

Rheological Characterization of 4,4'-Bis(diethylamino)benzophenone-Functionalized Polybutadienes with Low and Medium Vinyl Content

NORMA A. ALCÁNTAR,¹ MARÍA DEL R. SALINAS,² RAFAEL HERRERA,² and OCTAVIO MANERO^{1,*}

¹Instituto de Investigaciones en Materiales, UNAM, A.P. 70-360, México, D.F., 04510, and ²Industrias Negromex, S.A. de C.V., Ave. de los Sauces 3A, Parque Industrial Lerma, Lerma, México 15000

SYNOPSIS

In this article a mechanical spectroscopic study of a series of low ($\approx 8\%$) and medium ($\approx 70\%$) vinyl-content polybutadienes, some of them functionalized with 4,4'-bis(diethylamino)-benzophenone, is presented. Characterization of polymers with well-known structure by small-amplitude oscillatory shear flow enabled investigation of the effect of the vinyl content and functional groups on the rheological behavior of the samples in the linear viscoelastic region. The Doi-Edwards viscoelastic model, without any adjustable parameter, proved to be adequate to describe the relationship between the macro/micro structure of the polymers and their viscoelastic properties. Results indicate that the vinyl content and functional groups modify the rheological behavior extensively. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that the microstructure and composition of polymeric materials determine extensively the macroscopic behavior of such materials.^{1,2} In particular, in the case of polybutadienes, a high vinyl content provides properties related to rigidity and flow resistance.³ On the other hand, with regard to polymer functionalization, an increase in compatibility with other materials to form composites is obtained by introducing reactive groups along the main backbone of the macromolecule.⁴ The production of polybutadiene-based articles requires modified and functionalized elastomers to obtain an appropriate balance of properties sought, such as resistance and surface adhesion. These properties are associated with the vinyl content and compatibility degree of the elastomer, respectively.⁵ A given proportion of vinyl content and functionalized groups in the microstructure and specific topology of the polymeric chains will provide macroscopic characteristics of final products, which themselves are closely related to their viscoelastic properties. In this

regard, resistance is related to the value of the elastic modulus, and the adhesion properties are proportional to the value of the viscous modulus. Rheometrical information is thus necessary to account for an appropriate control of the products.

It has been reported that the use of chain-end functionalized polybutadienes shows marked improvements in the wear and traction properties of tires (see ref. 5 and references therein). Furthermore, it has been found that the use of polybutadienes with 4,4'-bis(diethylamino)benzophenone at the chain ends improves the rebound resistance without reducing the surface adhesion of tires in such a way that the resistance and adhesion properties of the compound can be harmonized. In addition, these functional groups promote increases in the amount of fillers used in vulcanization reactions (such as carbon black), resulting in enhancements of the abrasion resistance of the products.

In this article the relationship between molecular structure and rheological properties of various polybutadienes is studied in detail. In particular, we intend to elucidate the influence of functionalized and high-vinyl-content groups on the moduli and viscosity of the systems. In addition, predictions of the experimental data are carried out by using the reptation model of Doi and Edwards⁶ to provide a

* To whom correspondence should be addressed.

Table I List of Materials Used in the Synthesis

Sample	<i>n</i> -BuLi (mmol)	TMEDA (mmol)	DEAB (mmol)
PB	0.69	—	—
PBV	0.83	1.66	—
PBF	0.83	—	0.83
PBVF	0.89	1.66	0.83

physical explanation of the dynamic behavior of the systems. From this comparison, it is possible to predict the viscoelastic properties in a small-amplitude oscillatory motion without the use of adjustable parameters, which allow one to establish the aforementioned relationship between microstructure and the observed changes as this is modified by shear flow.

The polybutadiene samples used in this study are mainly monodisperse (i.e., the polydispersity index does not exceed 1.05). Although extensions of the Doi and Edwards theory have been made to include polydispersity,⁷⁻⁹ in the present study the rheological behavior is described without considering such extensions. The model used is the original Doi and Edwards model and does not take account of the constrained release mechanism. There is evidence to suggest that the contribution of this mechanism to the expressions of the rheological properties in near monodisperse polymers may be negligible. This is certainly true for a system with high values of M/M_e (M is the molecular weight and M_e is that within entanglements), typically greater than 10.^{10,11} In the present work these values are higher than 25.

Although numerous studies have discussed the relationships between rheological properties and the microstructure of polybutadienes, very few have dealt with the effect of functional groups at the chain ends on the rheology of these compounds. Furthermore, the combined effect of a high vinyl content and functional groups leads to an interesting flow behavior that needs a more thorough analysis. In this regard, this article is intended to provide elements to assess the aforementioned relations between rheology and microstructure in these compounds.

