in Figures 1 and 2. Inclusion of the z_{AB} terms in eq 9 raises or diminishes the potential energy level, so that the core–skin structure of $V(S_{12})$ is weakened or even destroyed according to the magnitude of k. Thus the effect of k on the systems of a fixed l has a resemblance to the effect of l on the systems of $k = 0$ shown in Figures 1 and 2.

As shown in the previous paper of this series, the repulsive interblock interaction, $z_{AB} > 0$, promotes the formation of a collapsed dumbbell form of the diblock copolymers if it is associated with negative intrablock interactions, $z_{AA} < 0$ and $z_{BB} < 0$. On the other hand, the attractive interblock interaction, $z_{AA} < 0$, promotes the formation of a collapsed ring form of the ABA triblock copolymers if z_{AB} is absent. The present theory based on the spherical potential given by eq 9 is insufficient for clarifying the behavior of A_2 in these states. Finally, we note that an analytical expression for $V(S_{12})$ obtainable at $S_{12} = 0$ is useful for a quick test of the sign of core potential.

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Configurations and Dynamics of Real Chains. 2. Internal Viscosity

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ABSTRACT: Intramolecular transmission of tensile force along a polymer chain can only occur via rotational rearrangements, which is the origin of internal viscosity. This is interpreted as the resistance to the propagation of configurational motions along the chain, caused by the rotational barriers around skeletal bonds. The relaxation mechanism occurs via traveling waves damping off as $e^{-t/\tau}$. Within the linear force approximation, each normal mode is characterized by two distinct relaxation times. The larger of them contains an internal viscosity contribution increasing with the normal mode coordinate, in essential agreement with what is currently assumed. A realistic, quadratic intramolecular potential is also incorporated in the theory, proceeding in analogy with the first paper of this series (Allegra, G.; Ganazzoli, F. *J. Chem. Phys.* 1981, *74*, 1310). With a suitable choice of the characteristic time τ_0 for bond-rotation relaxation, the complex modulus experimentally found for polystyrene is approximately reproduced. The dynamic structure factor departs in general from a single time exponential even more dramatically than in the absence of internal viscosity. Selecting a Q range where the actual stereochemical structure of the polymer comes into play ($0.1 \leq Q = 4\pi \sin(\theta/2)/\lambda \leq 0.4$ Å^{-1}) and ignoring the hydrodynamic interaction effects, we show that the approximate power law $t_{1/2}Q^{\beta}$ = constant is verified with $\beta \simeq 3$ for coherent scattering and with β between 2.4 and $\sim$3 for incoherent scattering, depending on the particular value chosen for τ_0 ($t_{1/2}$ = half-peak time width). Hence the suggestion proposed in the quoted paper that hydrodynamic interaction need not be invoked to explain a value of β close to 3 in this Q range is confirmed. The theory also predicts a Rouse-like spectrum of the relaxation times even in the ideal absence of external friction forces. Furthermore, in agreement with Fixman's computer simulation results, the incipient rate of chain relaxation is independent of internal viscosity.

Introduction

At sufficiently high frequencies of the alternating shear stress applied to a polymer solution, a peculiar behavior is observed which cannot be explained by the classical theories of polymer viscoelasticity.[1,2] In practice, the chains appear to stiffen, and a seemingly constant value of the component of the dynamic viscosity in phase with the velocity of deformation is observed through some frequency decades. This phenomenon is currently associated with the so-called "internal viscosity", but its molecular origins are still controversial. Kuhn and Kuhn[3] first suggested that it should be attributed to the dissipative effect connected with the rotational energy barriers surmounted during any configurational change; in analogy with Eyring's treatment of fluid viscosity, the faster the rate at which the energy barriers are crossed, the larger the extra force that is required. Cerf[4] and Peterlin[5] expressed in quantitative forms this plausible idea; although their mathematical formulation appeared to be quite successful in terms of numerical comparison with some experimental data,[6-8] it mainly rested on semiempirical criteria. More recently, Iwata,[9] Cerf,[10] and MacInnes[11] directed their attention to more sophisticated stochastic models. Bazua and Williams offered a detailed model of the rotational relaxation process,[12] while Allegra proposed an alternative nonequilibrium statistical mechanical approach where the hindered skeletal rotations are shown to slow down the propagation of configurational perturbations along the chain.[13]

While de Gennes suggests that intramolecular segment–segment friction may be the source of internal viscosity,[14] a still different approach is proposed by Adelman and Freed, who show that anharmonicity of the intramolecular potentials leads to mode-coupling effects reproducing at least qualitatively some typical features of the Cerf–Peterlin model.[15] Later, Adler and Freed obtain analogous results within the quadratic (harmonic) approximation through an appropriate energy interaction between side chains.[16] Fixman shows interesting computer simulation results on a chain model with fixed bond lengths and angles and threefold rotational potentials that leads inter alia to a plateau viscosity in the high-frequency region.[17]

In the present paper the theoretical approach to internal viscosity offered in ref 13 will be developed further. Specifically:

