Relaxation of Entangled and Partially Entangled Polymers in Melts: Time-Dependent Reptation

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ABSTRACT: The reptation theory founded on time-dependent diffusion and double reptation is valid for high masses in the entanglement domain. Here, this theory is extended to lower masses in the region where reptation and Rouse relaxation interfere. Equations describe relaxation in each domain separately, and we construct a theory which incorporates them. The theory depends on four constants, M_0, T, T_R, and T_i, which are functions of the nature of the polymer but not of its molecular mass M (two dimensionless constants). Here, M_0 is a normalizing factor; $T = \tau/M^3$, where τ is the reptation time; $T_R = \tau_R/M^2$, where τ_R is the Rouse time; and $T_i = \tau_i/M^2$, where τ_i is an intermediate Rouse time. Moreover, we assume that the effective Rouse time in the tube varies between τ_i in the entanglement domain and τ_R in the region of interference between the Rouse and reptation domains. The loss modulus $G''(\omega)$ is compared with experiments particularly for polystyrene, but also for polybutadiene, for poly(methyl methacrylate), and for polyisoprene. The corresponding viscosities are calculated for polystyrene and polybutadiene. All these comparisons lead to a good agreement.

1. Introduction

In a preceding article (I),[1] we calculated the stress relaxation function $G(t)$ associated with long entangled polymers constituting a melt. The so-called time-dependent diffusion was used, and this enabled us[2] to determine $G''(\omega)$

$$G''(\omega) = \omega \int_0^\infty dt \cos(\omega t) G(t) \tag{1}$$

The results were compared with experiments on polybutadiene (Rubinstein and Colby[3]).

In this article, we extend the preceding results to lower masses. In the entanglement domain, the interval between the long-time reptation and the short-time Rouse relaxation is large, and reptation can be considered separately (there is a large plateau region). When the mass of the polymers diminishes, the reptation levels come nearer to the Rouse continuum spectrum and are finally absorbed in it. Reptation results in a kind of bound state due to the fact that the polymers are confined in a tube consisting of the other polymers.

To describe this situation, we need a more complete model. Four constants, T, T_R, T_i, and a fixed molecular mass M_0, will be needed to construct it. In the monodisperse case, it will also depend on one parameter, the molecular mass M of the polymer.

The reptation time τ is proportional to M^3

$$\tau = TM^3 \tag{2}$$

The Rouse time τ_R is proportional to M^2

$$\tau_R = T_R M^2 \tag{3}$$

We introduce a third intermediate time τ_i, also proportional to M^2, which, for high masses (entanglement region), can be considered as the Rouse time of a polymer moving in its tube.

$$\tau_i = T_i M^2 \tag{4}$$

In the following, T, T_i, and T_R are constants independent of M.

Moreover, we introduce a molecular mass M_0 which is also a constant, independent of M, and which acts as a normalization factor.

In article I, where we considered pure reptation, we used only three parameters, τ, H, and G_0, which can be expressed in terms of T, T_i, and M_0 (and M)

$$H = \frac{\tau}{\tau_i} = \frac{T}{T_i}M$$

$$G_0/\rho A_v \beta^{-1} = 1/M_0 \tag{5}$$

Here, ρ is the density, A_v is the Avogadro number, and $\beta = 1/k_B T$ (T = temperature, k_B = Boltzmann's constant). In this case, $G_0 = G''(0)$.

Here, the expression of G_0 is suggested by theoretical considerations,[4] and this will appear clearly in the following. Therefore, we must consider $\rho A_v \beta^{-1}$ as a given value which is external to the theory. The real constant is the molecular mass M_0.

In the present article, we need another constant, T_R, i.e., the Rouse time $\tau_R = T_R M^2$.

We note that two constants are used to fix the coordinates; in addition, we have two dimensionless constants which are obtained by combining the four constants T, T_i, T_R, and M_0, namely, T_i/T_R and $M_0 T/T_R$.

The results will be compared with experiments on polystyrene (160 °C), poly(methyl methacrylate) (200 °C), and polyisoprene (21 °C) performed by Cassagnau[5] at Pau in the group of Ph. Monge.

The experimentalists made measurements on monodisperse and polydisperse melts. So here, we shall study the effects of polydispersity explicitly. The relaxation process will be described by mixing the double-reptation assumption[6] in the entanglement domain with a single-reptation representation in the Rouse region. In the following, we compare theoretical curves, shown by solid lines, with experimental results, appearing as dashed lines.

In section II, the double-reptation concept and the time-dependent diffusion method are recalled and applied in the pure reptation case to monodisperse and polydisperse polybutadiene of high masses. In section III, we introduce a new model covering simultaneously the reptation peak and the Rouse domain. In section IV, the theory is compared in the intermediate region where reptation and

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Rouse relaxation take place, with experiments on polystyrene (160 °C), poly(methyl methacrylate) (220 °C), and polyisoprene (21 °C). A good agreement with theory is obtained. Finally, a general expression of the viscosity of polymers is calculated in section V, and the obtained formula is compared with experiments in section VI.

