samples (F1703X and F1801X). In contrast, in the F3 series, deviations occur in the bimodal sample F3703, mainly along the terminal region, as depicted in Fig. 5c.

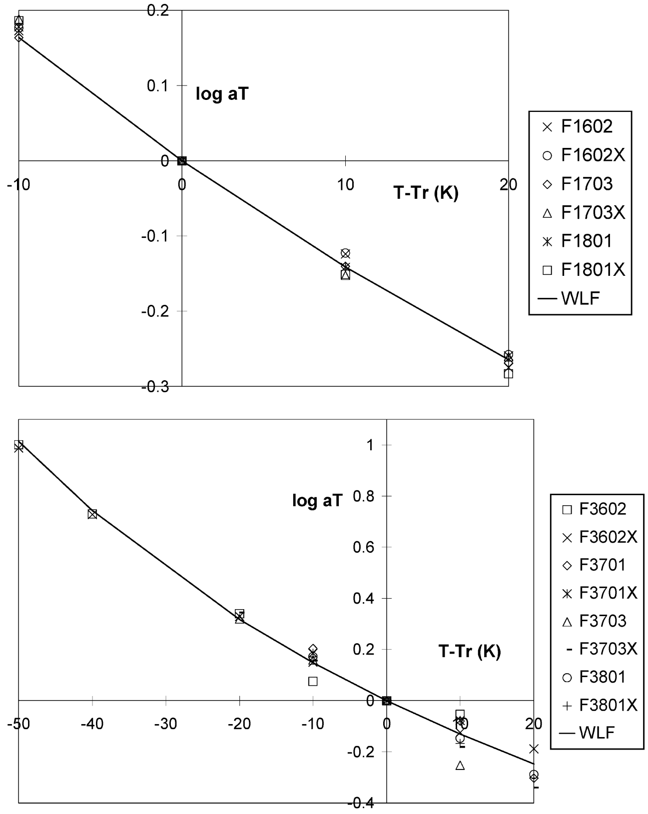

Fig. 4a,b Variation of the shifting factor a_T with temperature. Polybutadienes obtained with different initiators: **a** F1; **b** F3

Rheological modeling

As mentioned before, the rheological behavior obtained for the polybutadiene systems synthesized in this work has been modeled using three different rheological models. The models' predictions of the experimental data are compared and used to get a better understanding of the molecular characteristics of the polymeric systems.

The relaxation spectrum was initially analyzed using a discrete spectrum of relaxation times to estimate the contribution of additional relaxation times to the overall linear viscoelastic response. These expressions are based in the rubber-like liquid constitutive equation (Lodge 1968; Chang and Lodge 1972), and have been used by Wagner (1976) to describe non-linear behavior of branched polymers. The predictions for the dynamic moduli can be described by the following equations (Ferry 1980):

$$G'(\omega) = \sum_i a_i \tau_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \tag{13}$$

$$G''(\omega) = \sum_i a_i \tau_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \tag{14}$$

In addition, the reptation model proposed by Doi and Edwards (1978a, 1978b, 1978c, 1979) is also used in

