A COMPOSITION RULE TO PREDICT THE LINEAR VISCOELASTIC PROPERTIES OF POLYBUTADIENES WITH VARYING MICROSTRUCTURE

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ABSTRACT

A composition rule is proposed here to predict the glass transition temperature (T_g), the zero shear-rate dynamic viscosity (η'_0), the plateau modulus (G_0) and the terminal relaxation time (λ) of narrow molecular weight distribution (MWD) polybutadienes with various vinyl contents in solution and in the melt from the knowledge of the vinyl fraction, polymer fraction in solution and average molecular weight. The predictions of the composition rule are compared with data of a variety of narrow MWD polybutadienes with varying microstructure.

INTRODUCTION

It is well known that the anionic solution polymerization of 1, 3-butadiene yields three isomers (1,4 *trans*, 1,4 *cis* and 1,2 vinyl) and that the proportion of these isomers strongly affects the rheological, mechanical, thermal and structural properties of the polymer.[1-7] The *cis* isomer exhibits high resilience and abrasion resistance at low temperatures.[7] By contrast, the *trans* isomer possesses high tenacity, thermo-plasticity, and low resilience and it is slightly soluble in most solvents.[8] The high vinyl isomer content (ca. 95% atactic form) have fairly good tensile properties, low hysteresis, and poor low-temperature characteristics; T_g is approximately 0 °C.[9] The knowledge of the interactions among the different polybutadiene isomers is important to understand the relationship between the microstructure and the mechanical properties of these polymers.[10] Hence, it is important to relate molecular information with macro-structural characteristics of the polymers for many important applications. In particular, some rheological properties of polymers can be predicted with empirical correlations that relate macro-structural information (molecular weight, molecular weight distribution (MWD), topological entanglements, *etc.*) with molecular composition.[11-15] In the case of polybutadiene isomers, the prediction of the rheological properties from micro-structural parameters is still a challenge.

In this work, a composition rule is proposed to predict the glass transition temperature, zero shear-rate viscosity, the terminal relaxation time and the plateau modulus of polybutadienes with a wide range of microstructures in solution and in the melt from the knowledge of the vinyl fraction, the polymer fraction in solution and the molecular weight. The predicted values compare well with data obtained here and with literature data[4] of polybutadienes with varying microstructure made by anionic polymerization.

EXPERIMENTAL SECTION

Polybutadienes were synthesized via anionic polymerization of 1, 3-butadiene in hexane at 4 °C initiated with n-butyl lithium in a CEMCO batch reactor. In this case, polybutadiene with

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low 1,2 vinyl group content (ca. 8%) are obtained. Higher vinyl group contents were obtained when 1, 2-diethoxyethane was used as the reaction medium. Living chains were deactivated with dry 2-propanol free of dissolved oxygen. Excess solvent was removed by evaporation.

Molecular weight distributions were determined at 30 °C by gel permeation chromatography in a Hewlett Packard 1090-M HPLC equipped with three Shodex columns (with exclusion limits of 10^5, 10^6 and 10^7 g/mol) using HPLC-grade THF (Merck) as the mobile phase. The universal calibration curve with corrections of the Mark-Houwinks' parameters and of axial dispersion was obtained with polybutadiene standards (Polymer Laboratories).

The proportion of 1, 2 (vinyl), 1, 4 (*cis*) and 1, 4 (*trans*) groups was determined by FTIR spectroscopy using internal standards and following the usual procedures.[16] Measurements were made in 1 and 2 wt. % solutions of polybutadiene in carbon disulfide. Table I reports the average molecular weights and the vinyl composition determined for the eight polymer samples synthesized here. All samples have narrow molecular weight distributions ($M_w/M_n \approx 1.01$).

Linear viscoelastic properties (η'_0, G_0 and λ) were measured at 50 °C in a Rheometrics RDS-II dynamical spectrometer with a cone-and-plate geometry (25 mm in diameter and 0.1 radian angle).

THE COMPOSITION RULE

The rheological properties of solutions of polybutadienes depend strongly on their macrostructure (molecular weight, MWD, polymer fraction in solution, *etc.*) as well as on their microstructure (proportion of 1, 4 *trans*, 1, 4 *cis* and 1, 2-vinyl isomers). The proposed composition rule is based on investigations on mixing processes by Krauss and Rollman,[17] who assumed that the mechanical response of a polymer system can be predicted with mechanical models arranged in parallel or in series. These authors derived the corresponding constitutive equation in terms of the elastic modulus.

