# Monomeric friction coefficient of 1,2-polybutadienes

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The monomeric friction coefficient has been determined for 1,2-polybutadienes from dynamic measurements in the transition zone. These values are, respectively, $7.59 \times 10^{-5}$, $3.09 \times 10^{-6}$, $5.25 \times 10^{-7}$ and $2.95 \times 10^{-9}$ g s$^{-1}$ for 1,2-polybutadienes with vinyl contents of 91%, 76%, 53% and 14%. The structure-dependent behaviour of the monomeric friction coefficient has been discussed. 1,2-Polybutadienes with higher $T_g$, i.e. with higher vinyl content, have a larger monomeric friction coefficient. The fact that the monomeric friction coefficient increases with increase in cross-sectional area of the polymeric chains describes the effect of chain flexibility on the monomeric friction coefficient. The quantitative relationship between the shortest relaxation time, $\tau_A$, and the tube diameter, $d$, in Doi-Edwards theory has also been reported: $\log \tau_A = -17.24 + 0.38d$.

## INTRODUCTION

One acceptable molecular theory of viscoelasticity for entangled linear polymer liquids is Doi–Edwards theory[1], which is well known as the tube or reptation model[2]. Experimentally, the viscoelastic properties of high-molecular-weight polymers and their concentrated solutions exhibit more complex behaviour than the tube and reptation models predict. Thus, some modifications, e.g. contour-length fluctuation[3,4] and tube renewal[4,5], attempt to bring the theoretical model into better agreement with experiment. However, the basic parameters in Doi–Edwards theory are still used in those modifications. Our interest lies in being able to correlate the structural parameters of polymers with the basic parameters in Doi–Edwards theory and its modifications.

There are two basic parameters in Doi–Edwards theory. One is the monomeric friction coefficient, which characterizes the local dynamics, and the other is the step length of the primitive path, or the tube diameter, which characterizes the topology of the medium. Doi and Edwards take the primitive path step length and the tube diameter to be equal[1], although the latter is thought to be irrelevant except for discussion purposes[4]. Some methods have been given to evaluate the tube diameter from structural parameters of polymers. Graessley[6] expresses the tube diameter as:

$$d^2 = \frac{4}{5}\left(\frac{r^2}{M}\right)\left(\frac{cRT}{G_N^0}\right) \quad (1)$$

where $c$ is the polymer concentration (wt/mole), $R$ the universal gas constant, $G_N^0$ the plateau modulus, $T$ the temperature and $r^2$ the mean-square end-to-end distance of molecular weight $M$. The entanglement spacing:

$$R_c = N_c^{1/2} l_0 \quad (2)$$

where $l_0$ is average backbone length of a repeat unit and $N_c$ the critical number of entangled repeating units, is also

considered to be equivalent to the tube diameter[7,8]. He and Porter give a simple expression for the tube diameter:

$$d = 5.3 A^{1/2} \quad (3)$$

where $A$ is the cross-sectional area of the polymer chains.

The monomeric friction coefficient is usually deduced from dynamic measurements in the transition region of polymers. Few expressions for evaluation of the monomeric friction coefficient from structural parameters of polymers have been reported. In this paper, an attempt is given to set up a relationship between the monomeric friction coefficient, which is determined from dynamic measurements, and structural parameters of polymers, e.g. the cross-sectional area of polymer chains, for 1,2-polybutadienes.

## EXPERIMENTAL

1,2-Polybutadienes with various vinyl contents are the products of anionic polymerization. Microstructure was determined from the i.r. spectrum. Number-average molecular weight was measured with a Knauer membrane osmometer. Molecular-weight distribution obtained from g.p.c. for all samples is less than 1.3. Glass transition temperatures were determined with a linear dilatometer. The density of the samples at 20°C, measured with a density gradient column, was used to calculate the density at 25°C combining with the volume expansion coefficient above $T_g$ of the samples. The characteristic parameters of the 1,2-polybutadiene samples are listed in Table 1.