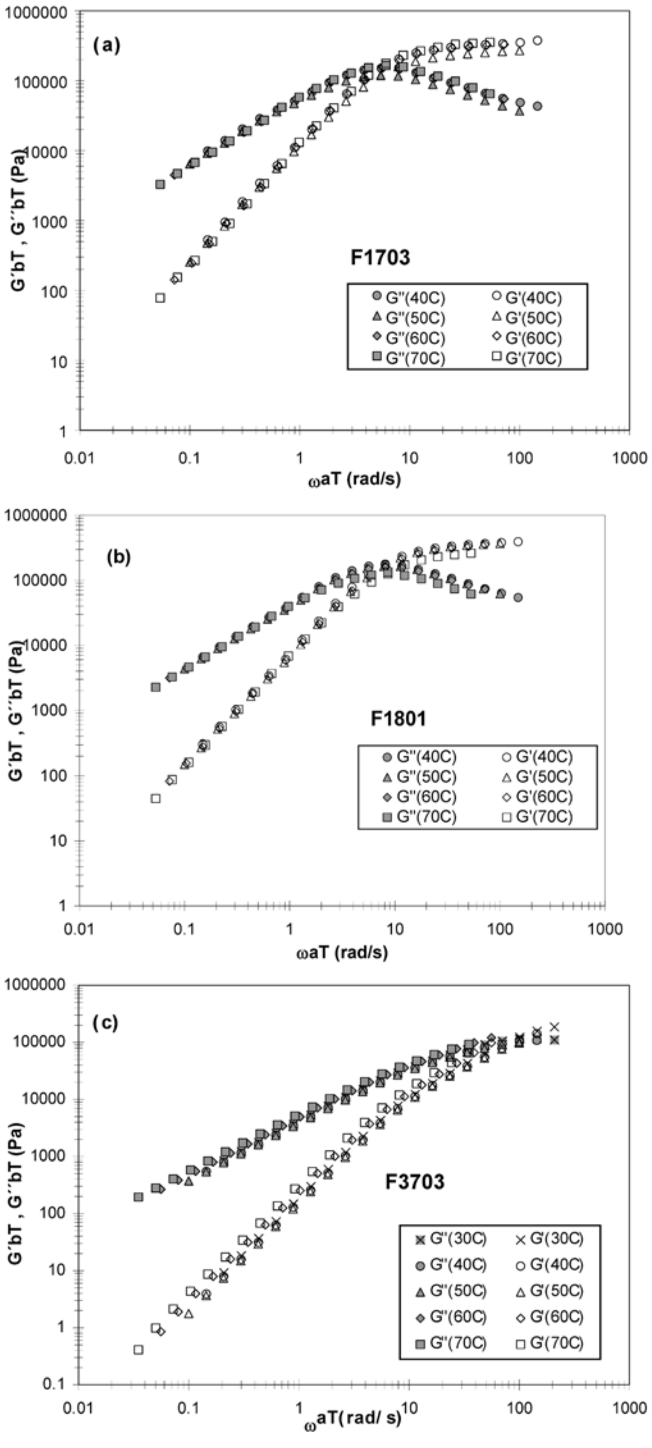

Fig. 5a–c Deviations from time-temperature superposition observed in some samples

this work. This model assumes that, due to the topological constraints, the motion of a chain in an entangled system is essentially confined in a tube-like region made of the surrounding polymers. This model has been proved to be useful when the relaxation process is dominated by a single relaxation time in the terminal region of the spectrum. This model suggests the following expressions for the dynamic moduli:

$$G'(\omega) = G_0 \sum_{p,odd} \frac{8}{\pi^2 p^2} \frac{\left(\frac{\omega\tau_d}{p^2}\right)^2}{1 + \left(\frac{\omega\tau_d}{p^2}\right)^2} \omega\tau_R < 1 \tag{15}$$

$$G''(\omega) = G_0 \sum_{p,odd} \frac{8}{\pi^2 p^2} \frac{\left(\frac{\omega\tau_d}{p^2}\right)}{1 + \left(\frac{\omega\tau_d}{p^2}\right)^2} \omega\tau_R < 1 \tag{16}$$

$$G'(\omega) = G''(\omega) = G_0 \left(\frac{\pi}{2}\omega\tau_R\right)^{1/2} \omega\tau_R > 1 \tag{17}$$

In these expressions τ_d is the longest relaxation time, which is often called the reptation or disengagement time. This characteristic time represent the required time for a chain to disengage from the tubular region it was confined to at a given initial time. In addition, τ_R is the Rouse relaxation time that defines the dynamics of a chain in dilute solutions. This time corresponds to the ratio of the constant contour length of the chain and its diffusion coefficient.

Polybutadiene (PB-701) modeling results are shown in Fig. 6 using both the Doi and Edwards reptation model and the discrete spectrum of relaxation times. Values of $G_o = 1.05$ MPa, $\tau_d = 0.77$ s, and $\tau_R = 0.0001$ s are used in the predictions of the reptation model. Deviations from the Doi and Edwards reptation model are primarily observed in the viscous modulus at high frequencies in the plateau region. Smaller deviations are also present in the viscous modulus at low frequencies as well as in the elastic modulus at high frequencies. The reason for these deviations is illustrated in the fit of the experimental data using the discrete spectrum. Along with the contribution of the main relaxation time (0.77 s), there are additional contributions of similar magnitude in the high frequency side and low frequency side of the spectrum, corresponding to relaxation times of 0.01 s and 1 s. When these contributions are accounted for, an improved fit is obtained, as shown in Fig. 6b.