EXPERIMENTAL PART

Synthesis

Polybutadienes used in this study were obtained by anionic polymerization, with cyclohexane

Table II Microstructure of 1-4 Polybutadienes

Characterization Results by GPC and IR				
Sample	Vinyl (%)	Trans (%)	\overline{M}_n	Polydispersity (I_d)
PB	8	50	80,000	1.02
PBF	8	49	79,000	1.02
PBV	70	—	76,000	1.01
PBVF	71	—	75,000	1.03

and *n*-butyl lithium (*n*-BuLi) as solvent and initiator, respectively. Medium vinyl polymers were obtained using *N,N,N',N'*-tetramethyl ethylene diamine (TMEDA) as modifier; and 4,4'-bis(diethylamino)benzophenone was used to functionalize the chain-end living polymers. Raw materials were provided by Industrias Negromex S.A.

PB T=50°C Viscoelastic properties

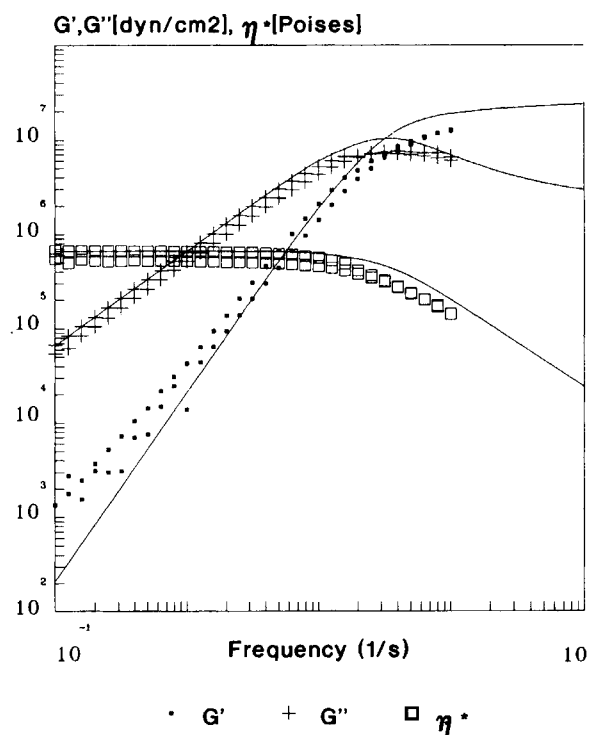


Figure 1 Variation of complex viscosity and moduli with frequency for the polybutadiene sample. Experimental results are compared with theoretical predictions (continuous lines).

PBF
T=50°C
Viscoelastic Properties

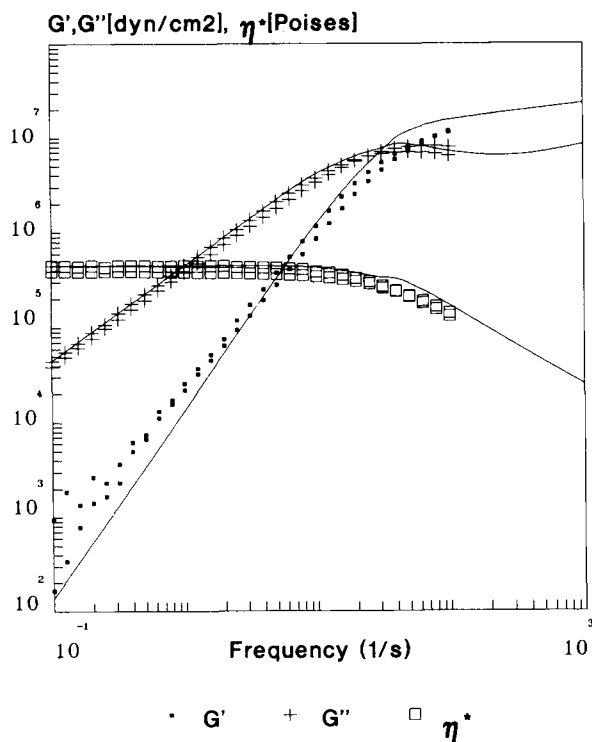


Figure 2 Same as in Figure 1, functionalized polybutadiene sample.

de C.V., and they were purified as follows: Cyclohexane and butadiene were treated with activated γ -alumina/molecular sieve No. 3 columns to reduce water and *tert*-butyl cathecol (monomers inhibitor) content; TMEDA (Aldrich, 99%) was purified by distillation in the presence of LiAlH_4 (lithium aluminum hydride); and DEAB (Aldrich, 99%) was recrystallized from anhydrous diethyl ether. Previous to polymerization, true active *n*-BuLi and scavenger initiator species contained in the butadiene/cyclohexane mixture were determined by a titration procedure⁵; therefore, it was possible to keep control of the molecular weight of the polymer as well as the TMEDA/*n*-BuLi and DEAB/*n*-BuLi ratios. Polymerization was conducted at $60 \pm 10^\circ\text{C}$ and 20 ± 10 atm, with a butadiene/cyclohexane ratio of about 10, allowing 1 h for the functionalization reaction of the poly(butadienyl) lithium with DEAB. Finally, polymers were deactivated and protected using 2,6-di-*tert*-butyl-*p*-cresol (BHT). Table I

shows the relative amount of *n*-BuLi, TMEDA, and DEAB used to produce the polymers.