The storage and loss moduli of the samples, $E'$ and $E''$, were measured with a Rheovibron Dynamic Viscoelastometer model DDV-II-EA. The moduli at four frequencies were measured from a temperature 30°C lower than $T_g$ to a temperature 50°C higher than $T_g$ at a heating rate of 2°C min$^{-1}$. The strain amplitude of the measurement is 0.02%. The accuracy of the moduli values was checked by repeating measurements twice at each frequency. Except for the glassy region the reproducibility

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**Table 1** Characteristic parameters of 1,2-polybutadienes

| Microstructure (vinyl/*cis*-1,4/*trans*-1,4) | 91/2/7 | 76/12/12 | 53/17/30 | 14/62/24 |
|---|---|---|---|---|
| $M_n \times 10^{-3}$ (g mol$^{-1}$) | 145 | 160 | 392 | 122 |
| $T_g$ (K) | 265 | 246 | 220 | 179 |
| $\rho_{25°C}$ (g cm$^{-3}$) | 0.884 | 0.885 | 0.888 | 0.889 |
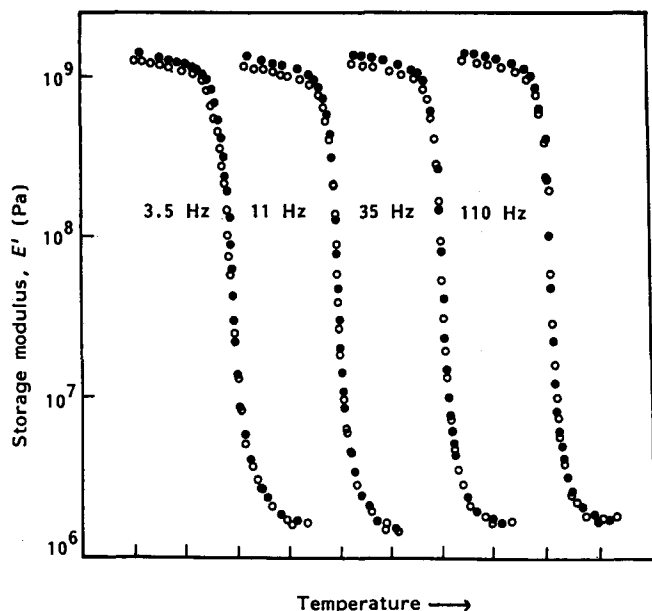


**Figure 1** The temperature dependence of the storage modulus at four frequencies for 1,2-polybutadiene with 91% vinyl content. Open and closed circles refer to different measurements. Data are reproducible at the transition zone

of the moduli is satisfactory (*Figure 1*). The non-reproducibility of the moduli in the glassy region in *Figure 1* is due to non-constant pre-tension with manually mounted samples.

## RESULTS AND DISCUSSION

The shift factors for the master curve of 1,2-polybutadiene can be expressed by the WLF equation. The general method to obtain the constants $C_1$ and $C_2$ in the WLF equation for 1,2-polybutadiene with various vinyl contents has been reported[10] as:

$$\log \alpha_T = \frac{5.78(T - T_g - 55)}{94.8 + (T - T_g - 55)} \tag{4}$$

The $C_1$ and $C_2$ values for the tensile moduli master curve of 1,2-polybutadiene samples in this work (*Table 2*) are determined with:

$$C_1 = \frac{5.78(C_2 + T_g - 298)}{C_2} \tag{5a}$$

$$C_2 = 94.8 - T_g + 298 \tag{5b}$$

$$T_s = T_g + 55 \tag{5c}$$

where 94.8, 5.78 and 55 are the constants in equation (4), 298 the reduced temperature for the master curve and $T_g$ the glass transition temperature of the samples. One of those master curves is shown in *Figure 2*. From the master curves of both storage and loss moduli, the method of Ferry and Williams[11] is used to obtain the relaxation spectra for 1,2-polybutadiene samples:

$$H(\tau) = AG' \, \mathrm{d} \log G'/\mathrm{d} \log \omega|_{1/\omega = \tau} \tag{6}$$

$$H(\tau) = BG''(1 - |\mathrm{d} \log G''/\mathrm{d} \log \omega|)|_{1/\omega = \tau} \tag{7}$$

where $G'$ and $G''$ are taken as one-third of the values of $E'$ and $E''$, respectively.