1. A new formulation of the intramolecular potential will be incorporated.[18,19] Although still confined within the quadratic approximation, it gives a realistic description of the polymer (*polyethylene*) chain. In particular, unlike the classical bead-and-spring model, it shows that the chain becomes progressively more rigid for more localized modes of configurational motion.
2. The Langevin equation approach will be followed, in a way that closely parallels Ronca's formulation.[20]
3. In addition to the complex modulus, which will be evaluated within the usual frequency range, we will also obtain the dynamic structure factor.[21] We will confine our attention to a particular range of the scattering vector where the specific stereochemical structure of the chain is relevant.[19]
4. The complex modulus will be obtained accounting for the hydrodynamic interaction effect, unlike the dynamic structure factor, where the observation length scale appears to be sufficiently small as to warrant its neglect.
5. Different chain lengths will be considered in the evaluation of the complex modulus, unlike the case of dynamic scattering, where the chain end effects give a negligible contribution to the intramolecular motions under investigation.

In ref 13 a particular assumption was introduced into the equations of chain motion under an oscillating external field. Namely, it was supposed that the frequency spectrum of any mode of motion reduces to the single applied frequency ω. While the assumption is formally incorrect, it is possible to see that it does not introduce any error in the ω range taken into consideration (i.e., $\omega\tau_0 \ll 1$, where τ_0 is the relaxation time for skeletal rotations; see following). No such assumption will be made in the present paper, where larger frequencies—i.e., smaller observation times—will also be considered.

An error implying a reduction by a factor of 2 of the internal viscosity force in the original formulation was pointed out later by one of us (see second paper in ref 13). Obviously enough, this will be taken care of in this paper.

Internal Viscosity and Force Propagation

In ref 13 the internal viscosity was obtained from nonequilibrium statistical mechanical considerations as a force acting on the general segment of a polyethylene chain when the end-to-end chain displacement along a given axis differs from the average value to be expected from the existing proportion of trans and gauche rotational states.[22]

In practice, the resulting physical pattern may be conveniently visualized as follows. Let us still refer for simplicity to the bead-and-spring model except for the introduction of internal viscosity. At first it will be expedient to consider the chain in an ideal state where both the viscous drag and the Brownian forces from the solvent become vanishingly small in comparison with the intramolecular elastic forces. If a pull is applied to the two chain ends along the x axis, an elongational deformation will be imparted to the end chain segments (or "springs"), which will be transmitted to the inner ones. Even neglecting the inertial effects, the rate at which the perturbation propagates along the chain must be finite because it involves skeletal rotations, which in turn take a finite time. The resulting internal viscosity force $\Phi(k,t)$ acting on the kth bead will be balanced by the elastic forces transmitted by the neighboring beads. Supposing that the strain propagates toward higher k values, we have from eq 29 of ref 13

$$[x(k+1,t) - x(k,t)] - [x(k,t) - x(k-1,t)] + \frac{\Phi(k,t)}{\alpha} = 0 \tag{1a}$$

$$\frac{1}{\alpha}\left[\frac{1}{\bar{\tau}_0}\Phi(k,t) + \dot{\Phi}(k,t)\right] = \frac{2}{3}[\dot{x}(k+1,t) - \dot{x}(k-1,t)] \tag{1b}$$

where

$$\alpha = 3k_{\mathrm{B}}T/b^2 \tag{1'}$$

$x(k,t)$ is the x coordinate of the kth bead at time t, and b^2 is the mean-square length of the segment. Each statistical segment (usually comprising few skeletal atoms) is supposed to be configurationally homogeneous, meaning that its statistical distribution of trans and gauche states corresponds to that existing at equilibrium for some value of its average elongation. The rotational relaxation time $\bar{\tau}_0$ is given by[13]

$$\bar{\tau}_0 = \frac{\exp(\Delta/k_{\mathrm{B}}T)}{2A}\left(\frac{f_{\mathrm{G}}^{\circ}f_{\mathrm{T}}^{\circ}}{2}\right)^{1/2} \tag{2}$$

where A is a frequency factor, Δ is the average effective energy barrier between gauche and trans states, and f_{G}° and f_{T}° are the respective fractions at equilibrium. It is possible to show that eq 1a,b represent a stretching perturbation that proceeds along increasing k's with a decreasing amplitude. The time rate of $d_1 = x(k+1,t) - x(k-1,t)$ is provided by the difference d_2 between the projections $x(k+1,t) - x(k,t)$ and $x(k,t) - x(k-1,t)$; if d_1 were constant with time, then d_2 would relax as $e^{-t/\bar{\tau}_0}$. Since a given statistical segment is assumed to undergo a uniform configurational change[23] in order to achieve the same average elongation as the preceding segment, it is implicit that a uniform tensile force should be transmitted to all of its skeletal bonds at a given time. This implies that a sort of rigidity is associated with the segment itself. We will see in the following how this limitation may be overcome.