In general, for the case of the functionalized polymers, just a few samples are described successfully using the reptation model. In fact, only sample F1602, a high molecular weight monodisperse sample, renders moderate fittings of the data. Figure 7 shows model predictions of the experimental data for the case of samples F1602 and F3602. The fitting parameters are $G_o = 0.4$ MPa, $\tau_d = 0.14$ s, $\tau_R = 5\text{X}10^{-6}$ s for F1602, and $G_o = 0.3$ MPa, $\tau_d = 0.0017$ s, $\tau_R = 1\times10^{-10}$ s for F3602. As shown, predictions for the F1602 sample are good; in

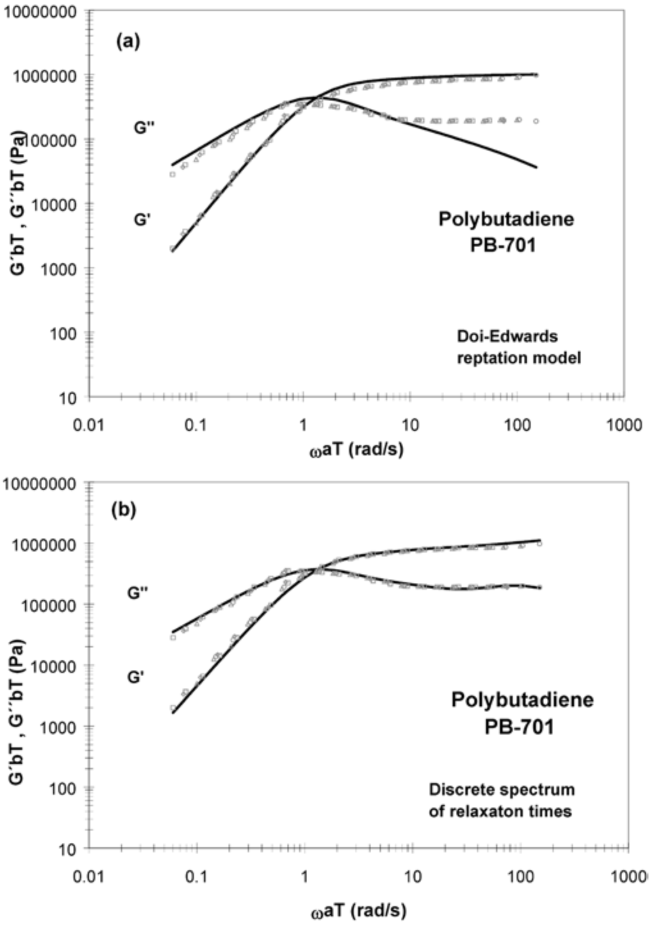

Fig. 6a,b Predictions for a polybutadiene synthesized with *n*-butyllithium (PB-701): **a** Doi and Edwards reptation model; **b** discrete spectrum of relaxation times