The relaxation spectra for all four 1,2-polybutadiene samples are shown in *Figure 3*. With decreasing vinyl content, the position of the transition shifts to shorter times, traversing nearly five decades of the logarithmic timescale. Similar to the methacrylate series[12], 1,2-polybutadiene with lower $T_g$, i.e. with lower vinyl content, is associated with shorter relaxation time for the transition zone.
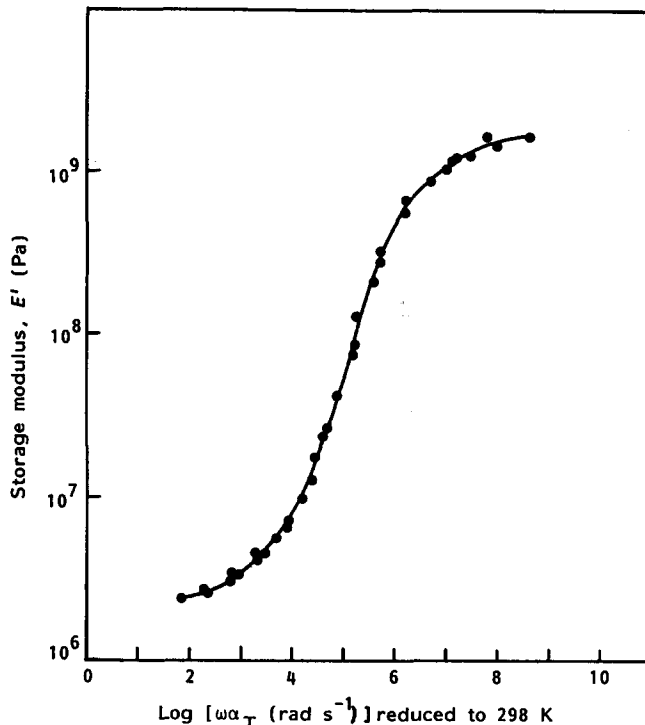


**Figure 2** Storage modulus master curve reduced to 298 K for 1,2-polybutadiene with 91% vinyl content. The $C_1$ and $C_2$ values for the shift factor are obtained with equation (5) in the text
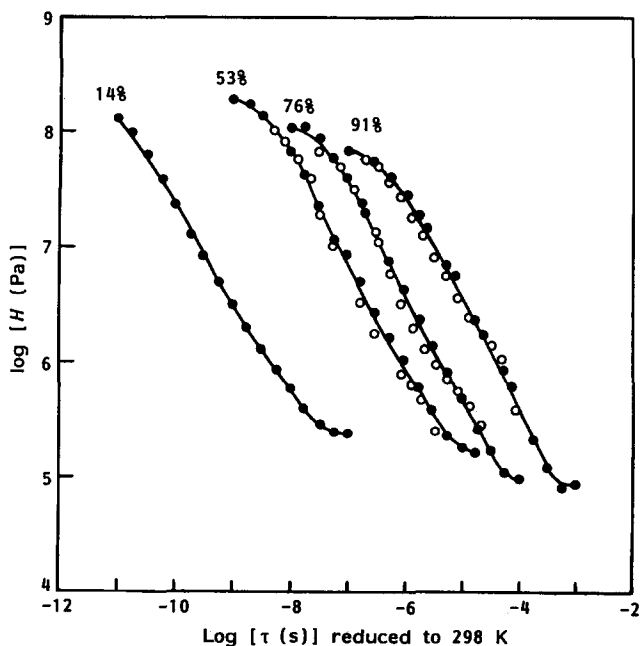


**Figure 3** Relaxation spectra for 1,2-polybutadienes. The figures refer to vinyl content. Closed circles obtained from storage modulus and open circles obtained from loss modulus

