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Effect of vinyl content on the viscoelastic properties of polybutadienes and polyisoprenes — monomeric friction coefficient

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The rheological behavior of a series of polybutadienes and polyisoprenes presenting various microstructures has been characterized over a wide range of temperatures. The polybutadienes vary in microstructure from 11% to 84% vinyl content. The viscoelastic coefficients resulting from the time–temperature superposition principle were determined. The Rouse theory modified for undiluted polymers was used to calculate the monomeric friction coefficient, ζ_0, from the transition zone. We determined that the WLF coefficients are the same, and that ζ_0 is a unique function of $(T - T_g)$ independently of chain microstructure. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Analysis of the rheological behavior of polymer systems is of fundamental importance in the study of the dynamic processes occurring in polymer melts. The monomeric friction coefficient, ζ_0, plays a crucial role in polymer dynamics. In the Rouse and Doi-Edwards molecular theories of viscoelasticity[1,2], the dynamics of all modes of chain motion scales with the monomeric friction coefficient. This coefficient represents the resistance encountered by one repeat unit moving through its environment.

However, chain microstructure is expected to influence the rheological behavior of polymers melts and essentially the friction coefficient. Some values of the monomeric friction coefficient were reported in the literature but because of the scattering of the data, we have carried out an analysis of the viscoelastic properties of elastomeric systems.

The purpose of the present work is to analyse the effect of local chain structure on the rheological behavior of polymer melts.

A series of polybutadienes with nearly the same cis:trans ratio but various vinyl contents were studied, as well as a polybutadiene containing 79% of cis configurations. Two polyisoprenes of different microstructures were also investigated. The viscoelastic properties of the different samples have been analyzed and the monomeric friction coefficient as well as the WLF parameters[3] have been determined.

EXPERIMENTAL PART

Materials

All the elastomers investigated were provided by Manufacture Francaise des Pneumatiques Michelin (Clermont-Ferrand, France). Their microstructures, molecular weight characteristics and glass transition temperatures are reported in *Table 1*.

Molecular weights were obtained by gel permeation chromatography (universal calibration). The glass transition temperatures T_g were determined by differential scanning calorimetry at the onset of the transition. Measurements were made at a heating rate of 5°C min^{-1}. As expected, in the polybutadienes, the glass transition temperature increases with the vinyl content[4–6].

Rheological measurements

Viscoelastic measurements were carried out with a Rheometrics Dynamic Analyser (RDA II) operating in the oscillatory strain mode and with parallel-plate geometry (25 mm diameter plates, 1–2 mm gap heights). In order to avoid slippage of the polymer, scattered plates were used. The maximum strain amplitude used (8%) was within the linear viscoelasticity zone of the material. The isothermal storage and loss moduli, G' and G'', were measured as functions of frequency from $\omega = 0{,}1$ to 100 rad s^{-1} for temperatures between about $(T_g + 30°C)$ and $(T_g + 110°C)$.

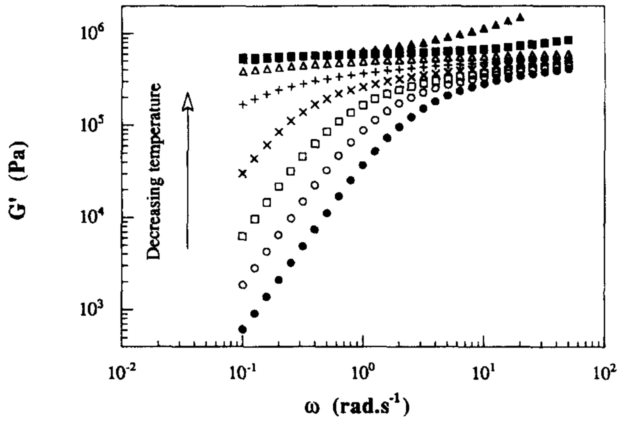

Figure 1 Storage modulus for PB(54v) versus angular frequency at different temperatures ranging from − 40°C to 55°C. Symbols: (●) 55°C, (○) 45°C, (□) 35°C, (×) 25°C, (+) 10°C, (△) − 10°C, (■) − 30°C, (▲) −40°C

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Figure 1 shows the storage modulus $G'(\omega)$ for the sample PB(54v) for temperatures varying from − 40°C to 55°C. Cooled nitrogen was continuously circulating in the sample chamber to obtain subambient temperatures. The plate distance was manually adjusted at each temperature to compensate for the thermal expansion of the fixtures and polymer. The reproducibility of the dynamic data was checked by repeating experiments at least twice with different samples of a given polymer.