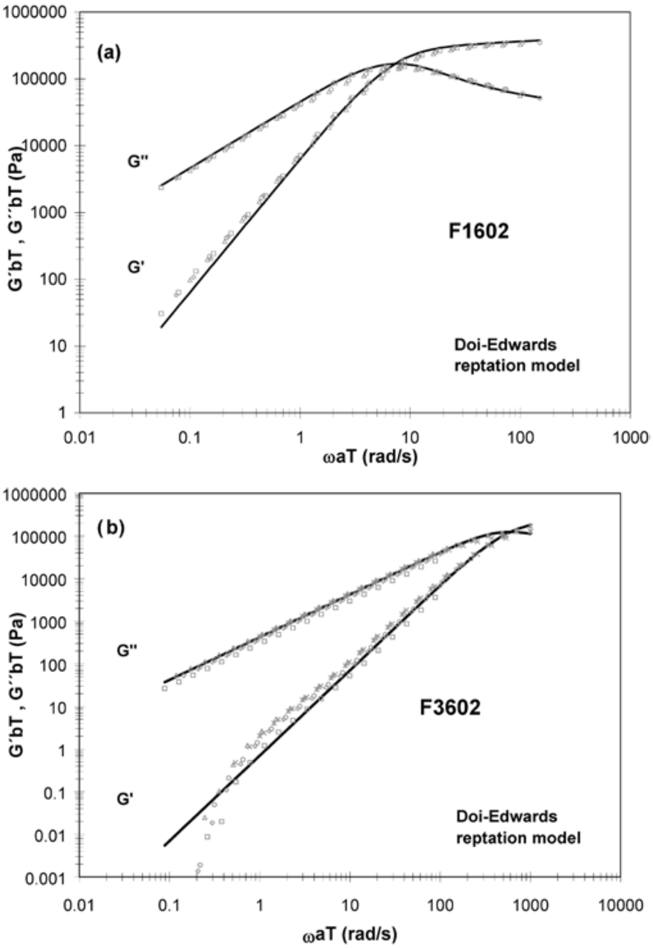

Fig. 7a,b Predictions obtained for two different samples using the Doi and Edwards reptation model

contrast, failure of time-temperature superposition is evident in the low frequency range where deviations are more pronounced due to polydispersity in the F3602 sample.

As mentioned before, samples in the F1 series show similar molecular weights and polydispersity values. However, it is interesting that only the F1602 sample can be fitted with the Doi and Edwards model. This is illustrated in Fig. 8 for the case of sample F1703, where it is evident that, despite the lack of complete superposition, there are important contributions of additional relaxation times in the relaxation spectrum of this sample. G_o values of F1703 are slightly higher than those of F1602 with small differences in molecular weight. An important observation, however, is that these subtle differences in molecular structure lead to additional relaxation times in the plateau region of the spectrum corresponding to different entanglement lengths, in addition to the main relaxation mechanism. Again these results support the idea of polydispersity being the predominant factor in the rheological response of these systems.

Polydispersity is higher in samples obtained with the silyl initiator (F3 series), particularly in the high molecular weight sample (F3701) and in the bimodal sample (F3703X). Figure 9 shows the prediction for these samples using the discrete set of relaxation times. In the high molecular weight sample, additional relaxation times in the plateau region of the spectrum, within the frequency range of 1–100 s^{-1} (0.01–1 s) are observed. These contributions arise from different molecular lengths between entanglement points, which are generally observed for frequencies higher than that of the main relaxation time. The reduced terminal region is only slightly affected by the polydispersity of the sample. On the other hand, F3703X sample has a low molecular weight component of 120,000 g/mol (86%) with a high molecular weight tail of 275,000 g/mol (14%). Results presented in Fig. 9b show that in this case the additional relaxation modes appear in the terminal region, around

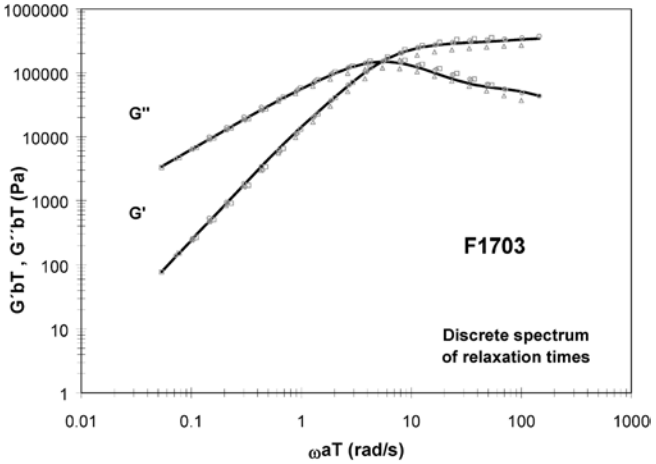

Fig. 8 Predictions for a polybutadiene sample synthesized with the F1 initiator using the discrete spectrum of relaxation times