Similarly to the model of Krauss and Rollman for mechanical properties,[17] here we propose the following correlation between a rheological parameter (P) of a polybutadiene and its micro- and macro-structure:

$$P_c(x_{12},\varphi,M_w) = \left[P_0(\varphi,M_w)\right]^{(1-x_{12})}\left[P_1(\varphi,M_w)\right]^{x_{12}} \tag{1}$$

Here P_c is the rheological parameter whose prediction is sought (i.e., η_0, λ or G_0), that depends on vinyl weight fraction (x_{12}), polymer fraction in solution (φ) and molecular weight (M_w). P_0 and P_1 represent the rheological parameters of polybutadienes with vinyl weight fraction equal to zero and one, respectively. P_0 and P_1 may depend on polymer fraction and/or molecular weight; for instance, the plateau modulus is known to be independent of the molecular weight, that is, $G_0(\varphi, M_W) = G_0(\varphi)$.[18]

Here we assume that the *cis* and *trans* isomers have similar relaxation behavior inasmuch as the have very similar structure and glass transition temperatures. Moreover, it has been proposed that the contributions of the various isomers to the overall relaxation behavior of polybutadienes can be predicted by the addition of the independent contributions from each isomeric group.[10] Hence, and by analogy to the Krauss and Rollman model,[17] we propose that the relaxation behavior of the *cis* and *trans* isomers can be modeled as a set of elastic moduli in series whereas that of the 1,2 isomer (vinyl groups) as an elastic modulus in parallel. The experimental evidence that validates the above assumption is given in the extensive study on the rheological characterization of polybutadienes with vinyl contents from 8 % to 99% carried out by Carella *et al.*[4,12]

In summary, our proposed composition rule assumes that the *cis* and the *trans* isomers have identical rheological behavior. As a consequence, the overall behavior of the isomer mixture can be envisaged as the sum of only two individual responses. In what follows, the weight fraction of the 1, 4 isomers (*cis* and *trans*) is $(1 - x_{12})$.

RESULTS AND DISCUSSION

GLASS TRANSITION TEMPERATURE

A number of equations for predicting the glass transition temperature (T_g) of polymer mixtures and copolymers have been reported in the current literature.[19-24] To demonstrate the potential of the proposed mixing rule, it is interesting to compare experimental glass transition temperatures of polybutadienes with a wide range of vinyl content[12, 20, 25-27] with the predictions of several popular equations with no adjustable parameters such as Gibbs-Dimarzio[19, 20] and Fox[21] and with adjustable parameters such as Kwei[24] and Brekner[28] and with those of the mixing rule proposed here. The Gibbs-Dimarzio equation for polybutadienes has the following form:

$$x_{cis}\left(T_{g,Blend} - T_{g,cis}\right) + x_{trans}\left(T_{g,Blend} - T_{g,trans}\right) = x_{12}\left(T_{g,Blend} - T_{g,12}\right) = 0 \quad (2)$$

Inasmuch as that the T_g of the *cis* and *trans* isomers are 167.15 and 166.15 K, respectively, we assume, similarly to Gibbs and Dimarzio.[19,20] that they are equal to 167.15 K. Moreover, because the polybutadiene with 100% vinyl has not been obtained, its T_g is unknown. However, by extrapolating the data in the literature and with the recent value of 273 K reported for a polybutadiene with 97% vinyl content,[29] a value of 275.5 K was estimated for the 100 % vinyl content isomer. With these considerations, Equation (2) can be written as:

$$T_{g,Blend} = 167.15 + 108.35x_{12} \quad (3)$$

The Fox equation, in turns, has the following form:

$$\frac{1}{T_{g,Blend}} = \frac{x_{12}}{T_{g1}} + \frac{\left(1 - x_{12}\right)}{T_{g0}} \quad (4)$$

where Tg_0 represents the glass transition temperature of the 1, 4 (*cis* and *trans*) isomers and Tg_1 is the glass transition of the vinyl isomer.

The Kwei equation, in turn, can be written for polybutadienes as[24]

$$T_{g,Blend} = q\left(x_{12} - x_{12}^2\right) + \frac{kT_{g0} + x_{12}\left(T_{g1} - kT_{g0}\right)}{x_{12} + k\left(1 - x_{12}\right)} \quad (5)$$

where Tg_0 and Tg_1 represents again the glass transition temperatures of the 1, 4 (*cis* and *trans*) isomers and of the vinyl isomer; respectively, and k and q are empirical (or fitting) constants.