RESULTS AND DISCUSSION

In materials which obey the time–temperature superposition principle[2], the dynamic moduli are rescaled to master curves at a reference temperature T_0 by using horizontal (a_{T/T_0}) and vertical (b_{T/T_0}) shift factors

$$G'(\omega, T) = b_{T/T_0} G'(a_{T/T_0}\omega, T_0) \tag{1}$$

$$G''(\omega, T) = b_{T/T_0} G''(a_{T/T_0}\omega, T_0) \tag{2}$$

Master curves resulting from time–temperature superposition of $G'(\omega)$ and $G''(\omega)$ for PB(54v) at the reference temperature $T_0 = 25°\mathrm{C}$ are presented in *Figure 2*. The behavior is typical for high molecular weight narrow distribution polymers[2,7,8]: it shows the terminal zone at low frequencies, the plateau zone at intermediate frequencies and entry into the transition zone at higher frequencies.

Viscoelastic coefficients

The temperature dependence of the horizontal shift factors, a_{T/T_0}, are well described by the WLF equation[3]

$$\log a_{T/T_0} = \frac{-C_1^0 (T - T_0)}{C_2^0 + (T - T_0)} \tag{3}$$

where C_1^0 and C_2^0 are the WLF parameters at the reference temperature T_0, which depend on the molecular structure of the polymer.

These viscoelastic coefficients are more easily determined from the intercept and slope of a linear plot of $(T_0 - T)/\log a_{T/T_0}$ versus $(T_0 - T)$ as shown in *Figure 3*.

T_0 corresponds to an arbitrarily chosen temperature reference. Varying T_0 from (T_g + 40°C) to (T_g + 110°C), one can obtain the temperature dependence of C_1^0 and C_2^0. These coefficients are related to the free volume theory[9] by the following expressions

$$C_1^0 = \frac{1}{2.303 f_{T_0}} \tag{4}$$

$$C_2^0 = \frac{f_{T_0}}{\alpha_f} \tag{5}$$

$$C_1 C_2 = \frac{1}{2.303 \alpha_f} \tag{6}$$

where f_{T_0} and α_f are respectively the fractional free volume at T_0 and the thermal expansion coefficient of the free volume.

The assumption of a linear relationship between the fractional free volume and temperature ($f_T = f_g) + \alpha_f (T - T_g)$, f_g being the fractional free volume at T_g, would lead to linear dependences of $1/C_1^0$ and C_2^0 against $(T_0 - T_g)$. These data are presented in *Figure 4* for the sample PB(54v).

As found earlier by Carella et al.[4] and more recently by Palade et al.[10], when T_0 is equally spaced from T_g for the polybutadienes with various vinyl contents, a master curve is obtained to represent the dependence of the frequency

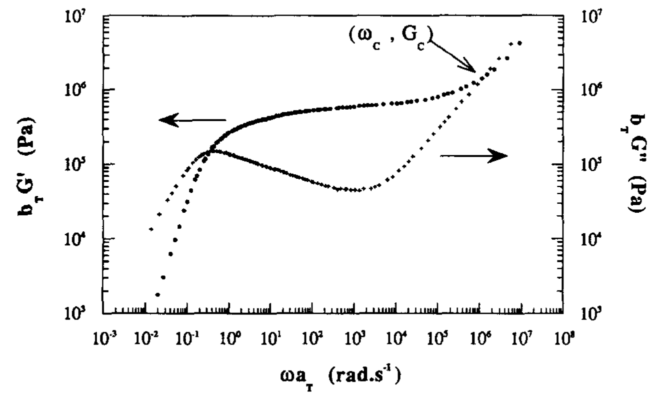

Figure 2 Dynamic moduli master curves for PB(54v) at the reference temperature $T_0 = 25°\mathrm{C}$

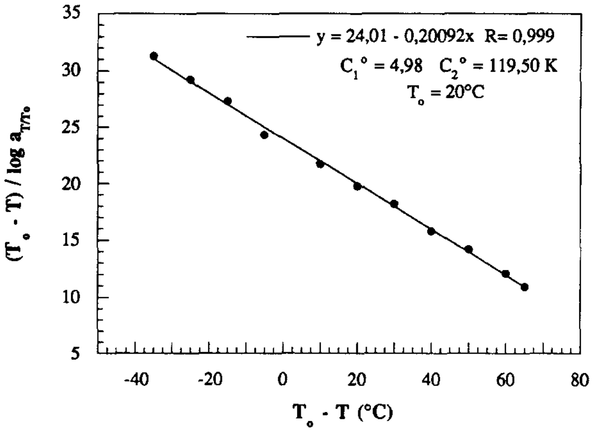

Figure 3 WLF plot for temperature dependence of frequency shift factor for PB(54v)