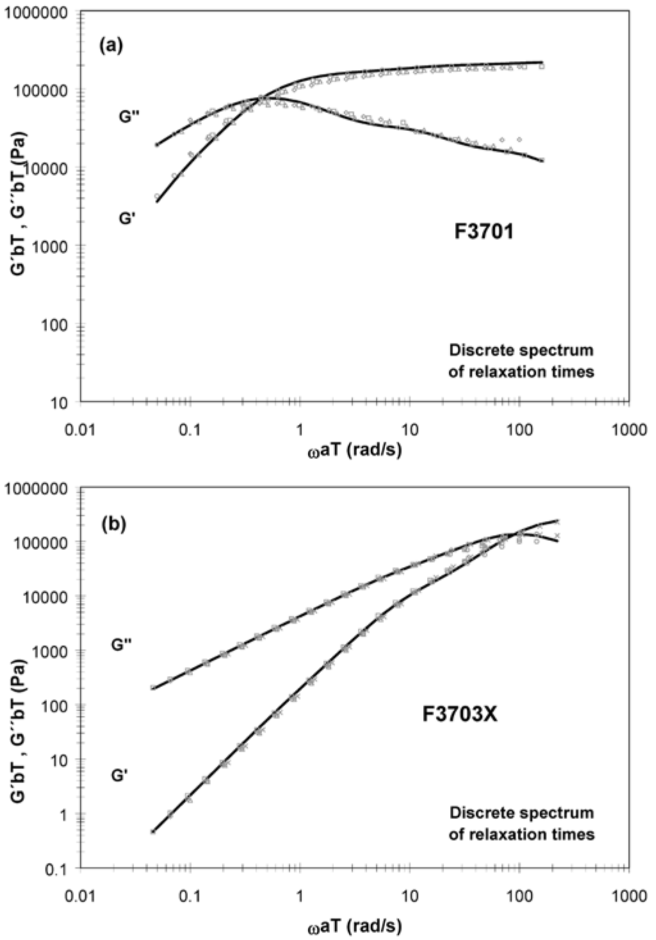

Fig. 9a,b Predictions of two polydisperse samples obtained with the F3 initiator using the discrete spectrum of relaxation times

0.1 s. The high molecular weight component causes additional relaxations in the terminal region. A complete set of the parameters used to predict the experimental data in Figs. 6, 8, and 9, using the discrete spectrum of relaxation times as included in the Electronic Supplementary Material of this paper.

Finally, predictions of linear viscoelastic data of some samples were obtained using generalized relations for the moduli considering analytical expressions of the spectrum of relaxation times. The expressions used in this study for the spectrum are those proposed by Baumgaertel et al. (1990) for the terminal-transition range, and the fractional Maxwell model (Friedrich 1991) modified by Palade et al. (1996) for the rest of the spectrum. The corresponding equations are presented below:

$$\begin{aligned} &H(\lambda) = H_\eta(\lambda) + H_\alpha(\lambda) \\ &\lambda\langle\lambda_{\max} \\ &H(\lambda) = 0 \\ &\lambda\rangle\lambda_{\max} \end{aligned} \tag{18}$$

$$H_\eta(\lambda) = n_\eta G_0 \left[\frac{\lambda}{\lambda_{\max}}\right]^{n_\eta} \tag{19}$$

$$H_\alpha(\lambda) = \frac{G_\alpha}{\pi}\left[\frac{\lambda}{\lambda_\alpha}\right]^{a-b} \frac{\sin(\pi b) + \left[\frac{\lambda}{\lambda_\alpha}\right]^{-a}\sin(\pi[b-a])}{\left[\frac{\lambda}{\lambda_\alpha}\right]^{-a} + 2\sin(\pi a) + \left[\frac{\lambda}{\lambda_\alpha}\right]^{a}} \tag{20}$$

$$G'(\omega) = \int_0^\infty H(\lambda)\frac{(\omega\lambda)^2}{1+(\omega\lambda)^2}\frac{d\lambda}{\lambda} \tag{21}$$

$$G''(\omega) = \int_0^\infty H(\lambda)\frac{\omega\lambda}{1+(\omega\lambda)^2}\frac{d\lambda}{\lambda} \tag{22}$$

The model includes seven parameters, two of them (G_o and $\lambda_{\max}$) obtained from the experimental data. The glassy modulus ($G_\alpha = 0.8$ GPa) and the power law in the glassy region (b–a = 0.25) are taken from the literature (Palade et al. 1996). The remaining parameters (n_η, b, and λ_α) are determined in the fitting process. Some of the results are shown in Table 4. This table includes results of a sample with a single relaxation time in the terminal region (F1602), and two samples with similar molecular weights but with different viscosity values (F1801 and F3801). In the single relaxation time sample (F1602) the value of n_η is lower (3.4) than in the samples with additional relaxation times. Furthermore, values of b are related to the transition region and are higher in the sample with the lowest G_o and $\lambda_{\max}$ (F3801). This result suggests once again the important contribution of low molecular weight fractions in the relaxation process of this sample.