Characterization

The polymers were characterized according to the following techniques:

1. Gel permeation chromatography (GPC), from which the molecular weight averages and distribution were obtained. The molecular weight distribution was obtained by using the universal calibration (polystyrene) and experimentally measured Mark-Houwink-Sakurada (MHS) parameters for 1,4-polybutadiene.
2. Fourier-transform infrared (FTIR) spectroscopy, to determine the proportion of vinyl and trans groups, and the functionalization degree. The presence of functional groups in the polymeric chains was detected by FTIR

PBV
T=50°C
Viscoelastic properties

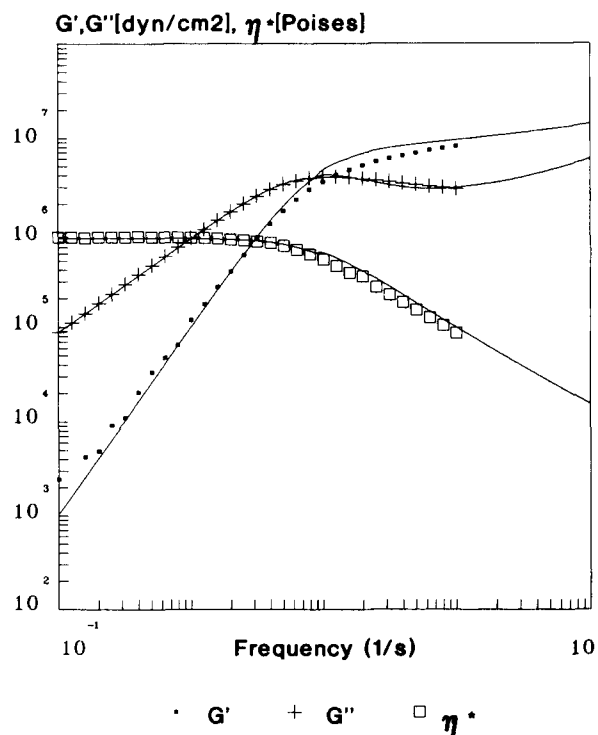


Figure 3 Same as in Figure 1, high-vinyl-content polybutadiene sample.

Table III Doi and Edwards Model Predictions

	PB	PBF	PBV	PBVF
Relaxation times:				
τ_d (s)	0.0322	0.0306	0.1190	0.099
τ_e (s)	1×10^{-6}	0.0001	0.00025	0.0001
Zero shear viscosity Temperature: 50°C				
η_0 (Poises)	530,000	360,000	700,000	650,000
Molecular parameters				
Molecular weight between entanglements				
Me (g/mol)	1000	1400	2800	2500
$Me = \frac{\rho RT}{G_N^0}$				
Number average molecular weight				
M (g/mol)	80,000	79,000	76,000	75,000
Average number of displacements by molecule				
M/Me	80	56.43	27.14	30
Number of displacements of primitive chain				
$Z = \frac{5}{4} \frac{M}{Me}$	100	70.54	33.93	37.5

using a Fourier Transform Infrared Spectrometer Nicolet 20-SXB.

- Mechanical spectroscopy (small-amplitude oscillatory shear flow) was used to determine the influence of the vinyl content and functional groups on the rheological behavior of the samples in the linear viscoelastic region. Rheological measurements were performed in the melt using a Rheometrics Dynamic Spectrometer model VE.

The rheological measurements were made on samples for which the functional groups do not participate in clustering, and evaluation of their rheological properties was done prior to vulcanization or related chemical reactions. As will be discussed later, these groups provide the chain ends with a more rigid conformation in comparison with the non-functionalized samples.

Results of GPC and FTIR are presented in Table II. The degree of functionalization was difficult to quantify, but the analysis allowed evidence of grafting of functional groups to the polymeric chain. The vinyl and trans contents were determined by

^1H , ^{13}C nuclear magnetic resonance (NMR) in a Varian XL-300.

THEORETICAL DESCRIPTION

The Doi and Edwards model⁶ essentially describes the dynamic properties of concentrated polymer solutions and melts (or elastomers) on the basis of a reptation motion of individual polymer chains. These are confined in a tubular region determined by topological constraints due to the presence of the other chains. The spatial distribution of temporary entangled network of polymer chains is modified by deformations or stresses imposed on the system, which induce the diffusion of individual chains.

The time scale associated with the molecular dynamics depends on the magnitude of the relative displacement of the individual chains in such a way that the diffusion of the chains is characterized by a specific length of magnitude a . This characteristic length represents in the Doi and Edwards model the diameter of the constrained tubular region along which the diffusion of chains takes place. In this