Table 1 Molecular characteristics of the considered elastomers

Polymer	Sample	Microstructure				M_w	$\frac{M_w}{M_n}$	T_g (°C)
		% cis	% trans	% vinyl	% 3.4			
Polybutadienes	PB(11v)	40	49	11		141700	1.1	− 93
	PB(24v)	38	38	24		128900	1.1	− 85
	PB(34v)	29	37	34		123000	1.2	− 75.5
	PB(54v)	21	24	54		140900	1.6	− 59
	PB(69v)	14	17	69		116100	1.2	− 44
	PB(76v)	10	14	76		158700	2.3	− 32.5
	PB(84v)	3	13	84		159600	1.7	− 23.5
	PB(79c)	79	17	4		276300	3.7	− 100
Polyisoprenes	PI(92c)	92	5		3	1820000		− 62
	PI(30%3,4)	53	17		30	192900	1.2	− 43

shift factors with the temperature. We chose $T_0 = T_g + 70°C$ as the reference temperature in *Figure 5* and observed a master curve as it was reported in the literature. This indicates that the viscoelastic coefficients at the glass transition temperature, i.e. C_1^g and C_2^g, are the same in all these systems.

To minimize experimental errors, C_1^g and C_2^g were determined by extrapolating the lines in *Figure 4* to $(T_0 - T_g) = 0$. For all the elastomers studied, the same procedure was used. For the polybutadienes with nearly the same cis:trans ratio and differing in vinyl content, we calculated an average of the C_1^g and C_2^g values corresponding to the different samples. Finally, we obtained

$$C_1^g = 13.9 \pm 0.2 \ C_2^g = 44 \pm 3 \text{ K and } C_1C_2 = 610 \pm 50 \text{ K}$$

These results are in reasonable agreement with values previously reported[4,11].

For the polybutadiene with 79% of cis units, the C_1^g and C_2^g values are slightly different and are respectively 13.4 ± 0.4 and 37 ± 4 K. This difference may be ascribed to the strong polydispersity of this sample PB(79c).

Concerning the two polyisoprenes, we also obtained an a_{T/T_0} master curve and the following WLF parameters

$$C_1^g = 13.5 \pm 0.2 \ C_2^g = 45 \pm 3 \text{ K and } C_1C_2 = 606 \pm 50 \text{ K}$$

This is in good agreement with the conclusion of Gotro et al.[12], Roovers et al.[13], that the temperature dependence of a_{T/T_0} is rather insensitive to the microstructure of polyisoprenes.

It is concluded that, within experimental error, a single set of WLF parameters at T_g is obtained to characterize the relaxation dynamics irrespective of the vinyl content of the polybutadienes and polyisoprenes.

This is equivalent to assuming that the free volume expansion coefficient is identical for all the elastomers investigated and that the fractional free volume is the same for each polymer at its own T_g.

Monomeric friction coefficient

Different methods[2] are available to calculate the monomeric friction coefficient ζ_0: one involves measurement of the zero-shear melt viscosity of polymers. Since the newtonian plateau was not accessible in all the polymers (because of sample degradation), this method was not used.

Hence, the monomeric friction coefficient was determined from experimental data in the transition zone, where $G' = G'' = G_c$ and both are proportional to the square root of frequency, according to the following equation derived from the Rouse theory modified for undiluted polymers[2]

$$\zeta_0 = \frac{48 M_0^2 G_c^2}{a^2 \rho^2 RNT \omega_c} \tag{7}$$

(ω_c, G_c) represents the crossover point coordinates (see *Figure 2*), M_o the monomer molecular weight, ρ the polymer density, R the universal gas constant, T the temperature, N Avogadro's number and a the root-mean-square end-to-end length per monomer unit. This approach is subject to approximations, for example the exact value of a may not be known. However, this method is largely used for estimating the monomeric friction coefficient.

For this range of microstructures[4], the density of polybutadienes at 25°C is 0.895 g cm^{-3}. The value of 0.913 g cm^{-3} is considered at 25°C for the two polyisoprenes[14].