2. Double Reptation and the Time-Dependent Diffusion Model

The double-reptation concept has been presented elsewhere,[6] but let us sketch the idea. If two polymers A and B exert a stress on each other at time zero, this stress still holds at time t if neither A nor B slipped through the stress point. Let $p_A(t)$ be the probability that A did not slip between times 0 and t ($p_A(0) = 1$) through this point which is assumed to remain fixed. Then the probability of persistence of stress is proportional to $p_A(t)p_B(t)$. Consequently, the stress relaxation function can be written in the form[1,6]

$$G(t) = G_0 \sum_A [\varphi_A p_A(t)]^2 \qquad (6)$$

where φ_A is the volume fraction of polymers of type A

$$\sum_A \varphi_A = 1$$

This formula defines double reptation.

It may seem that double reptation does not differ much from constraint release,[7] but in fact it is a simpler and more exact concept. The experiments show that as a first-order approximation, double reptation should be preferred.[1,6] Moreover, this approach is supported by many intuitive arguments. For instance, consider a simple fluid and its pressure; the first term where the interaction plays a role is a two-body term, just as in double reptation. For these reasons (and others), we adopt double reptation in this section.

Incidentally, it will be convenient to write

$$G_0/\rho A_v \beta^{-1} = 1/M_0 \qquad (7)$$

a formula which defines a molecular mass M_0 (expressed in daltons) and establish a connection with the Rouse model, as will be shown in the next section.

Now the probability $p_A(t)$ has to be calculated in a proper way. This difficult problem can be solved in an easy way by application of the time-dependent diffusion method,[1] which we may sum up as follows. The stress point being assumed to be fixed, the polymer moves along it. Then we may consider the abscissa s ($0 < s < S$) of the stress point on the polymer (counted from the polymer origin) as changing with time. This apparent motion of the stress point on the polymer is a complicated result of the time evolution of all the polymer modes. The method consists in simulating this evolution by a time-dependent diffusion of the stress point characterized by s on the polymer considered as fixed. Here, S is the linear end-to-end distance along the tube; the polymer being Brownian in the direction of the tube, S is proportional to the number of links, or to the length L of the polymer. Thus dropping the index A for convenience, we deduce $p(t)$ by setting

$$p(t) = \int_0^S \mathrm{d}s\, P(t,s)$$

where $P(t,s)$ is the solution of the equation

$$\frac{\partial}{\partial t} P(t,s) = \mathcal{D}(t) \frac{S^2}{L^2} \frac{\partial^2}{\partial s^2} P(t,s) \qquad (8)$$

with the boundary conditions

$$P(0,s) = 1$$
$$P(t{>}0,0) = P(t{>}0,S) = 0$$

It is clear that such an equation cannot represent a real process, since the laws of dynamics are time invariant. But, it may simulate a complicated process involving all the modes, and, in this equation, $\mathcal{D}(t)$ is given in terms of $x(t,s)$ by

$$\mathcal{D}(t) = \frac{\partial}{\partial t}\left[\frac{1}{2S}\int_0^S \mathrm{d}s\, \langle [x(t,s) - x(0,s)]^2 \rangle\right]$$

where $x(t,s)$ is the solution of the Langevin equation

$$\frac{\partial}{\partial t} x(t,s) = \gamma \frac{\partial^2}{\partial s^2} x(t,s) + f(t,s) \qquad (9)$$

with

$$\langle f(t,s) \rangle = 0$$

$$\langle f(t,s) f(t',s') \rangle = 2\gamma \delta(t-t')\delta(s-s')$$

We set

$$\tau = L^2 S/\pi^2 \gamma$$
$$\tau_i = S^2/\pi^2 \gamma \qquad (10)$$

which shows that τ is proportional to M^3 and τ_i is proportional to M^2, in agreement with eqs 2 and 3, since S and L are both proportional to M. We find

$$\mathcal{D}(t) = \frac{\gamma}{S}[1 + \sum_{n=1}^{\infty} e^{-n^2 t/\tau_i}]$$

Finally, our calculations lead to

$$p(t) = \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-(2n+1)^2 U(t)] \qquad (11)$$

$$U(t) = \frac{t}{\tau} + \frac{\tau_i}{\tau} g(t/\tau_i) \qquad (12)$$

$$g(x) = \sum_{n=1}^{\infty} \left(\frac{1 - e^{-nx}}{n^2}\right) \qquad (13)$$

Thus, eqs 6 and 7 with eqs 11, 12, and 13 give $G(t)$ explicitly in terms of M_0, τ, and τ_i. The loss modulus $G''(\omega)$ is obtained directly from $G(t)$ by Fourier transformation (and analytic continuation in order to ensure a good convergence).

We reproduce here a comparison of the results with experiments on polybutadiene (see Figure 1) for two samples of molecular masses 355 000 and 70 900 at 25 °C. For polybutadiene, we have $\rho = 0.96$ g/cm^3 and $\rho A_v \beta^{-1} = 2.377 \times 10^{10}$ (cgs). Consequently, the constants are

$$T = 1.5 \times 10^{-16}\ \mathrm{s/Da^3}$$
$$T_i = 3.6 \times 10^{-12}\ \mathrm{s/Da^2}$$
$$M_0 = 1900\ \mathrm{Da}$$

Now we can study mixtures at the same temperature by using the same constants, and the result (plotted in Figure 2) shows the validity of the double-reptation assumption.