PBVF
T=50°C
Viscoelastic Properties

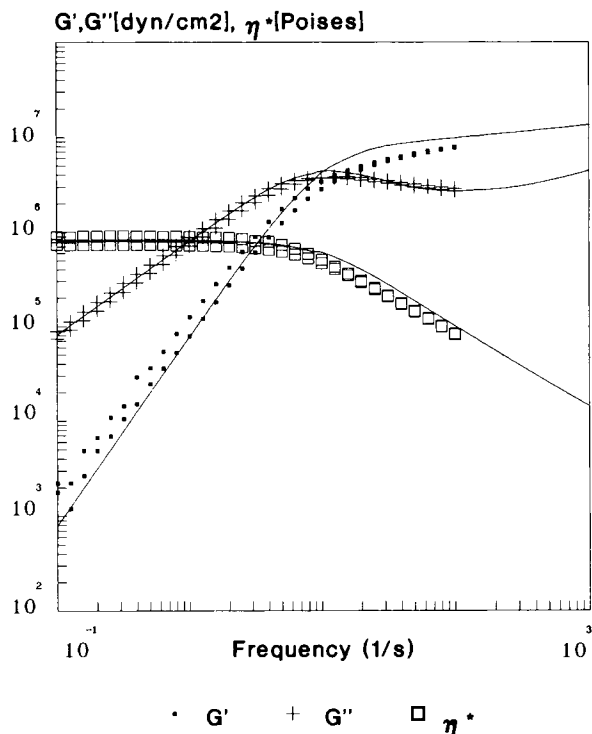


Figure 4 Same as in Figure 1, high-vinyl-content functionalized polybutadiene sample.

regard, for displacements larger than a , the dynamics are reptational, whereas for motions smaller than a , the response of molecular segments is not restricted by the tube boundaries and each segment behaves as free Rouse molecules without entanglements. This behavior also takes place when the polymer molecular weight is lower than that corresponding to the critical value for the entanglement onset.

On the basis of the previous premises, it is then possible to define a characteristic time τ_e , such that for time scales smaller than τ_e , the dynamics are described by the Rouse model, with the following expressions for the dynamic moduli:

$$G'(\omega) = G''(\omega) = G_N^0 \left(\frac{\pi}{2} \omega \tau_e \right)^{1/2} \quad \omega \tau_e > 1 \quad (1)$$

For times scales larger than τ_e , the molecular dynamics are influenced by the presence of molecular entanglements and the Rouse model is no longer

valid. The reptation and the relaxation processes take place in this regime. Accordingly, the dynamics for time scales larger than τ_e are characterized by the disentanglement process from the tubular region, where the complex moduli are expressed as

$$G'(\omega) = G_N^0 \sum_{p \text{ odd}} \frac{8}{\pi^2 p^2} \frac{(\omega \tau_d / p^2)^2}{1 + (\omega \tau_d / p^2)^2} \quad \text{for } \omega \tau_e < 1 \quad (2a)$$

$$G''(\omega) = G_N^0 \sum_{p \text{ odd}} \frac{8}{\pi^2 p^2} \frac{\omega \tau_d / p^2}{1 + (\omega \tau_d / p^2)^2} \quad \text{for } \omega \tau_e < 1 \quad (2b)$$

The characteristic time τ_d (disentanglement time) is the largest relaxation time and signals the time scale of the reptation process. It governs the dynamics along the low-frequency region up to the onset of the plateau region.

STORAGE MODULUS, G'
T=50°C

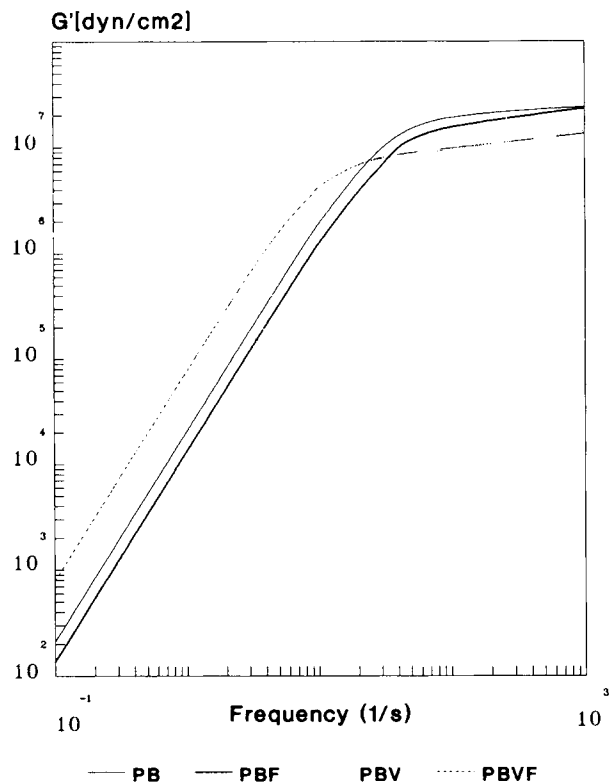


Figure 5 Theoretical predictions for the four samples. Elastic modulus as a function of frequency.