The root-mean-square end-to-end length per monomer unit, a, is defined by

$$a^2 = \frac{\langle r_0^2 \rangle}{M_n} M_0 \tag{8}$$

where $\langle r_0^2 \rangle$ represents the mean-square unperturbed end-to-end distance, and M_n the number-average molecular weight.

In the case of polybutadienes of various microstructures, Fetters et al.[15] as well as Zhongde et al.[16] presented values of $(\langle r_0^2 \rangle / M)$ which are reported on *Figure 6* against the vinyl content, $x_{1,2}$. It appears that, except for a polybutadiene containing 96% of cis units, one can propose a linear equation to describe this evolution. With $M_0 = 54$ g mol^{-1}, a^2 (in Å^2) may be written as

$$a^2 = 49.2 - 0.162 x_{1,2} \tag{9}$$

The calculated values of a for the series of our polybutadienes are given in *Table 2*. It should be noticed that these values disagree with those proposed by Liu et al.[17]. The value of a for the two polyisoprenes[2] was considered to be 6.8 Å.

The monomeric friction coefficients determined at 25°C are also listed in *Table 2* for the elastomers investigated. It is quite reasonable that 1,2-polybutadienes with higher vinyl

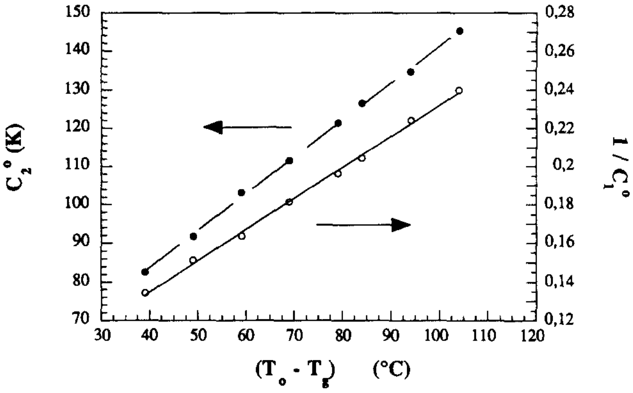

Figure 4 $1/C_1^0$ (open symbols, right axis) and C_2^0 (filled symbols, left axis) plotted versus $(T_0 - T_g)$ for PB(54v)

Table 2 Calculated values of monomeric friction coefficient for the studied elastomers

Sample	a/(Å)	log ζ_0 at 298 K/ (dyn s cm^{-1})	log ζ_{00}/ (dyn s cm^{-1})
PB(11v)	6.9	− 7.13	− 10.8
PB(24v)	6.7	− 6.97	− 10.6
PB(34v)	6.6	− 6.77	− 10.9
PB(54v)	6.4	− 6.33	− 11.2
PB(69v)	6.2	− 5.76	− 11.4
PB(76v)	6.1	− 5.17	− 11.2
PB(84v)	6	− 4.67	− 11.1
PB(79c)	6.4	− 7.07	− 10.0
PI(92c)	6.8	− 6.25	− 10.4
PI(30%3,4)	6.8	− 5.57	− 10.4

contents correspond to higher monomeric friction coefficients because the vinyl group is much stiffer than the 1,4 group at any given temperature. The temperature dependence of ζ_0 is also described by the WLF equation

$$\log\frac{\zeta_0(T)}{\zeta_0(T_g)}=\frac{-C_1^g(T-T_g)}{C_2^g+(T-T_g)} \qquad (10)$$

where $\zeta_0(T)$ and $\zeta_0(T_g)$ are respectively the monomeric coefficient friction values at T and T_g.

The above equation can be written as

$$\log\zeta_0(T)=\log\zeta_{00}+\frac{C_1^gC_2^g}{T-T_g+C_2^g} \qquad (11)$$

where ζ_{00} is called the intrinsic monomeric friction coefficient.

It is of interest to compare these coefficients at temperatures equally spaced from T_g. Therefore, we have determined ζ_0 at temperatures where the viscoelastic measurements were carried out, by applying temperature shifts factors, and plotted in *Figure 7* log ζ_0 versus $(T - T_g)$ for all the investigated polymers. A master curve is obtained. Despite the differences in the microstructure of the various samples, they all exhibit nearly the same value of the monomeric friction coefficient at a given $(T - T_g)$ value and consequently the same value of $\log \zeta_0(T_g)$. *Figure 8* shows some discrepancies between our data and some data taken from the literature[11,17-21] (see caption for the references).