3. Reptation and Rouse Motions in the Intermediate Range

Until now, we described $G(t)$ in the reptation range by eq 6 (with eqs 7, 8, 10, 11, 12, and 13); on the other hand, in the Rouse domain, we have according to Doi and Ed-

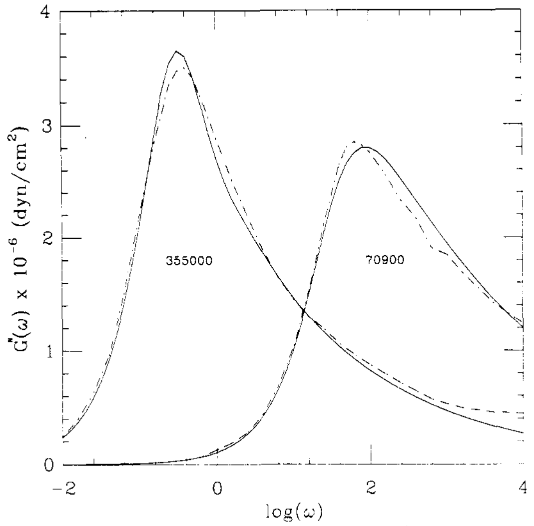

Figure 1. Loss modulus of two monodisperse polybutadiene samples. The curves on the left-hand side correspond to a molecular mass 355 000; the curves on the right-hand side correspond to a molecular mass 70 900. The dashed lines represent experimental results at 25 °C by Colby.[3] The solid lines are theoretical curves obtained with the time-dependent method and double reptation. Constants: $T = 1.5 \times 10^{-16}$ s/Da^3, $T_i = 3.6 \times 10^{-12}$ s/Da^2, $M_0 = 1900$ Da. On the other hand, we have $\rho A_v/\beta = 2.377 \times 10^{10}$ (cgs).

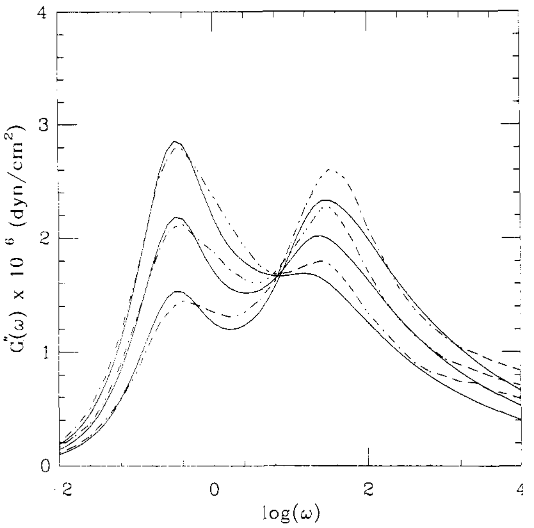

Figure 2. Loss modulus of three mixtures of two polybutadiene samples of molecular masses 355 000 and 70 900. The volume fraction of polybutadiene of molecular mass 355 000 is ϕ. Here the volume fractions are $\phi = 0.882$, $\phi = 0.768$, and $\phi = 0.638$. The peaks on the left-hand side decrease and the peaks on the right-hand side increase as ϕ decreases. The dashed lines represent experimental results at 25 °C by Colby.[3] The solid lines are theoretical curves obtained with the time-dependent diffusion model and double reptation. The constants are the same as in Figure 1. This curve shows the (approximate) validity of double reptation.

wards[8] (for a monodisperse polymer)

$$G(t)/\rho A_v\beta^{-1} = \frac{1}{M}\sum_{p=1}^{\infty}\exp[-2p^2t/\tau_R] \qquad (14)$$

where τ_R is the Rouse time with

$$\tau_R = T_R M^2 \qquad (T_R = \text{constant})$$

The corresponding loss modulus $G''(\omega)$ increases proportionally to $\omega^{1/2}$ when ω goes to infinity. Of course, there is a cutoff but we are not interested here in cutoff-dependent phenomena and the formula should be valid in the intermediate range. Thus, this equation has to be combined with the reptation equation which in the monodisperse case reads

$$G(t)/\rho A_v\beta^{-1} = \frac{1}{M_0}p^2(t) \qquad (15)$$

It is clear that to describe reality, we cannot simply add up eqs 14 and 15. The modes which participate in reptation are already present in eq 14. Reptation modes play the role of a bound state corresponding to the localization of a polymer in its tube. Moreover, we remark that, in the intermediate range, $M_0 \ll M$; therefore by comparing eqs 14 and 15, we see that a large but finite number of levels of the continuum are transferred to the reptation modes.

Moreover, we established that reptation is a two-body process, i.e., a cooperative process involving simultaneously two polymers (double reptation) instead of one. Therefore, we must bridge over this difficulty.