LOSS MODULUS, G''
 $T=50^\circ\text{C}$

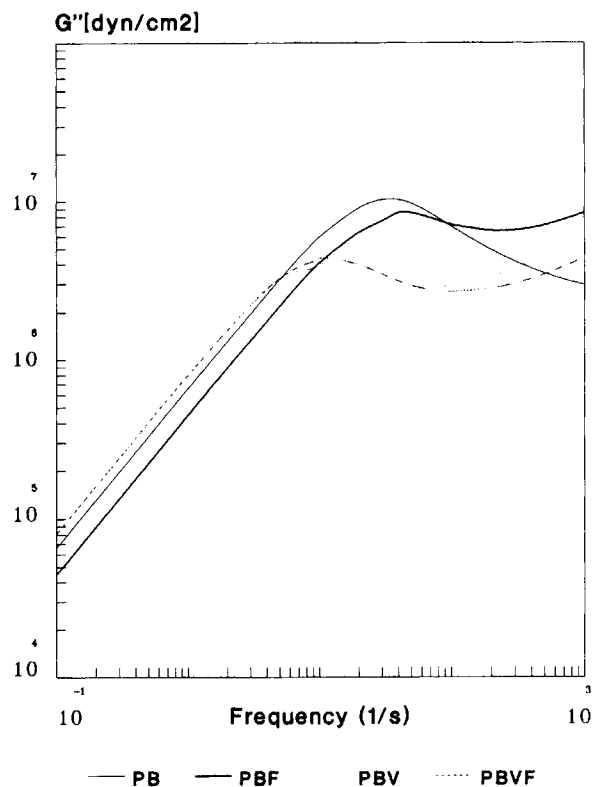


Figure 6 Theoretical predictions for the four samples. Viscous modulus as a function of frequency.

In molecular terms, the characteristic times τ_e and τ_d derived from the theory are

$$\tau_e = \frac{12M_e^2}{\pi^2\rho RT} \quad (3)$$

$$\tau_d = \frac{12M^3}{\pi^2\rho RTM_e} \quad (4)$$

where ρ , T are the density and temperature, R is the gas constant, and M , M_e are the molecular weight and molecular weight between entanglements, respectively. M_e may be calculated from the value of the elastic modulus in the plateau region (G_N^0), according to the rubber elasticity theory:

$$M_e = \frac{\rho RT}{G_N^0} \quad (5)$$

The viscosity at zero shear rate may be found from the following expression similar to that of the Maxwell model of linear viscoelasticity:

$$\eta_0 = \frac{\pi^2}{12} G_N^0 \tau_d \quad (6)$$

Equations (4) and (6) show that the viscosity and the main relaxation time are proportional to M^3 , which indicates a strong dependence on molecular weight determined by the dynamics of the whole polymer chain. Similarly, Eq. (5) shows that the largest modulus corresponds to the more entangled system.

RESULTS AND DISCUSSION

Experimental results of four samples—polybutadiene (PB), functionalized polybutadiene (PBF), polybutadiene with high vinyl content (PBV), and functionalized polybutadiene with high vinyl content

COMPLEX VISCOSITY, η^*
 $T=50^\circ\text{C}$

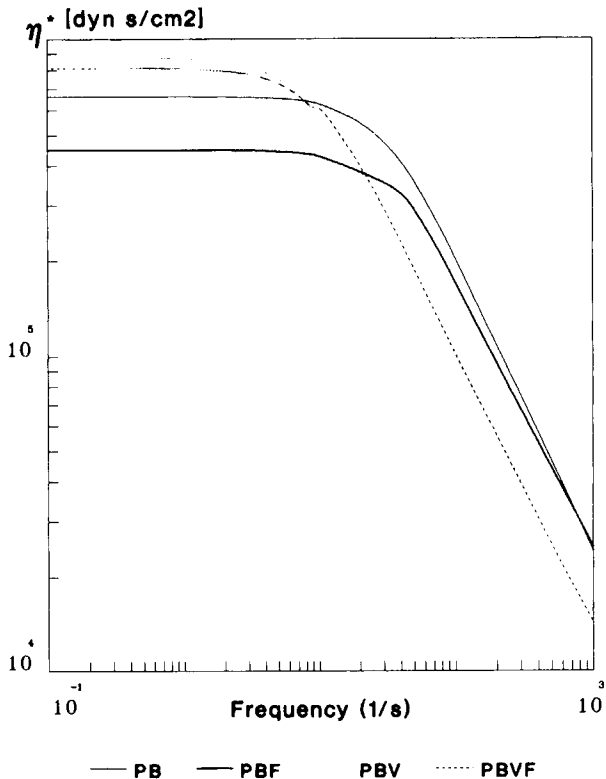


Figure 7 Theoretical predictions for the four samples. Complex viscosity as a function of frequency.