The monomeric friction coefficients for 1,2-polybutadiene samples are calculated with:

$$\log \zeta_0 = 2 \log H + \log \tau + \log(6/kT) + 2 \log(2M_0\pi/a\rho N_A) \quad (8)$$

where $a$ is the root-mean-square end-to-end length per square root of the number of monomer units, $\rho$ the density of the polymer and $M_0$ the monomer molecular weight. The experimental relaxation spectra for all four 1,2-polybutadiene samples are matched to the theoretical slope of $-1/2$ only by drawing a tangent. In equation (8), $\log H = 5.75$ at $\log \tau = -3.67$, $\log H = 5.81$ at $\log \tau = -5.17$, $\log H = 5.76$ at $\log \tau = -5.83$ and $\log H = 5.54$ Pa at $\log \tau = -7.62$ s are, respectively, used for 1,2-polybutadienes with vinyl contents of 91%, 76%, 53% and 14%. From the values of unperturbed end-to-end distance for 1,2-polybutadiene in the literature[13], the vinyl-content-dependent unperturbed end-to-end distance is:

$$(r_0^2/M)^{1/2} = 1.033 - 0.0598 X_{1,2} \quad (\text{Å mol}^{1/2}\,\text{g}^{-1/2}) \quad (9)$$

with correlation coefficient $-0.957$. Thus, the values of $a$ in (8) are obtained with:

$$a \equiv (r_0^2/M)^{1/2} = (r_0^2/N)^{1/2}(M_0)^{1/2}$$

The monomeric friction coefficients $\zeta_0$ for 1,2-polybutadiene are listed in *Table 2*. The monomeric friction coefficient for 1,2-polybutadiene with vinyl content of 91% in *Table 2*, $7.59 \times 10^{-5}$ g s$^{-1}$, is very close to the reported value of $7.76 \times 10^{-5}$ g s$^{-1}$. But the monomeric friction coefficient for polybutadiene with vinyl content of 14% in *Table 2* is two orders of magnitude lower than that for 1,2-polybutadiene with 8% vinyl content[14-16].

The significance of the monomeric friction coefficient is the average force per monomer unit required for a chain segment to push its way through its local surroundings at unit velocity. Thus, the monomeric friction coefficient depends on intermolecular forces and chain flexibility of polymer chains. It has long been recognized[17] that a high glass transition temperature is characteristic of a polymer with strong intermolecular forces and high chain stiffness. Therefore, it is not unexpected that 1,2-polybutadiene with higher $T_g$, i.e. with higher vinyl content, corresponds to higher monomeric friction coefficient. The logarithmic values of the monomeric friction coefficient (in g s$^{-1}$) and $T_g$ (in K) satisfy:

$$\log \zeta_0 = -17.29 + 0.049 T_g \quad (10)$$

with correlation coefficient $-0.992$.

In the case of the 1,2-polybutadiene series, chain flexibility is the sole factor that determines the glass transition temperature[13]. The nature of the relationship in equation (10) indicates the dependence of the

monomeric friction coefficient on the chain flexibility of 1,2-polybutadienes. One structural parameter describing chain flexibility is the cross-sectional area of polymer chains[18]. The cross-sectional area of polymer chains can be determined from many methods[18-20], e.g. directly from the unit-cell parameters or indirectly from empirical correlations. From $T_g$ in *Table 1* and the cohesive energy density $E_c$ in ref. 13, the cross-sectional area of polymer chains for 1,2-polybutadiene, $A$ were determined using[18]:

$$T_g = 116 + 4.33 E_c A \quad (11)$$

where $E_c$ is taken as $72.3\,\text{cal cm}^{-3}$ for all 1,2-polybutadiene samples[13]. Equation (12) gives a correlation of logarithmic value of monomeric friction coefficient with cross-sectional area of polymer chains, $A$ (in Å$^2$), for 1,2-polybutadiene:

$$\log \zeta_0 = -11.59 + 0.15 A \quad (12)$$

with correlation coefficient 0.992. The meaning of (12) is that for the 1,2-polybutadiene series the resistance to driving per monomer unit through the local surroundings at unit velocity depends on the chain flexibility.