Another equation that employs two adjustable parameters, K_1 and K_2, and which has been proved to describe well blend glass transition temperatures, is the Breckner equation.[28] For the case under study, this equation can be written as:

$$T_{g,Blend} = T_{g0} + \left(T_{g1} - T_{g0}\right)\left[\left(1 + K_1\right)x_{12} - \left(K_1 + K_2\right)x_{12}^2 + K_2 x_{12}^3\right] \qquad (6)$$

Our mixing rule for the glass transition temperature reads:

$$T_{g,Blend} = \left(T_{g0}\right)^{\left(1-x_{12}\right)}\left(T_{g1}\right)^{x_{12}} \qquad (7)$$

Figure 1 clearly shows that, as expected, the equations with adjustable parameters, *i.e.*, the Kwei and Brekner equations, fit quite well the experimental data whereas the Gibbs-Dimarzio equation fails to reproduce the data in the whole vinyl fraction range, except of course, when x_{12} is 0 or 1. The mixing rule proposed here also reproduces quite well experimental data in the whole composition range. However, the mixing rule does not require any adjustable parameters whereas the Kwei equation needs two (k and q) fitting parameters. Interestingly, the Fox equation, which does not required fitting parameters, predict reasonably the experimental data.

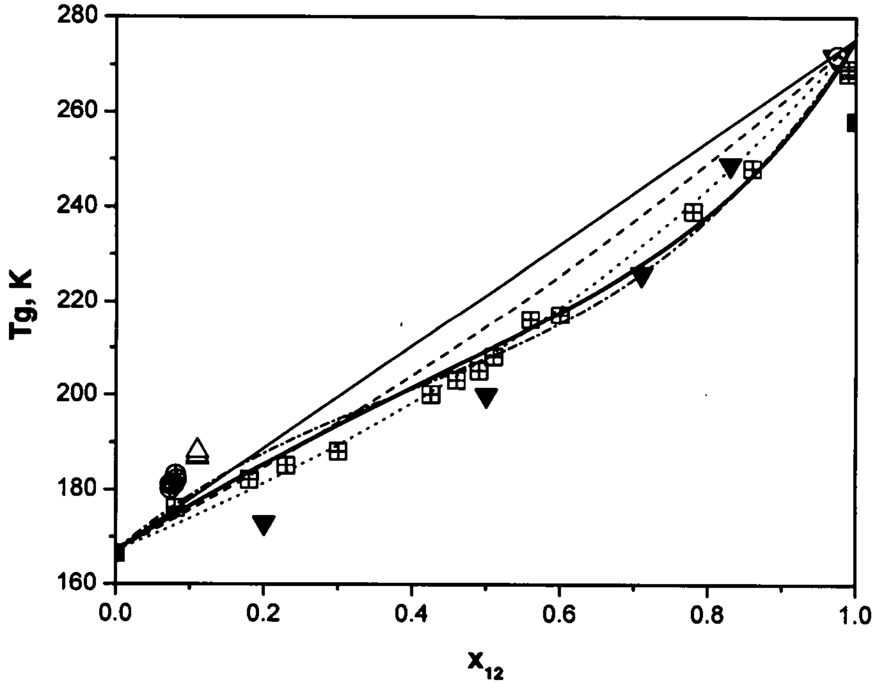

FIG. 1 — Glass transition temperature (K) plotted as a function of vinyl content (weight fraction). Predictions are shown from Eq. 3 (thin line), Eq. 4 (dotted line), Eq. 5 (thick solid line), Eq. 6 (dashed-dotted line) and from Eq. 7 (dashed line). Data from several authors are shown: ■ Bahary, 1967,[19] △ Palade *et al.*, 1996,[24] ⊕ Jackson *et al.*, 1994,[25] ▼ Roland and Ngai, 1991,[26] ⊞ Carella *et al.*, 1984,[3] and ○ Wang and Roland, 2005.

PLATEAU MODULUS

Since the plateau modulus (G_0) of polybutadienes in solution is independent of molecular weight and depends only on the vinyl fraction and the polymer weight fraction in solution,[4,12] Equation (1) can be written as:

$$G_0(x_{12},\varphi) = \left[G_{0,0}(\varphi)\right]^{(1-x_{12})}\left[G_{0,1}(\varphi)\right]^{x_{12}} \tag{8}$$

Here, $G_{0,0}(\varphi)$ and $G_{0,1}(\varphi)$ are the plateau modulus of the polybutadiene solution with vinyl weight fraction of 0 and 1, respectively.