Finally, to be accurate, we must assume that reptation relaxation, in the intermediate domain, is produced by disentanglement followed by Rouse relaxation.

Taking all these requirements into account, we write $G(t)$, for a polydisperse system, in the following form:

$$G(t)/\rho A_v\beta^{-1} = \sum_{A}\frac{\varphi_A}{M_A}R_A(t) - \sum_{AB}\frac{\varphi_A\varphi_B}{M_A}\int_0^t dt'\, p_A(t-t')p_B(t-t')\frac{d}{dt'}F_A(t') \qquad (16)$$

In this expression, the convolution indicates that, when reptation occurs, stress release is produced by disentanglement plus Rouse relaxation.

Here, φ_A is the volume fraction of polymers of type A

$$\sum_{A}\varphi_A = 1$$

The function $R_A(t)$ is defined as follows:

$$R_A(t) = \sum_{p=1}^{\infty}e^{-2p^2t/\tau_{RA}} \qquad (17)$$

where $\tau_{RA} = T_R M_A{}^3$. Thus the first term $\sum_A(\varphi_A/M_A)R_A(t)$ is just the contribution of the Rouse relaxation in the absence of any reptation. (Note however that the second term gives a contribution $-\sum_A(\varphi_A/M_A)F_A(t)$ to the Rouse relaxation).

The function $F_A(t)$ is defined as follows:

$$F_A(t) = \sum_{p=1}^{\infty}e^{-pM_0/M_A}e^{-2p^2t/\tau_{RA}} \qquad (18)$$

where it is assumed that, for each level p, e^{-pM_0/M_A} is the fraction which is transferred from the Rouse to the reptation modes.

Finally, $p_A(t)$ is given by the time diffusion

$$p_A(t) = \sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2U_A(t)] \qquad (19)$$

$$U_A(t) = \frac{t}{\tau_A} + \frac{\tau_{mA}}{\tau_A}g(t/\tau_{mA}) \qquad (20)$$

$$g(x) = \sum_{n=1}^{\infty}\left(\frac{1-e^{-n^2x}}{n^2}\right) \qquad (21)$$

These equations would coincide with eqs 11–13 if we had $\tau_{mA} \equiv \tau_{iA} = T_i M_A{}^2$. However, the experimental evidence, as well as our intuition, leads us to admit that the Rouse

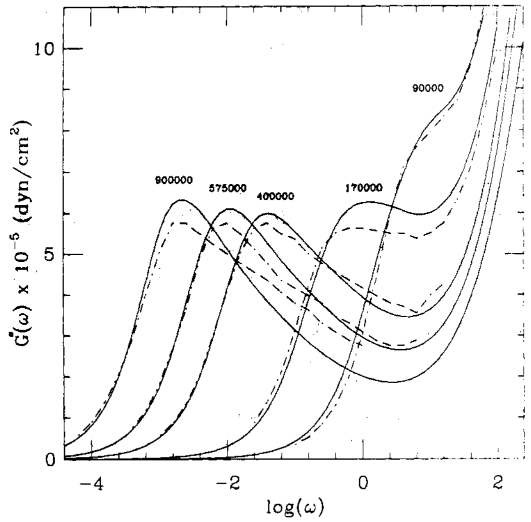

Figure 3. Loss modulus of five monodisperse polystyrene samples of molecular masses 900 000, 575 000, 400 000, 170 000, and 90 000. The dashed lines represent experimental results at 160 °C by Cassagnau.[5] The solid lines are theoretical curves. Constants: $T = 2.2 \times 10^{-15}$ s/Da^3, $T_i = 6.4 \times 10^{-10}$ s/Da^2, $T_R = 1.9 \times 10^{-11}$ s/Da^2, $M_0 = 14\,000$ Da. On the other hand, we have $\rho A_v/\beta = 3.992 \times 10^{10}$ (cgs).

time in a tube is not a constant; for large masses, it must be equal to τ_i but for small masses, it is equal to τ_R. As the transition must take place when the reptation peak merges into the Rouse continuum, we may interpolate by defining τ_m, for a monodisperse polymer, as follows:

$$\tau_m = \tau_i\left(\frac{\tau_R + \tau}{\tau_i + \tau}\right) \tag{22}$$

or, in the polydisperse case (polymer of type A)

$$\tau_{mA} = \tau_{iA}\left(\frac{\tau_{RA} + \tau_A}{\tau_{iA} + \tau_A}\right) \tag{23}$$

The introduction of these τ_{mA} produces a shift in the times and is quite necessary to obtain an agreement.

Equations 16, 17, 18, 19, 20, 21, and 23 define our new theory, where we determine τ_A, τ_{RA}, and τ_{iA} as usual by

$$\tau_A = TM_A^{\,3}$$

$$\tau_{RA} = T_R M_A^{\,2}$$

$$\tau_{iA} = T_i M_A^{\,2}$$

As the reader will realize, this theory is founded on simple arguments which should be tested. A comparison with experimental results is given in the next section. There remain four constants, M_0, T, T_i, and T_R, and the molecular masses of the polymers play the role of variables.