Table 4 Model parameters used in Eqs. (18), (19), (20), (21), and (22) in the prediction of experimental data of some representative samples

Sample	n_η	G_0 (MPa)	$\lambda_{\max}$ (s)	b	λ_α (s)	G_α (GPa)	a	b−a
F1602	3.43	0.4	0.13891	0.82	5E–8	0.8	0.795	0.025
F1602X	3.19	0.4	0.14264	0.78	3E–8	0.8	0.755	0.025
F1801	4.6	0.42	0.12732	0.74	1E–8	0.8	0.715	0.025
F1801X	4.01	0.42	0.12657	0.71	6E–9	0.8	0.685	0.025
F3801	4.61	0.33	0.08366	0.87	9E–8	0.8	0.845	0.025
F3801X	4.69	0.33	0.08274	0.9	2E–7	0.8	0.875	0.025
PB-701	5.81	1.05	0.76602	0.72	2E–7	0.8	0.695	0.025

Dynamic moduli vs frequency curves of the model predictions and the corresponding experimental data for samples obtained with different initiators are depicted in Fig. 10. As shown in this figure, the beginning of the transition region in the viscoelastic spectrum is also predicted by this model. An important observation is that negligible differences are observed for the propylene oxide-modified samples with respect to the rest of the samples.

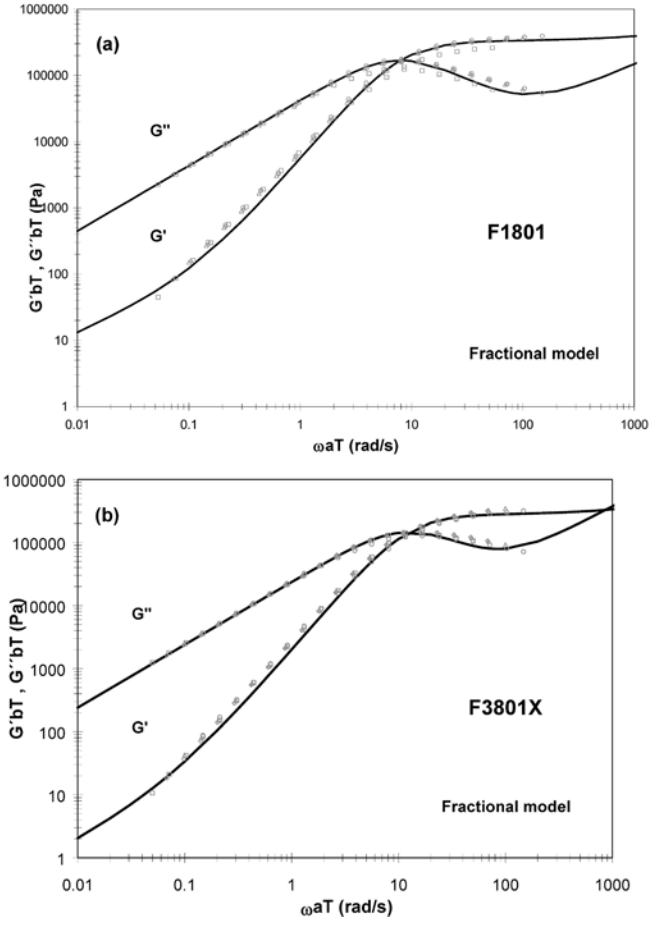

Fig. 10a,b Predictions obtained for two polybutadiene samples obtained with different functionalized initiators using the fractional model defined in Eqs. (18), (19), (20), (21), and (22)

Conclusions

In this work, the anionic polymerization of butadiene with two different functionalized initiators is used to obtain polymers with a well-defined structure. Initiators used in this work include either a silyl-type group (F3) or a larger and more polar silyloxy group (F1). Significant changes are observed in the rheological behavior of polymers synthesized with different initiators, which are mainly related to their polydispersity differences. Samples resulting from the silyloxy-initiator (F1) possess similar molecular weights and are monodisperse ($M_w/M_n < 1.073$). The silyl initiator (F3) was used to produce polymers within a relative wide range of molecular weights (65,000–667,000 g/mol) and in general polydispersity is increased in these materials ($M_w/M_n = 1.17+$).