Carella *et al.*[4,12] and other authors[11,30,31] reported the plateau modulus of polybutadienes with various vinyl contents in the melt. Figure 2 shows that these data can be fitted to an equation of the form:

$$G_0(x_{12},1) = G_0(0,1)10^{B_1 x_{12}} \tag{9}$$

where $G_0(0,1)$ is the plateau modulus of the polybutadiene with zero vinyl fraction in the melt state, which amounts to 1.22×10^6 ($\pm 2.3 \times 10^3$) Pa,[11-12,30,31] and the best fitting value of B_1 is -0.363 ($\pm$ 0.03) with $R^2 = 0.993$. The predictions of Equation (9) are shown as a solid thick line in Figure 2.

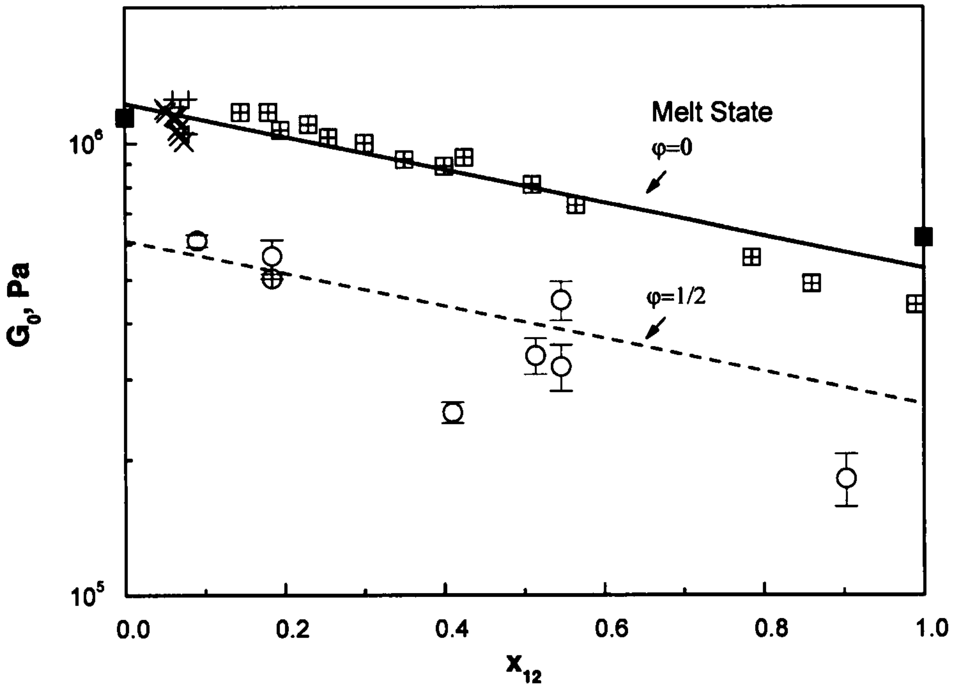

FIG. 2. — Plateau modulus as a function of vinyl contents (weight fraction). The solid thick line shows predictions from Eq. 9, and those from Eq. 10 are shown as a dotted line, for a polymer fraction in solution of $\varphi = (1/2)$. Experimental data of polybutadienes in the melt: X Rahalkar, 1990,[27] ⊞ Carella *et al.*, 1984,[3] ■ Pearson, 1987,[28] + Struglinski, 1985,[10] and data of polybutadienes in solution from the present work ○.

The following correlation has also been proposed to estimate the plateau modulus of concentrated solutions of polybutadienes in cyclohexane:[18,32]

$$G_0(x_{12},\varphi) = G_0(0,1)\varphi^{2.12} \tag{10}$$

Notice that the polymer fraction in solution (φ) can be estimated from Equation (10) and the knowledge of the plateau modulus of the polymer solution, $G_0(x_{12},\varphi)$ and that of the polymer in the melt with the same vinyl fraction, $G_0(x_{12},1)$. The values of φ from of all samples prepared here are reported in Table I. Predictions of Equation (10) for polybutadienes solutions with $\varphi = 1/2$ are shown as a dashed line in Figure 2. The predictions overlap reasonably well the experimental data.