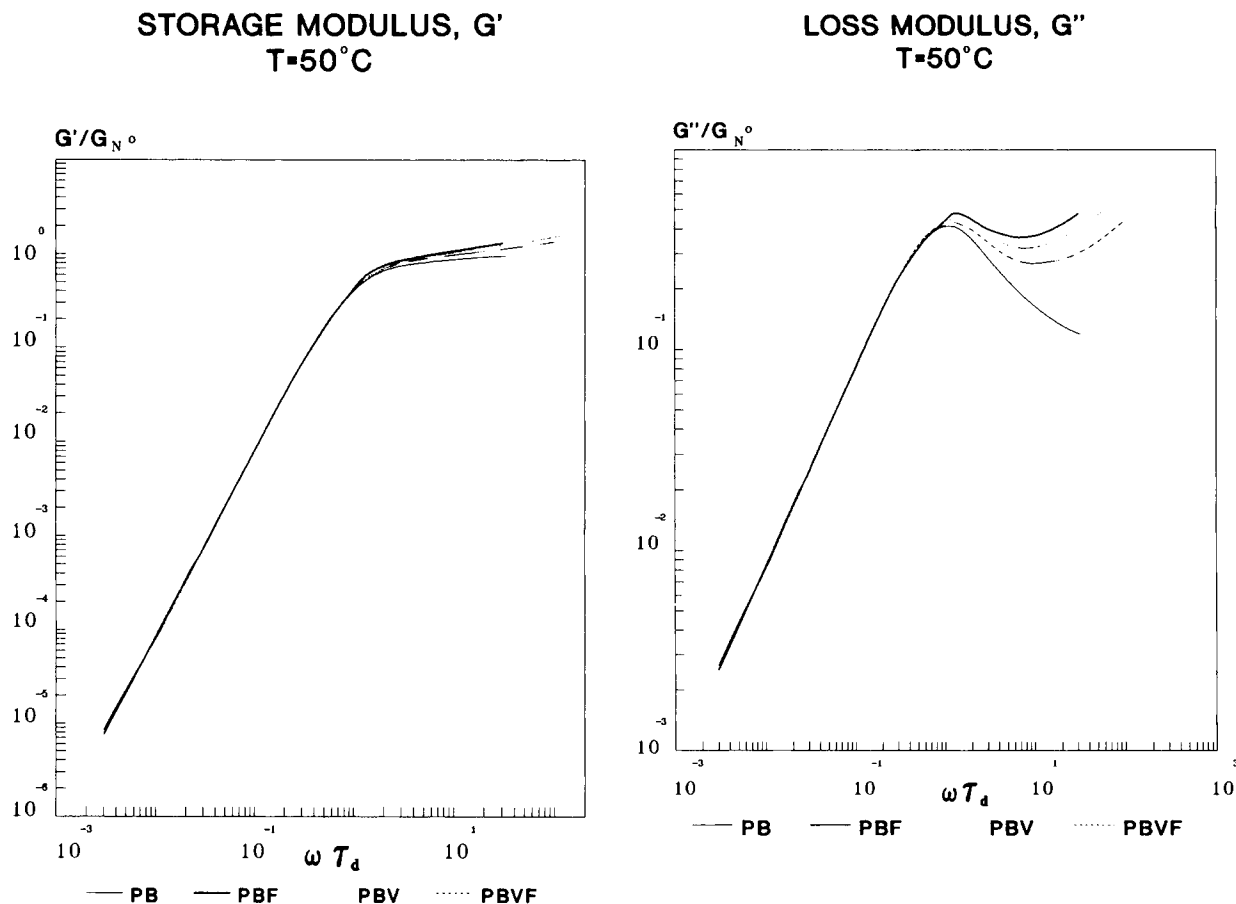


Figure 8 Normalized elastic modulus (a), viscous modulus (b), and complex viscosity (c), as a function of reduced frequency $\omega\tau_d$. Results for the four samples.

(PBVF)—are shown in Figures 1 through 4, together with predictions of the Doi and Edwards model [Eqs. (1) and (2)]. Two experimental runs at 50°C for the moduli G' , G'' , and the viscosity η' as a function of frequency are shown with the predictions as continuous lines. The range along which Eq. (1) governs the behavior of the moduli covers frequencies larger than $1/\tau_e$ and vanishes at the onset of the terminal region, where $\omega \ll 1/\tau_e$.

As observed, a good quantitative agreement is found without using adjustable parameters. The characteristic times τ_d and τ_e were quantified from the variation of the viscoelastic properties at low and high frequencies together with Eqs. (3) through (6). From this adjustment, it is possible to analyze the molecular information that the model provides, and this is shown in Table III. Similarly, Figures 5 through 7 show the predictions for the four systems depicting the variation of the moduli and viscosity with frequency, respectively. With these results, a comparative analysis of the four systems may be performed systematically.

As mentioned, the characteristic time τ_d (disentanglement time) is the main relaxation time of the system which governs the dynamics along the low-frequency region up to the onset of the plateau region. Figures 8(a) through 8(c) show the variation of the normalized viscosity and moduli as a function of $\omega\tau_d$. Within the low-frequency region, the predictions for the four systems lie on a single curve independent of their own molecular structure, indicating that the rheological properties of these systems are indeed effectively governed by τ_d . Similarly, Figure 9 shows the region where the influence of molecular entanglements gradually vanishes at high frequencies and the dynamics are governed by the time τ_e . As before, in this case the normalized rheological functions are plotted with the normalized frequency $\omega\tau_e$ and curves superimposed at the onset of the Rouse regime. Here, moduli vary as $(\omega\tau_e)^{1/2}$ in accordance with Eq. (1).