A termination reaction with propylene oxide is used to introduce a hydroxyl group at the end of the chain. In general, the presence of this functional group promotes negligible differences in the rheological behavior. However, samples with additional relaxation modes in the terminal or plateau regions present slight changes in their rheological response when this functionality is introduced, showing the significant effect of polydispersity.

Differences in the dynamic behavior of polybutadienes synthesized with different initiators (F1 and F3) become apparent when samples with similar molecular weights are compared. Samples obtained with the bulkier F1 initiator present a higher zero-shear rate viscosity than those obtained with the smaller F3 initiator. As a consequence, the difference in the viscosities between samples F1801 and F3801 cannot be related to their slight difference in molecular weight, and suggests a possible combination between the contributions of the functionality at the chain ends and their intrinsic differences in polydispersity. In addition, the magnitudes of the plateau moduli reveal that systems obtained with the F1 initiator are found to create a more entangled or structured system. Therefore, lower molecular weights between entanglements are found in the F1 samples and the resulting degree of flexibility of the systems in the F3 group is larger than that in the F1 samples when comparing samples of similar molecular weight. An interesting observation is that the sample with the largest molecular weight (F3701) presents a high viscosity with low modulus, suggesting that non-linear viscoelastic functions, such as the yield stress, may be affected by the interplay of modulus and viscosity at small deformations.

The shear compliance is mostly affected by small proportions of high molecular weight components and by the distribution of relaxation times. The influence of polydispersity in the shear compliance and in the rheological response in general is analyzed using samples with a bimodal distribution of molecular weights synthesized with F3 (F3703 and F3703X). Larger values of J_o are found in these samples, despite the fact that the high molecular weight component is only about 14%. This suggests that there is a strong contribution of the molecular weight distribution to the rheological response of the functionalized polybutadienes analyzed in this work. Polydispersity appears to dominate in many ways the rheological response of these systems. This observation is in agreement with the results obtained by Kasehagen and Macosko (1998) on the nonlinear shear and uniaxial extensional measurements on randomly branched polybutadienes with varying amounts of long-chain branching that show that the extensional behavior is mostly affected by changes in the relaxation spectra due to branching and increases in the high-end of the molecular weight distribution.

It has been shown that in polymers of the F3 group, viscosity variation with molecular weight follows closely a cubic relationship, and so the main relaxation time. In fact, with a ten times increase in the molecular weight, i.e., from 60,000 to 600,000 g/mol, the zero shear-rate viscosity increases correspondingly from 0.4 to 400 kPa s, and the relaxation time increases from 0.002 to 2.2 s. In contrast, the shear compliance follows a linear relation with the molecular weight.

Finally, the rheological modeling reveals interesting features of the molecular structure of these materials and its relation to their relaxation behavior. Even though polymers from the F1 group show similar molecular weights, viscosity, and moduli, a more detailed analysis reveals that only one sample of this series (F1602) can be fitted by the reptation model of Doi and Edwards. It is well known that this model suggests that a single relaxation mode dominates the viscoelasticity in the terminal and plateau regions from low to moderate frequencies, and as a general result, this is not true for the end-functionalized polybutadiene systems analyzed in this work. A good example of this is sample F1703, which displays a slightly higher viscosity, suggesting the presence of an important relaxation mode within the plateau region as shown in Fig. 8. Additional contributions to the relaxation spectrum at low and high frequencies are revealed, depending on the molecular structure of the polybutadiene systems. In addition, as observed in Table 4, deviations from a single relaxation time behavior in the flow region promote changes in the fitting parameters of a fractional type of model. Expected deviations due to polydispersity are observed when additional relaxations are included as suggested by Baumgaertel et al. (1992). This is illustrated by an increase in n_η and a decrease in the power law indices b and a. For the F3 group, simple viscoelastic behavior is only found in the low molecular weight sample, suggesting once again a strong influence of polydispersity and molecular weight on the viscoelastic behavior of these functionalized polybutadienes.

These results overall suggest that the intrinsic features of the molecular weight distribution of the samples analyzed in this work, along with a possible effect due to the presence of a given functionality at the chain-ends, brought about in this study by the two functionalized initiators (F1 and F3), dominate the relaxation process of a polybutadiene system inducing significant changes to its rheological behavior.

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