TABLE I

AVERAGE MOLECULAR WEIGHTS, VINYL COMPOSITION, POLYMER WEIGHT FRACTIONS IN SOLUTION, ZERO SHEAR-RATE VISCOSITY, PLATEAU MODULUS AND RELAXATION TIME OF THE POLYBUTADIENE SAMPLES

Sample	M_w Dalton	x_{12}	φ	η_0,*Pa.s*	G_0,*Pa*	λ,s^{-1}
PB-1	85,116	0.090	0.75	5,878	610,937.0	0.012
PB-2	89,182	0.184	0.71	10,547	503,049.0	0.025
PB-3	92,377	0.184	0.75	10,504	564,177.5	0.025
PB-4	95,277	0.546	0.59	25,837	253,840.5	0.130
PB-5	101,586	0.546	0.68	29,756	338,601.5	0.114
PB-6	122,071	0.514	0.65	53,546	320,062.0	0.217
PB-7	126,716	0.410	0.73	50,620	450,159.5	0.147
PB-8	96,278	0.903	0.58	83,398	181,407.5	0.625

Figure 3 depicts experimental data of the plateau modulus of polybutadienes with various vinyl contents as a function of the polymer fraction in solution. The predictions of Equation (10) for the plateau modulus versus φ (dotted lines in Figure 3) are quite good for the polybutadienes with different vinyl content in solution. The solid line in Figure 3 represents the prediction of Raju *et al.*[32] for polybutadienes with $x_{12} = 0$. Notice that for $\varphi = 1$, the modulus reaches the value of $G_0(0,1)$.

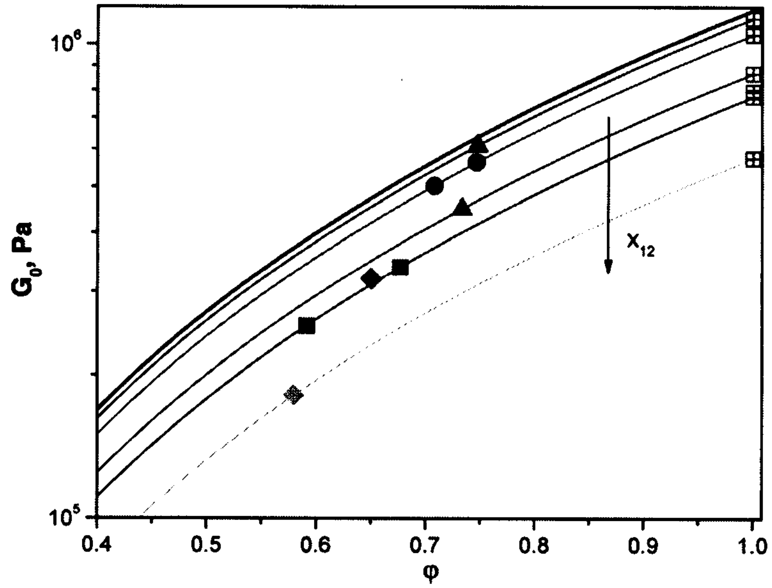

FIG. 3 — Plateau modulus of polybutadienes with various vinyl contents as a function of polymer fraction in solution. Predictions from the equation $G_0 = 1.18\times 10^6\varphi^{2.12}$ [29] are shown as a solid thick line. Those predictions from Eq. 11 for several vinyl fractions are indicated as follows: ▲ 0.090, ● 0.180, ▲ 0.410, ◆ 0.514, ■ 0.546, ◆ 0.903, and data from Carella *et al.* ⊞[3]

The combination of Equations (9) and (10) yields:

$$G_0(x_{12},\varphi) = G_0(0,1)\varphi^{2.12}10^{B_1 x_{12}} \tag{11}$$

Notice that by setting x_{12} equal to zero and one in Eq. (11) gives the values of the plateau modulus at zero- and one-vinyl fractions, respectively. Substitution of Equation (11) ($x_{12} = 0$ and 1) in Equation (8) yields the final form of the composition rule for the plateau modulus:

$$G_0(x_{12},\varphi) = \left[G_0(0,1)\varphi^{2.12}\right]^{(1-x_{12})}\left[G_0(0,1)\varphi^{2.12}10^{B_1}\right]^{x_{12}} \tag{12}$$

Figure 4 shows a plot of the experimental plateau modulus versus the estimations of Equation (12) for polybutadienes with varying vinyl content in solution and in the melt state. The experimental G_0 in this figure includes data measured here as well as data from the literature.[4,12] Clearly, the predictions of the composition rule agree with experimental data for the different values of vinyl content and polymer fraction in solution. The correlation coefficient of the log-log plot between the experimental and the predicted plateau modulus is better than 0.990 for all the polybutadienes examined.