A simple way to determine log ζ_{00} is to represent the evolution of log $\zeta_0(T)$ versus $1/(T - T_\infty)$, with $T_\infty = T_g - C_2^g$, as shown in *Figure 9* for PB(54v). A straight line is obtained with log ζ_{00} as intercept. Values of log ζ_{00} are listed in *Table 2* for all the elastomers. When taking into account experimental errors, one can consider that these values are quite similar.

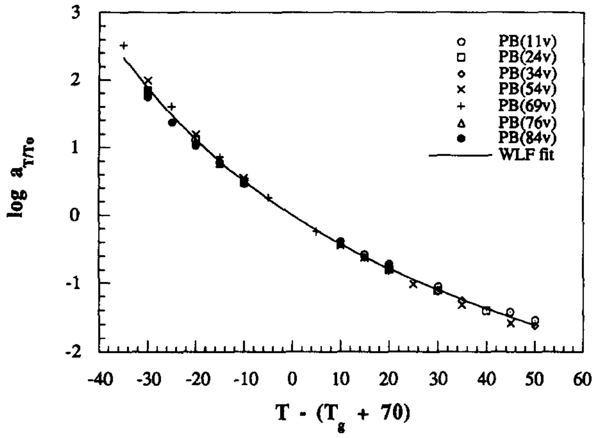

Figure 5 Logarithmic plot of frequency shift factors versus $(T - T_0)$ with $T_0 = T_g + 70°C$. The solid curve corresponds to the WLF fit for a_{T/T_0} in all the polybutadienes

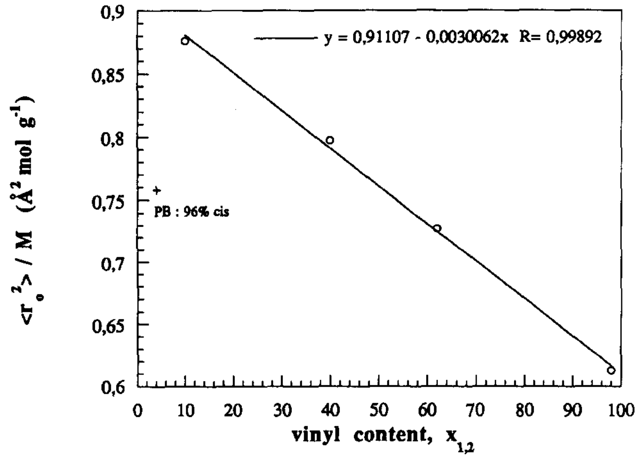

Figure 6 Dependence of $\langle r_0^2\rangle/M$ on the vinyl content for 1,2-polybutadienes (open circles). Data are taken from Refs. [15,16]

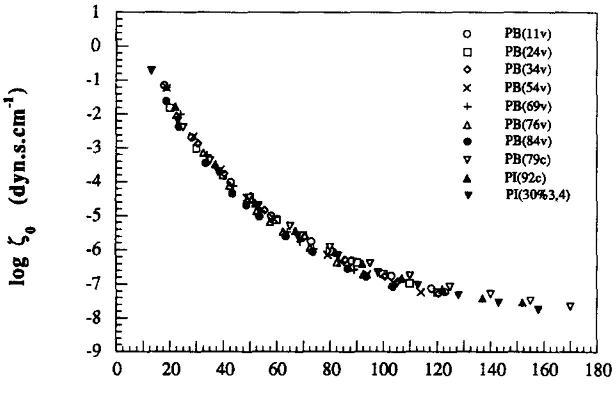

Figure 7 Plot of log ζ_0 as a function of $(T - T_g)$ for various polybutadienes and polyisoprenes

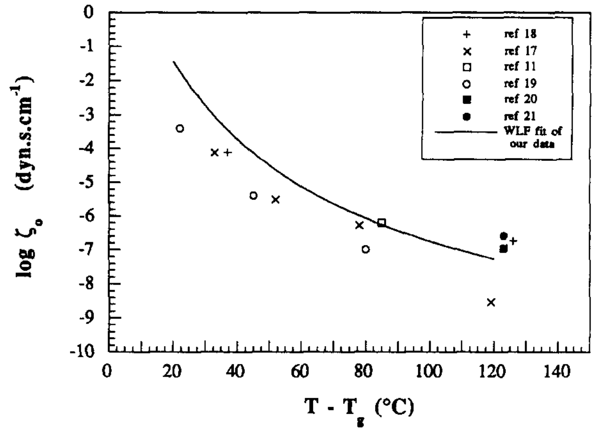

Figure 8 Log ζ_0 plotted versus $(T - T_g)$ for various polybutadienes. The symbols are relative to values of the monomeric friction coefficient reported previously by different authors[11,17-21]. The solid curve corresponds to the WLF fit for our 1,2-polybutadienes