4. Comparisons with Experiments

It is difficult to test the theory with polybutadiene because there are uncertainties in the measurements;[9] from values of $G''(\omega)$ at high ω, we cannot deduce the value of τ_R precisely (actually τ_R will be obtained from data on the viscosity of polybutadiene). However, we can as well use other polymers, for which we have data covering regions of passage of reptation to the Rouse regime.

We find it convenient to compare our theoretical results with experiments on polystyrene at 160 °C, poly(methyl methacryalte) at 220 °C, and polyisoprene at 21 °C performed by Cassagnau.[5] The best data are obtained with polystyrene. In each case, we cover the intermediate region.

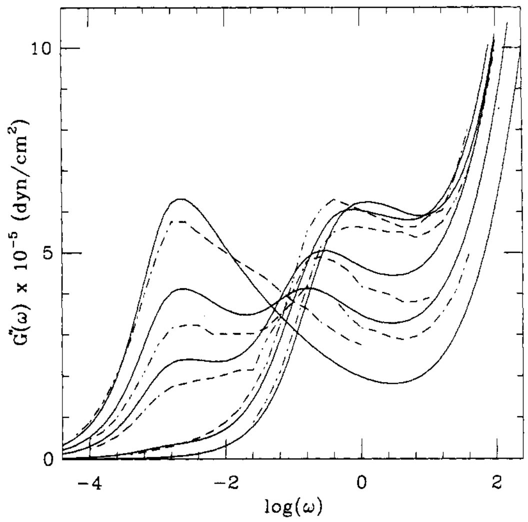

Figure 4. Loss modulus of mixtures of polystyrenes of molecular masses 900 000 and 170 000. The volume fractions of polystyrene of molecular mass 900 000 are $\phi = 1, 0.8, 0.6, 0.2$, and 0, and the curves appear in this order from left to right. The dashed lines represent experimental results (160 °C) by Cassagnau.[5] The solid lines are theoretical results. The constants are the same as in Figure 3.

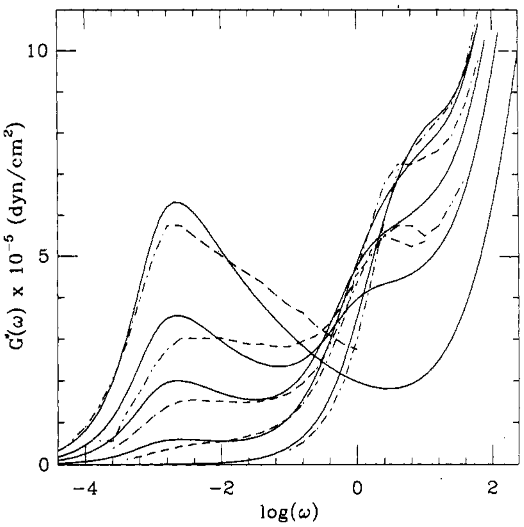

Figure 5. Loss modulus of mixtures of polystyrenes of molecular masses 900 000 and 90 000. The volume fractions of polymer of molecular mass 900 000 are $\phi = 1, 0.75, 0.56, 0.3$, and 0, and the curves appear in this order from left to right. The dashed lines represent experimental results (160 °C) by Cassagnau.[5] The solid lines are theoretical results. The constants are the same as in Figure 3.

Simultaneous fits for polystyrene of molecular masses M = 900 000, 575 000, 400 000, 170 000, and 90 000 at 160 °C appear in Figure 3. The constants are $T = 2.2 \times 10^{-15}$ s/Da^3, $T_i = 6.4 \times 10^{-10}$ s/Da^2, $T_R = 1.9 \times 10^{-11}$ s/Da^2, and $M_0 = 14\,000$ Da. Moreover, we know that $\rho = 1.11$ g/cm^3 and $\rho A_v \beta^{-1} = 3.992 \times 10^{10}$ (cgs).

The agreement obtained is good, and we would like to verify that this agreement still holds true when we deal with mixtures of polystyrene of various masses. The results are presented in Figure 4 for mixtures of polymers of molecular masses 900 000 and 170 000 and in Figure 5 for mixtures of polymers of molecular masses 900 000 and 90 000. Without being perfect, the agreement is very satisfactory. We must note that the constants are the same as in Figure 3 and that no other constant is added. The result confirms that double reptation should be valid in the reptation domain.

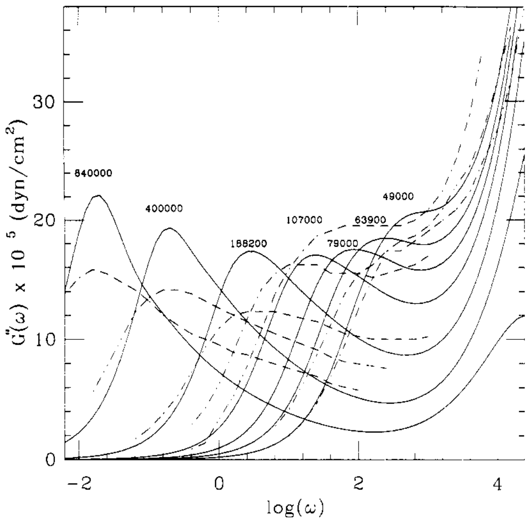

Figure 6. Loss modulus of seven monodisperse poly(methyl methacrylate) samples of molecular masses 840 000, 400 000, 188 200, 107 000, 79 000, 63 900 and 49 000. The dashed lines represent experimental results at 200 °C by Cassagnau.[5] The solid lines are theoretical results. Constants: $T = 2.0 \times 10^{-16}$ s/Da^3, $T_i = 1.3 \times 10^{-11}$ s/Da^2, $T_R = 1.1 \times 10^{-12}$ s/Da^2, $M_0 = 5600$ Da. On the other hand, we have $\rho A_v/\beta = 4.418 \times 10^{10}$.