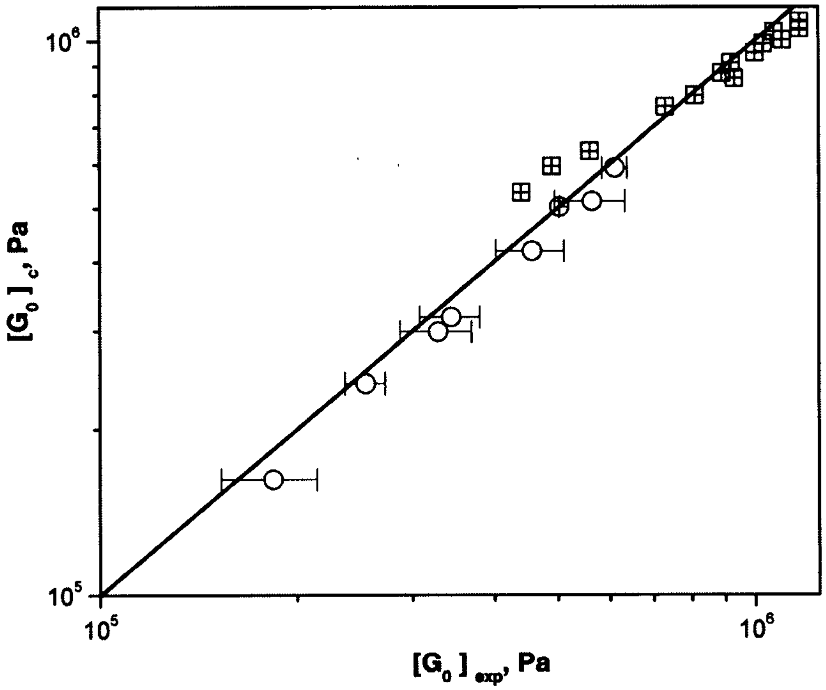

FIG. 4. — Plateau modulus predictions (using Eq.12) versus experimental data. The solid line indicates a correlation with $R^2 = 1.0$. Data from Carella et al. ⊞ [3] is shown, as well as data from the present work for polybutadienes with various vinyl contents in solution ○.

TERMINAL RELAXATION TIME

According to the scaling laws of polymer solutions, the terminal relaxation time varies with polymer volume fraction and molecular weight as, $\lambda \sim M^3\varphi^{3/2}$.[33] However, as demonstrated below, for the solutions of polybutadienes examined here (*i.e.*, with varying vinyl content), their relaxation times depends very weakly on the polymer fraction. On the other hand, the terminal relaxation time depends strongly on molecular weight and molecular weight distribution (MWD). Hence, as a first approximation, we neglect the dependence of λ on φ and since the MWD of the polybutadienes examined here is very narrow ($M_w/M_n \approx 1.01$), the composition rule (Equation 1) takes the following form:

$$\lambda\left(x_{12}, M_w\right) = \left[\lambda_0\left(M_w\right)\right]^{\left(1-x_{12}\right)}\left[\lambda_1\left(M_w\right)\right]^{x_{12}} \qquad (13)$$

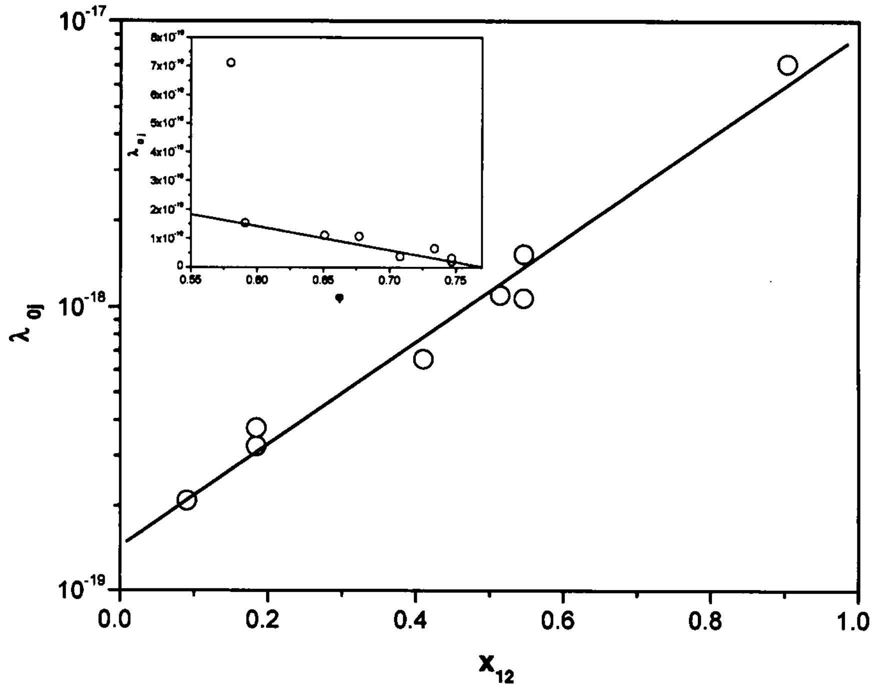

FIG. 5 — Correlation of $\lambda_i/M_w^{3.4}$ versus vinyl content (x_{12}), for polybutadienes in solution. The solid line represents the best fit, with correlation coefficient of 0.980.