The resistance to segment mobility through its local surroundings determines the relaxation process. The relaxation process corresponding to the transition zone of the relaxation spectrum can be described by the shortest relaxation process of Doi–Edwards theory[15]. The shortest relaxation time in Doi–Edwards theory is:
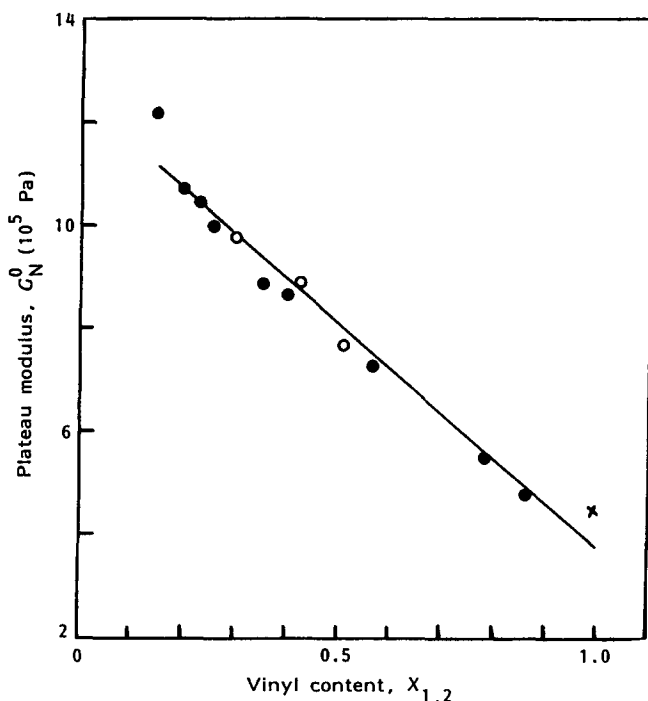


**Figure 4** Dependence of plateau modulus on the vinyl content for 1,2-polybutadienes. Data are taken from ref. 10. Closed circles were measured at 25°C, open circles at 24°C and crosses at 50°C

Table 2 Relative values of monomeric friction coefficient for 1,2-polybutadienes

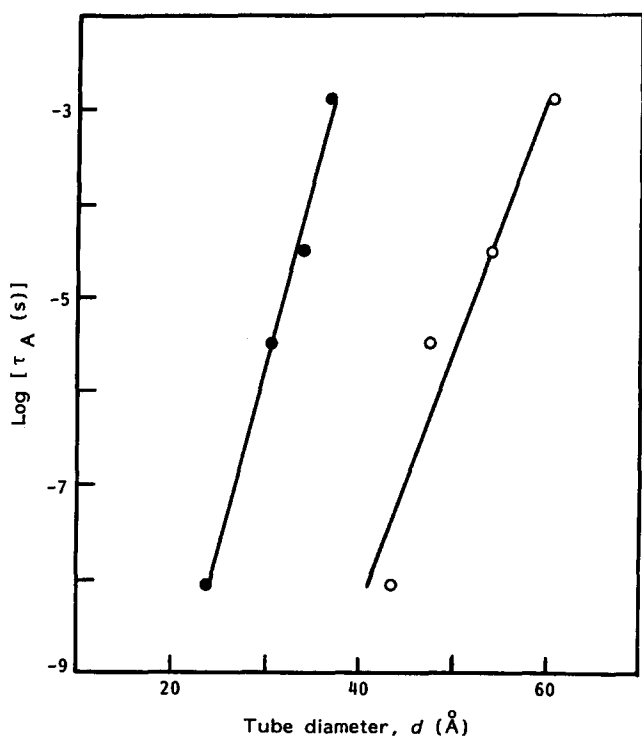| Vinyl content (%) | 91 | 76 | 53 | 14 |
|---|---|---|---|---|
| $C_1, C_2$ in WLF equation | 7.19, 73.11 | 5.99, 91.25 | 4.65, 117.8 | 3.46, 158.3 |
| $a$ (Å) | 7.19 | 7.26 | 7.36 | 7.53 |
| $\log[\zeta_0 \text{ (g s}^{-1})]$ | $-4.12$ | $-5.51$ | $-6.28$ | $-8.53$ |
| $N_c$ | 89 | 70 | 52 | 36 |
| $\log[\tau_A \text{ (s)}]$ | $-2.89$ | $-4.49$ | $-5.50$ | $-8.04$ |
| $d$ (Å) from equation (3) | 36.6 | 34.1 | 30.1 | 23.8 |
| $d$ (Å) from equation (1) | 60.8 | 54.1 | 47.4 | 43.5 |