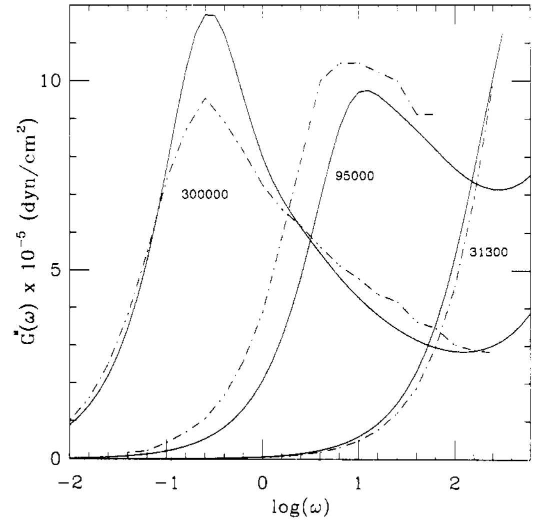

Figure 7. Loss modulus of three monodisperse polyisoprene samples of molecular masses 300 000, 95 000, and 31 300. The dashed lines represent experimental results at 21 °C by Cassagnau.[5] The solid lines are theoretical curves. Constants: $T = 2.9 \times 10^{-16}$ s/Da^3, $T_i = 5.2 \times 10^{-12}$ s/Da^2, $T_R = 3.0 \times 10^{-12}$ s/Da^2, $M_0 = 5600$ Da. On the other hand, we have $\rho A_v/\beta = 2.277 \times 10^{10}$.

Simultaneous fits for poly(methyl methacrylate) of molecular masses $M = 840\,000$, 400 000, 188 200, 107 000, 79 000, 63 900, and 49 000 performed at 220 °C appear in Figure 6. The constants are $T = 2.0 \times 10^{-16}$ s/Da^3, $T_i = 1.3 \times 10^{-11}$ s/Da^2, $T_R = 1.1 \times 10^{-12}$ s/Da^2, and $M_0 = 5600$ Da. In addition, we know that $\rho = 1.078$ g/cm^3 and $\rho A_v\beta^{-1} = 4.418 \times 10^{10}$ (cgs).

Simultaneous fits for polyisoprene of molecular masses $M = 80\,000$, 95 000, and 31 300 at 21 °C appear in Figure 7. The constants are $T = 2.9 \times 10^{-16}$ s/Da^3, $T_i = 5.2 \times 10^{-12}$ s/Da^2, $T_R = 3.0 \times 10^{-12}$ s/Da^2, and $M_0 = 5600$ Da. In addition, we take $\rho = 0.913$ g/cm^3 and $\rho A_v\beta^{-1} = 2.274 \times 10^{10}$.

The results are not quite as good for poly(methyl methacrylate) and for polyisoprene as for polystyrene, probably because the intrinsic polydispersity of the samples is rather high. However, we note, especially on poly(methyl methacrylate) (Figure 6), a very strong variation of the relaxation times which occurs when the reptation levels and the beginning of the Rouse spectrum are very near to one another. This effect appears also for polystyrene (Figure 3) and polyisoprene (Figure 7). This might be due to a change of density. Anyway, this shows that a more precise theory of the transition is needed.

5. Viscosity: Theoretical Value

From the expression of the stress relaxation function, we deduce a value of the viscosity

$$\eta = \int_0^\infty \mathrm{d}t\, G(t) \tag{24}$$

The viscosity has two regimes. For low masses, it is proportional to M; for higher masses, it behaves like M^α, where $\alpha \simeq 3.4$, but this power appears to be an effective exponent; finally, for very high masses, it behaves like M^3. We note that, for pure reptation (if we forget Rouse relaxation) and for low masses, $\eta \propto M^4$; thus the passage from 4 to 3 produces the effective index 3.4. However, when we deal with the full expression, the regime changes at low mass and η becomes proportional to M.