It has been reported that the terminal relaxation time of many polymers varies as a power law with molecular weight as:

$$\lambda = A_1\left(M_w\right)^{\beta} \qquad (14)$$

where β is reported to be ca. 3.0 - 3.4 and depends on the MWD.[34] Here we choose the most accepted value of 3.4.[34] From our data and those reported in the literature, a correlation among λ, M_w and vinyl content was found by plotting $\lambda_i/M_w^{3.4}$ versus x_{12} (Figure 5) of the form:

$$\frac{\lambda_i\left(x_{12}\right)}{M_w^{3.4}} = \lambda_0 10^{B_2 x_{12}} \text{ (for i = 0, 1)} \qquad (15)$$

where the terminal relaxation time of the polybutadiene with zero vinyl content (λ_0), was found to be 1.55 (± 0.12) x 10^{-19} s and B_2 = 1.684 (± 0.055). The inset of Figure 5 depicts a plot of $\lambda_i / M_w^{3.4}$ versus φ for the polybutadienes solutions examined here (see Table I). Clearly, the dependence of $\lambda_i / M_w^{3.4}$ on polymer fraction is quite small and so, it can dropped without affecting our mixing ruke.

The substitution of Equation (15) in Equation (13) yields:

$$\lambda\left(x_{12}, M_w\right) = \varphi^{a}\left[\lambda_0\left(M_w\right)^{3.4}\right]^{\left(1-x_{12}\right)}\left[\lambda_0 10^{B_2}\left(M_w\right)^{3.4}\right]^{x_{12}} \tag{16}$$

Figure 6 depicts the experimental terminal relaxation time of the polybutadienes in solution with varying vinyl content and molecular weight versus the predictions of Equation (16). Again, agreement is outstanding (the correlation coefficient is better than 0.998). The lineal model, given by $\lambda = \lambda_0(1 - x_{12}) + \lambda_1 x_{12}$, gives worst predictions with a correlation coefficient equal to 0.601.

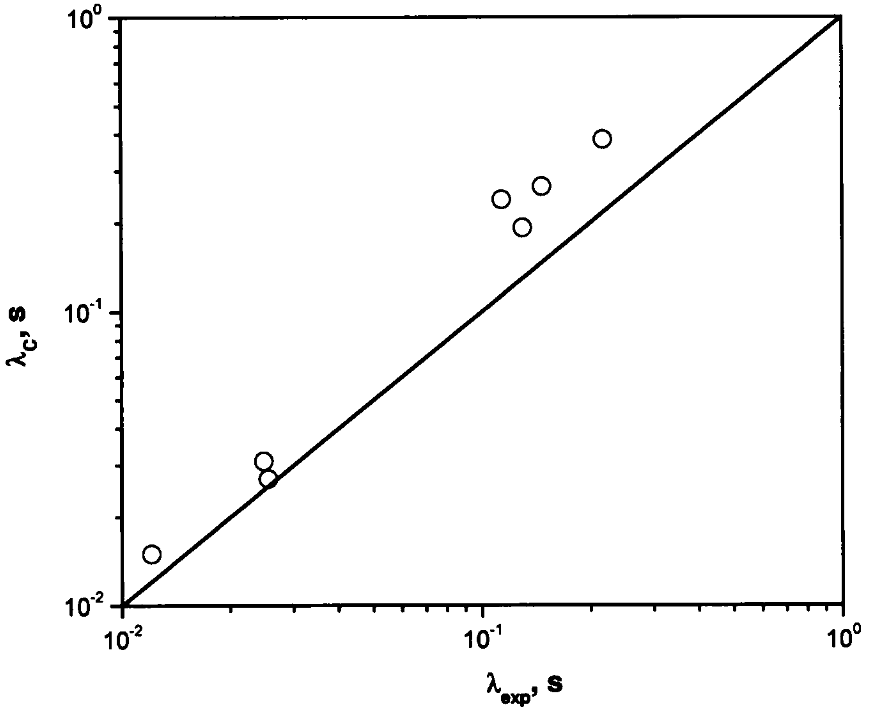

FIG 6. — Predictions of the main relaxation time for polybutadienes with various vinyl contents in solution (using Eq. 16) versus experimental data ○. The solid line indicates a correlation with R^2 = 1.0.