The relaxation times τ_d shown in Table III indicate that the highest values correspond to compounds with high vinyl content, and thus the plateau

COMPLEX VISCOSITY, η^*
T=50°C

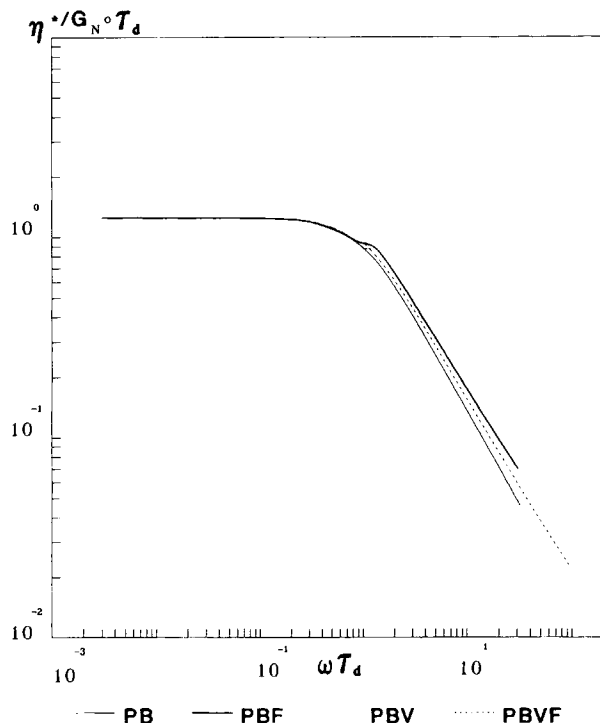


Figure 8 (Continued from the previous page)

region of the elastic modulus and the maximum in the viscous modulus are observed at lower frequencies than those of the other samples (see Figs. 5 and 6). Similarly, the onset for viscosity variation with frequency is observed at lower frequencies in these compounds, as shown in Figure 7.

It is interesting to observe in Figures 8(a) and 8(c) that with the knowledge of τ_d it is possible to predict practically the whole variation of viscosity and moduli with frequency for the four systems. However, it is necessary to know τ_e to predict the full behavior of the viscous modulus, as observed in Figure 8(b), where the correlation with $\omega\tau_d$ breaks down in the high-frequency region. In addition, the minimum in G'' is observed at lower frequencies in the compounds with high vinyl content (see Fig. 6). On the contrary, in PB, the minimum in G'' is not observable but at very high frequencies ($\omega > 10^3 \text{ s}^{-1}$), which were not accessible with the present experimental facilities. Within the frequency range covered, PB is practically a system with a single relaxation time τ_d .

From the values provided by the elastic modulus at high frequencies (Fig. 5), it may be observed that the compounds with higher entanglement density

are those with a low proportion of vinyl groups, inasmuch as the mean molecular weight between entanglements for those compounds is lower, as shown in Table III. Similarly, these systems possess a higher viscous modulus and higher viscosity at high frequencies, as observed in Figures 6 and 7. In contrast to this behavior, the compounds with higher vinyl contents present moduli and viscosity with larger magnitudes within the low-frequency region.

Compounds with higher vinyl content present higher magnitudes of their rheological properties at low frequencies and lower values at high frequencies. This is certainly valid even though their molecular weight is slightly lower, according to data in Table III. Consequently, the mean molecular weight between entanglements doubles those of the compounds with low vinyl content.

By observation of Figures 5 through 7, it is clear that the existence of a functional group at the chain ends has a substantial effect on the linear viscoelastic properties in the terminal region, where the reptation motion occurs. In comparison with the corresponding nonfunctionalized samples, the functionalized ones present the shorter relaxation times, as seen in Table III. This observation is related with experimental evidence which indicates that the end segments of a polymer chain relax faster than the

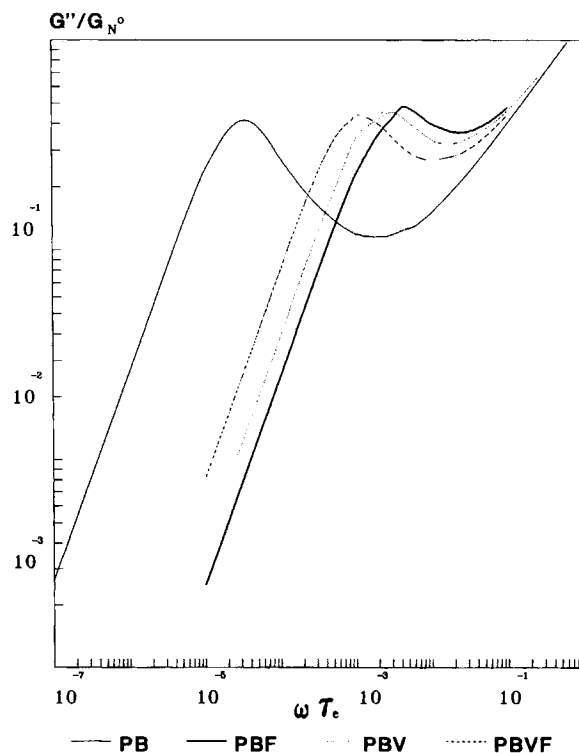


Figure 9 Normalized viscous modulus as a function of reduced frequency $\omega\tau_e$. Results for the four samples.