For a monodisperse polymer, eq 16 reads

$$G(t)/\rho A_v\beta^{-1} = \frac{1}{M}R(t) - \frac{1}{M}\int_0^t \mathrm{d}t'\, p^2(t-t')\, \frac{\partial}{\partial t'}F(t') \tag{25}$$

with

$$R(t) = \sum_{p=1}^{\infty} e^{-2p^2t/\tau_R}$$

$$F(t) = \sum_{p=1}^{\infty} e^{-pM_0/M} e^{-2p^2t/\tau_R}$$

The function $p(t)$ is equal to

$$p(t) = \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{-(2n+1)^2\left[\frac{t}{\tau} + \frac{\tau_m}{\tau}g(t/\tau_m)\right]\right\}$$

with

$$g(x) = \sum_{n=1}^{\infty}\left(\frac{1 - e^{-n^2x}}{n^2}\right) \tag{26}$$

where τ_m is given in terms of τ_i, τ_R, and τ by eq 22

$$\tau_m = \tau_i\left(\frac{\tau_R + \tau}{\tau_i + \tau}\right) \tag{27}$$

Applying eq 24, we find

$$\eta/\rho A_v\beta^{-1} = \frac{\tau_R}{2M}\sum_{q=1}^{\infty}\frac{1}{q^2} - \frac{1}{M}\int_0^\infty \mathrm{d}t \int_0^t \mathrm{d}t'\, p^2(t-t')\, \frac{\partial}{\partial t'}F(t') \tag{28}$$

We use

$$\sum_{q=1}^{\infty}\frac{1}{q^2} = \frac{\pi^2}{6}$$

and we write

$$\int_0^\infty \mathrm{d}t \int_0^t \mathrm{d}t' ... = \int_0^\infty \mathrm{d}t' \int_{t'}^\infty \mathrm{d}t ...$$

in eq 28. Thus, we get

$$\eta/\rho A_v\beta^{-1} = \frac{\pi^2}{12}\frac{\tau_R}{M} + \frac{F(0)}{M}\int_0^\infty \mathrm{d}t\, p^2(t)$$

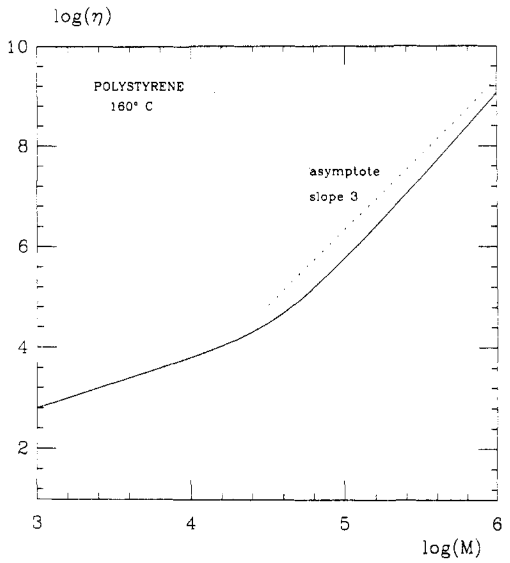

Figure 8. Viscosity of monodisperse polystyrene at 160 °C; η is expressed in poises, M in daltons. Constants: $T = 2.2 \times 10^{-15}$ s/Da^3, $T_i = 6.4 \times 10^{-10}$ s/Da^2, $T_R = 1.9 \times 10^{-11}$ s/Da^2, $M_0 = 14\,000$ Da. On the other hand, we have $\rho A_v/\beta = 3.992 \times 10^{10}$.

or more explicitly

$$\eta/\rho A_v\beta^{-1} = \frac{\pi^2}{12}\frac{\tau_R}{M} + \frac{1}{M(e^{M_0/M}-1)}\int_0^\infty dt \left[\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} \times \exp\left\{-(2n+1)^2\left[\frac{t}{\tau} + \frac{\tau_m}{\tau}g(t/\tau_m)\right]\right\}\right]^2$$

where τ_m is given by eq 27.

Using eqs 2–4 and putting $\tau_m = T_m M^2$, we obtain the equations

$$\frac{\eta}{\rho A_v\beta^{-1}} = \frac{\pi^2}{16}T_R M + \frac{TM^2}{e^{M_0/M}-1}\int_0^\infty d\theta \left[\frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n+1)^2} \times \exp\left\{-(2n+1)^2\left[\theta + \frac{T_m}{MT}g\left(\theta\frac{MT}{T_m}\right)\right]\right\}\right] \qquad (29)$$

with

$$T_m = T_i\left(\frac{T_R + MT}{T_i + MT}\right) \qquad (30)$$

where $g(x)$ is given by eq 26.

6. Viscosity: Comparisons with Experiments

The expression of viscosity given by eqs 29 and 30 is plotted for polystyrene at 160 °C with $T = 2.2 \times 10^{-15}$ s/Da^3, $T_i = 6.4 \times 10^{-10}$ s/Da^2, $T_R = 1.9 \times 10^{-11}$ s/Da^2, and $M_0 = 14\,000$ Da. On the other hand, we took $\rho A_v/\beta = 3.992 \times 10^{10}$. The results appear in Figure 8. The results cannot be easily compared with those given by Graessley[10] which correspond to a different temperature and are given in arbitrary units but we note a qualitative agreement.