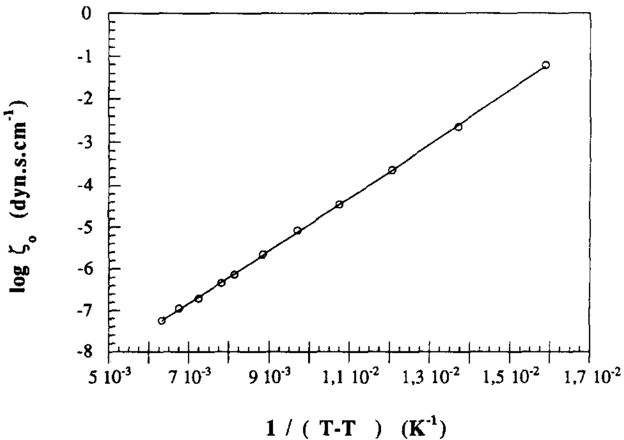

Figure 9 Log ζ_0 plotted versus $1/(T - T_\infty)$ for PB(54v)

CONCLUSION

Polybutadienes and polyisoprenes of various microstructures were studied by rheological measurements. The monomeric friction coefficient, ζ_0, was determined from the transition zone. It was shown that, in all these systems, the viscoelastic coefficients determined at T_g were identical. Moreover, a master curve was obtained to represent the evolution of ζ_0 versus $(T - T_g)$. This means that log $\zeta_0(T_g)$ is the same, irrespective of the microstructure.

REFERENCES

1. Doi, M. and Edwards, S. F., *J. Chem. Soc., Faraday Trans. II*, 1978, **74**, 1789.
2. Ferry, J. D., *Viscoelastic Properties of Polymers*, 3rd edn. Wiley, New York, 1980.
3. Williams, M. L., Landel, R. F. and Ferry, J. D., *J. Am. Chem. Soc.*, 1955, **77**, 3701.
4. Carella, J. M., Graessley, W. W. and Fetters, L. J., *Macromolecules*, 1984, **17**, 2775.
5. Zorn, R., McKenna, G. B., Willner, L. and Richter, D., *Macromolecules*, 1995, **28**, 8552.
6. Hofmann, A., Alegria, A., Colmenero, J., Willner, L., Buscaglia, E. and Hadjichristidis, N., *Macromolecules*, 1996, **29**, 129.
7. Vinogradov, G. V., Malkin, A. Y., Yanovskii, Y. G., Borisenkova, E. K., Yarlykov, B. V. and Berezhnaya, G. V., *J. Polym. Sci., A-2*, 1972, **10**, 1061.
8. Graessley, W. W., *Adv. Polym. Sci.*, 1974, **16**, 1.
9. Doolittle, A. K., *J. Appl. Phys.*, 1951, **22**, 1471.
10. Palade, L. I., Verney, V. and Attane, P., *Macromolecules*, 1995, **28**, 7051.
11. Zawada, J. A., Fuller, G. A., Colby, R. H., Fetters, L. J. and Roovers, J., *Macromolecules*, 1994, **27**, 6861.
12. Gotro, J. T. and Graessley, W. W., *Macromolecules*, 1984, **17**, 2767.
13. Roovers, J. and Toporowski, P. M., *Macromolecules*, 1992, **25**, 3454.
14. Brandrup, J. and Immergut, E. H., eds., *Polymer Handbook*. John Wiley, New York, 1975.
15. Fetters, L. J., Lohse, D. J., Richter, D., Witten, T. A. and Zirkel, A., *Macromolecules*, 1994, **27**, 4639.
16. Zhongde, X., Hadjichristidis, N., Carella, J. M. and Fetters, L. J., *Macromolecules*, 1983, **16**, 925.
17. Liu, W., Yang, Y. and He, T., *Polymer*, 1988, **29**, 1789.
18. Chen, S. P. and Ferry, J. D., *Macromolecules*, 1968, **1**, 270.
19. Arendt, B. H., Kannan, R. M., Zewail, M., Kornfield, J. A. and Smith, S. D., *Rheol. Acta*, 1994, **33**, 322.
20. Roovers, J., *Polymer*, 1985, **26**, 1091.
21. Colby, R. H., Fetters, L. J. and Graessley, W. W., *Macromolecules*, 1987, **20**, 2226.