segments at the center.¹²⁻¹⁵ This particular behavior is predicted by the Doi and Edwards model, in which reptation motion causes chain relaxation to occur first at the ends and then later in the center.^{16,17} In the present experiments, the functional group at the chain ends causes a first relaxation of the polymer chains in the terminal region, and eventually this effect vanishes at higher frequencies in the plateau region. It is then possible that the functional groups promote changes in the reptation behavior of the chains, inducing a higher orientation in the chain ends. This effect shows the presence of short-range interactions between segments of functionalized molecules and the polymeric network, the so-called orientational coupling.¹⁸⁻²³ The functional group imparts the chain ends a more rigid, nematic-like structure, which increases the end-segment orientation and hence decreases the relaxation times.

Orientalional coupling effects have been accounted for in a model proposed by Doi et al.,²⁴ which is based on the assumption that orientation correlations act on the bond level and do not interfere with the overall reptation process of the chain. On the contrary, in the present case, the existence of functional groups at the chain ends affects the reptation process, decreasing the overall relaxation times. Of course, the Doi et al. model is not directly applicable to this case but nevertheless illustrates a possible mechanism by which reptation occurs in functionalized chains.

CONCLUSIONS

The structural properties and the dynamic response of the systems treated in this study manifest themselves in several forms according to the time scales of specific processes. For instance, in those processes that involve relaxations at long times, the presence of vinyl groups in their macromolecular structure induces a certain level of rigidity, which produces a higher flow resistance and elasticity. On the other hand, for processes in which the strain rate is higher with small characteristic times corresponding to the processing operations of elastomers, the presence of vinyl groups promotes the formation of a temporary entangled network less dense, less viscous, and with high processability.

N. A. Alcántar acknowledges the support received from DGAPA-UNAM during the period of this research.

REFERENCES

1. M. Morton, *Anionic Polymerization: Principles and Practice*, Academic Press, New York, 1983, Chap. 11.
2. M. van Beylen, S. Bywater, G. Smets, M. Szwarc, and D. J. Worsfold, *Adv. Polym. Sci.*, **86**, 87 (1988).
3. A. Yoshioka, K. Komuro, A. Veda, H. Watanabe, S. Akita, A. Masuda, and A. Nakajima, *Pure & Appl. Chem.*, **58**, 12, 1697 (1986).
4. D. E. Bergbreiter and C. R. Martin, Eds., *Functional Polymers*, Plenum Press, New York, 1989.
5. R. P. Quirk, J. Yin, S. Guo, X. Hu, G. J. Summers, J. Kim, L. Zhu, J. Ma, T. Takazawa, and T. Lynch, *Rubber Chem. Technol.*, **64**, 648 (1991).
6. M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford Science Publications, Clarendon Press, Oxford, England, 1986.
7. R. R. Rahalkar, *Rheol. Acta*, **29**, 88 (1990).
8. R. R. Rahalkar, J. Lamb, G. Harrison, A. J. Barlow, W. Hawthorne, J. A. Semleyn, A. M. North, and R. A. Pethrick, *Proc. Roy. Soc. Lond. A.*, **334**, 207 (1986).
9. R. R. Rahalkar, C. Javanand, P. Richmond, I. Melville, and R. A. Pethrick, *J. Rheol.*, **29**, 955 (1985).
10. J. Rooves, *Polymer J.*, **18**, 153 (1986).
11. Y. H. Lin, *Macromolecules*, **22**, 3080 (1989).
12. K. Osaki, E. Takatori, M. Kurata, H. Ohnuma, and T. Kotaka, *Polym. J.*, **12**, 947 (1986).
13. J. F. Tassin, L. Monnerie, and L. J. Fetters, *Polym. Bull.*, **15**, 165 (1986).
14. J. F. Tassin, L. Monnerie, and L. J. Fetters, *Macromolecules*, **21**, 2404 (1988).
15. A. Lee and R. P. Wool, *Macromolecules*, **20**, 1924 (1987).
16. M. Doi, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1005 (1980).
17. M. Doi and S. F. Edwards, *J. Chem. Soc. Faraday Trans II*, **74**, 1789 (1978).
18. B. Deloche and E. T. Samulski, *Macromolecules*, **14**, 575 (1981).
19. M. Jacobi, R. Stadler, and W. Gronski, *Macromolecules*, **19**, 2884 (1986).
20. J. F. Tassin, A. Baschwitz, J. Y. Moise, and L. Monnerie, *Macromolecules*, **23**, 1879 (1990).
21. P. Sotta, B. Deloche, J. Herz, A. Lapp, D. Durand, and J-C. Rabadeux, *Macromolecules*, **20**, 2769 (1987).
22. P. Schmidt and B. Schneider, *Makromol. Chem.*, **184**, 2075 (1983).
23. E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, **104**, 2075 (1982).
24. M. Doi, D. S. Pearson, J. Kornfield, and G. G. Fuller, *Macromolecules*, **22**, 1488 (1989).

Received July 15, 1994

Accepted January 15, 1995