However, in the case of polybutadiene, more recent measurements by Colby, Fetters, and Graessley[11] are available, and they afford a means to determine T_R with sufficient precision (for 25 °C). Thus, we have $T = 1.5 \times 10^{-16}$ s/Da^3, $T_i = 3.6 \times 10^{-12}$ s/Da^2, and $M_0 = 1900$ Da and we take $T_R = 3.0 \times 10^{-13}$ s/Da^2. On the other hand, we have $\rho A_v/\beta = 2.377 \times 10^{10}$. The results appear in Figure 9. The data are taken from Table XI of ref 11, and the theory is fitted with the corrected data for low masses.

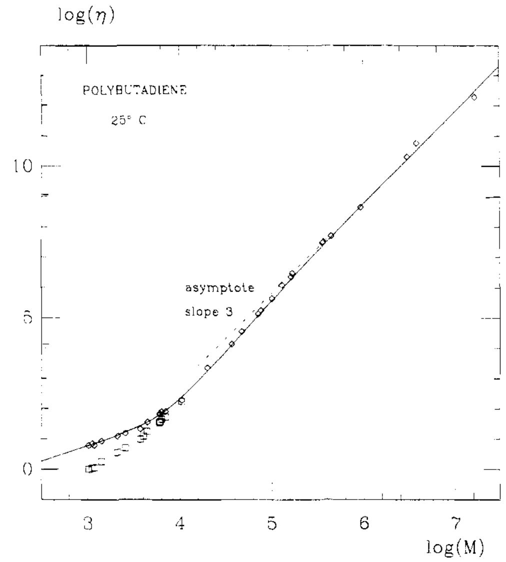

Figure 9. Viscosity of monodisperse polybutadiene at 25 °C; η is expressed in poises, M in daltons. The theoretical results appear as solid lines. Constants: $T = 1.5 \times 10^{-16}$ s/Da^3, $T_i = 3.6 \times 10^{-11}$ s/Da^2, $T_R = 3.0 \times 10^{-13}$ s/Da^2, $M_0 = 1900$ Da. On the other hand, we have $\rho A_v/\beta = 2.377 \times 10^{10}$. The experimental points of Colby, Fetters, and Graessley[11] are given by diamonds (values corrected by these authors) and squares (uncorrected values).

7. Conclusion

A new theory of relaxation valid for reptation levels and the beginning of the Rouse modes has been presented and the agreement is rather good, if one takes into account the lack of reliability of the experiments and the theoretical uncertainties.

Fits were made for the loss modulus $G''(\omega)$ of four polymers, polybutadiene (25 °C), polystyrene (160 °C), poly(methyl methacrylate) (220 °C), and polystyrene (21 °C). The loss modulus $G''(\omega)$ of mixtures has also been fitted, and the validity of double reptation was confirmed.

Four independent constants were used, T, T_i, T_R and M_0. These constants have a dimension, and therefore only two pure numbers, M_0T/T_i and M_0T/T_R, can be extracted from them. Thus, we obtain

	T_i/T_R	M_0T/T_R
polybutadiene (25 °C)	12	0.95
polystyrene (160 °C)	34	1.62
poly(methyl methacrylate) (220 °C)	12	1.02
polyisoprene (21 °C)	1.7	0.54

The reason for calculating these numbers is our belief that, in some sense, the theory might be universal for all polymer masses (with a cutoff in the Rouse domain). However, the numbers obtained are rather uncertain: they cannot give us any clue concerning universality.

To give a precise answer to this question, progress has to be made in both experiment and theory. We noted that the reptation modes appeared as bound states, the Rouse modes representing the continuous spectrum. To get a completely nonphenomenological theory, this idea should be exploited. However, we must realize that, the experiments being now described in a fairly realistic way, the theory has already a precise predicting value, which any theoretical change should maintain.

References and Notes

(1) des Cloizeaux, J. *Macromolecules* **1990**, *23*, 4678. See also: des Cloizeaux, J. *Makromol. Chem., Macromol. Symp.* **1991**, *45*, 153.

(2) It would also be possible but less significant to study $G'(\omega) = \omega\int_0^\infty dt \sin(\omega t)G(t)$.

(3) Rubinstein, M.; Colby, R. H. *J. Chem. Phys.* **1989**, *89*, 529.

(4) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.

(5) Cassagnau, Ph. Thèse de Doctorat, Université de Pau et des Pays de l'Adour, 1988.

(6) des Cloizeaux, J. *Europhys. Lett.* **1988**, *6*, 475.

(7) Viovy, J. L.; Rubinstein, M.; Colby, R. H. *Macromolecules* **1991**, *24*, 3873.

(8) See ref 4; the number of the equation is (7.3) on p 226.

(9) Colby, R. J., private communication.

(10) Graessley, W. W. *The Entanglement Concept in Polymer Rheology*; Advances in Polymer Science; Springer: New York, 1976; Vol. 16.

(11) Colby, R. H.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2226.

Registry No. $PhCH{=}CH_2$ (homopolymer), 9003-53-6; $H_2C{=}CHCH{=}CH_2$ (homopolymer), 9003-17-2; $MeOC(O)C(Me){=}CH_2$ (homopolymer), 9011-14-7; $H_2C{=}C(Me)CH{=}CH_2$ (homopolymer), 9003-31-0.