ZERO-SHEAR RATE DYNAMIC VISCOSITY

For the zero-shear rate dynamic viscosity, Equation (1) reads:

$$\eta_0'\left(x_{12}, \varphi, M_w\right) = \left[\eta_{0,0}'\left(\varphi, M_w\right)\right]^{\left(1-x_{12}\right)}\left[\eta_{0,1}'\left(\varphi, M_w\right)\right]^{x_{12}} \tag{17}$$

where $\eta'_{0,0}$ and $\eta'_{0,1}$ are the zero-shear rate dynamic viscosities of the polymers with zero and one vinyl content, respectively. Moreover, the zero-shear viscosity is proportional to the product of the plateau modulus and the terminal relaxation time according to:[34]

$$\eta'_{0,i}(\varphi, M_w) = \frac{\pi^2}{12} G_{0,i}(\varphi)\lambda_i(M_w) \quad (\text{for } i = 0,1) \tag{18}$$

The combination of Equations (11), (15) and (18) yields the composition rule for the zero-shear rate dynamic viscosity:

$$\eta'_{0,i}(x_{12}, \varphi, M_w) = \left[\frac{\pi^2}{12} G_0(0,1)\lambda_0 \varphi^{2.12} M_w^{3.4}\right]^{(1-x_{12})} \left[\frac{\pi^2}{12} G_0(0,1)\lambda_0 \varphi^{2.12} M_w^{3.4} 10^{(B_1 + B2)}\right]^{x_{12}} \tag{19}$$

Figure 7 shows a double-logarithm plot of the experimental versus the predicted zero-shear rate dynamic viscosity. Again, the agreement between the experimental data and the predictions of the composition rule (Equation 19) are excellent with a correlation coefficient better than 0.992.

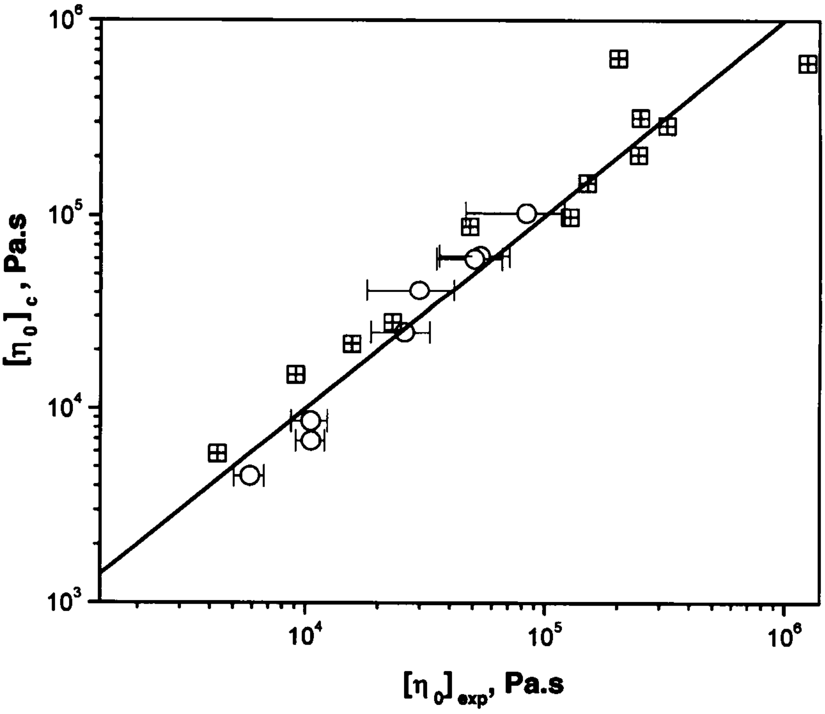

FIG. 7. — Predictions of the zero-shear rate dynamic viscosity for polybutadienes with various vinyl contents in solution (○), and in the melt (⊞)[3] calculated using Eq. 19, versus experimental data. The solid line indicates correlation with $R^2 = 1.0$.

CONCLUSIONS

A standing problem in the rheology of polybutadienes is the prediction of the linear viscoelastic properties of samples with very different vinyl contents. The composition rule proposed in this paper is a useful tool that relates the zero shear-rate dynamic viscosity, the plateau modulus and the terminal relaxation time, with the vinyl fraction, molecular weight and polymer fraction in solution. Extensive comparisons of the predictions of the composition rule with data from the current literature demonstrate a good agreement.

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