**Figure 5** Dependence of logarithmic shortest relaxation time on the tube diameter in Doi–Edwards theory for 1,2-polybutadienes. Closed circles refer to the tube diameter obtained from equation (3) and open circles from equation (1)

$$\tau_A = \frac{1}{6\pi^2} \frac{\zeta_0 a^2}{kT} N_e^2 \tag{13}$$

where $N_e = M_e/M_0$ and $M_e$ is the entanglement molecular weight, which is equal to

$$M_e = \rho RT / G_N^0 \tag{14}$$

The plateau modulus for polybutadiene samples varies with the vinyl content as shown in *Figure 4*. All the data in *Figure 4* are taken from ref. 10; except for the lowest and the highest vinyl contents, all the other values fall reasonably close to the same line. The line in *Figure 4* can be formulated to:

$$G_N^0 = 12.42 - 8.65X_{1,2} \ (10^5 \, \text{Pa}) \tag{15}$$

with correlation coefficient $-0.986$. Combining (15) with (13), the shortest relaxation time of 1,2-polybutadiene samples is obtained and listed in *Table 2*. Those values correspond to $\tau$ values at the transition zone in *Figure 3*.

The shortest relaxation process in Doi–Edwards theory involves equilibration of the chain over the

distance of the tube diameter. This means that the larger the tube diameter, the longer is the relaxation time. The relationship between the shortest relaxation time and the tube diameter for 1,2-polybutadienes is:

$$\log \tau_A = -17.24 + 0.38d \tag{16}$$

where the correlation coefficient is 0.992 and the tube diameter is obtained from equation (3). The tube diameter obtained from equation (1) can also be expressed in terms of the shortest relaxation time with a similar formula:

$$\log \tau_A = -19.20 + 0.27d \tag{17}$$

with correlation coefficient 0.958. *Figure 5* shows $\tau_A$ vs. $d$ plots with $d$ obtained from equations (1) and (3).

## CONCLUSIONS

The monomeric friction coefficient for 1,2-polybutadiene is related to $T_g$ and the cross-sectional area of polymeric chains. The quantitative relationship between the shortest relaxation time and the tube diameter in Doi–Edwards theory has been found for 1,2-polybutadienes.

## ACKNOWLEDGEMENT

## REFERENCES

1  Doi, M. and Edwards, S. F. *J. Chem. Soc., Faraday Trans. II* 1978, **74**, 1789, 1802, 818
2  de Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572
3  Doi, M. *J. Polym. Sci., Polym. Lett. Edn.* 1981, **19**, 256; *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 667
4  Graessley, W. W. *Adv. Polym. Sci.* 1982, **47**, 67
5  Klein, J. *Macromolecules* 1978, **11**, 852
6  Graessley, W. W. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 27
7  Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn., Wiley, New York, 1980, p. 372
8  Klein, J. *Macromolecules* 1986, **19**, 105
9  He, T. and Porter, R. S. unpublished work
10  Carella, J. M., Graessley, W. W. and Fetters, L. J. *Macromolecules* 1984, **17**, 2775
11  In ref. 7, Ch. 4
12  In ref. 7, Ch. 12, Sect. A
13  He, T., Li, B. and Ren, S. *J. Appl. Polym. Sci.* 1986, **31**, 873
14  In ref. 7, Ch. 12, Sect. B
15  Roovers, J. *Polym. J.* 1986, **18**, 153
16  Colby, R. H., Fetters, L. J. and Graessley, W. W. *Macromolecules* 1987, **20**, 2226
17  Boyer, R. F. *Rubber Chem. Technol.* 1963, **36**, 1303
18  Miller, R. L. and Boyer, R. F. *Polym. News* 1978, **4**, 255
19  He, T. *J. Appl. Polym. Sci.* 1985, **30**, 4319
20  He, T. *J. Appl. Polym. Sci.* 1986, **31**, 152