Let us now integrate eq 1b over the time variable; then eliminating Φ from (1a) and (1b), we get

$$x(k+1,t) - 2x(k,t) + x(k-1,t) + {}^{2}\!/_{3}\, e^{-t/\bar{\tau}_0}\int_{-\infty}^{t} e^{\tau/\bar{\tau}_0}[\dot{x}(k+1,\tau) - \dot{x}(k-1,\tau)]\,\mathrm{d}\tau = 0 \tag{3}$$

If the applied motion is a harmonic oscillation with an angular frequency $\omega \ll \bar{\tau}_0^{-1}$, it is easy to check that the stationary solution of eq 3 is[13]

$$x(k,t) = H\exp\left[i\left(\frac{2\pi k}{\lambda} - \omega t\right) - kK\right] \tag{4}$$

where

$$\lambda = 3\pi/2\omega\bar{\tau}_0 \quad \text{(beads)} \qquad K = {}^{4}\!/_{3}\,\omega^2\bar{\tau}_0^{\,2} \tag{5}$$

Equation 4 represents a damped wave propagating toward higher k values with a velocity (in beads/s)

$$v = \omega\lambda/2\pi = 3/4\bar{\tau}_0 \tag{6}$$

It is noteworthy that eq 3 does not contain any parameter related with the geometrical or physical features of the relaxing sequence except for its characteristic time $\bar{\tau}_0$, thus suggesting a general validity. On the other hand, although the current assumption that the chain statistical segments are configurationally independent *from an equilibrium viewpoint* may qualitatively justify their identification with the relaxing sequences, this choice is basically arbitrary. More than that, it would impose the bead-and-spring configurational description of the chain, which appears to miss some relevant physical features at sufficiently short observation times.[19] For these reasons we will here assume that the relaxing sequence is the single bond itself, with a single relaxation time τ_0, identifying henceforth $x(k,t)$ with the coordinate of the kth skeletal *atom* at time t (see eq 1 and 3, $\bar{\tau}_0 \rightarrow \tau_0$). Although some degree of coupling between skeletal rotations must clearly exist, and the rotational relaxation may proceed through a spectrum rather than via a single relaxation time, our assumption should permit a substantially correct although approximate evaluation of the internal viscosity effect insofar as it does not suppress any configurational degree of freedom. From inspection of eq 4 and 5, it may be observed that the present description should differ from the previous one in the high-frequency range (i.e., for $\omega \sim \tau_0^{-1}$ or more), while at low frequencies the two approaches are equivalent as long as the single-bond relaxation time τ_0 is related to $\bar{\tau}_0$ by

$$\tau_0 = \bar{\tau}_0/\nu \tag{7}$$

where ν is the number of skeletal atoms per statistical segment ($\sim$10 for polyethylene under usual Θ conditions).

It must be stressed that eq 1 and 3 imply that an internal motion propagates along the chain toward higher k values. In practice, it is obvious that both directions of propagation are equally probable; if the direction is reversed, the sign of the right-hand side in eq 1b changes, and so does the sign of the time integral in eq 3. (Such a dependence of the internal viscosity force from the history of the chain motion is in keeping with its nonequilibrium character.[13]) We will decompose any chain configurational motion into two oppositely traveling motions, in analogy with the splitting of a standing sinusoidal wave into two identical waves traveling along opposite directions. Correspondingly, our results show that each traveling motion is constituted by a superposition of elementary contributions relaxing as damped waves that propagate along the chain. Each traveling motion, or perturbation, may be considered as associated with its own set of Brownian forces, so that the two opposite motions will be treated as statistically independent. In practice, we will limit ourselves to considering the propagation direction chosen above (i.e., along increasing k's), although we bear in mind that it accounts for only 50% of the overall chain motion. As an example, under isotropic conditions the correlation function $B(k,t) = \langle[\mathbf{r}(k,t) - \mathbf{r}(0,0)]^2\rangle$ will be correctly given within our scheme by the average of the values corresponding to $+k$ and $-k$, i.e.

$$B(k,t) = \tfrac{1}{2}[3\langle[x(k,t) - x(0,0)]^2\rangle + 3\langle[x(-k,t) - x(0,0)]^2\rangle] \tag{8}$$

so that the two directions of propagation are treated as equally probable. Recourse to "traveling" perturbations is perhaps not unavoidable, but it appears to make the physicomathematical representation of internal viscosity clearer.

Let N be the (very large) number of chain bonds and assume at first the chain to be connected ringwise for simplicity, so that $x(N + k,t) \equiv x(k,t)$. We will introduce the Fourier transformations (indicated with primes)[20]

$$x'(q,t) = \sum_{k=1}^{N} x(k,t)e^{iqk} \qquad x(k,t) = N^{-1}\sum_{\{q\}} x'(q,t)e^{-iqk} \tag{9a}$$

$$\{q\} \equiv \left(0, \frac{2\pi}{N}, 2\left(\frac{2\pi}{N}\right), 3\left(\frac{2\pi}{N}\right), ..., (N-1)\left(\frac{2\pi}{N}\right)\right) \tag{9b}$$

Multiplying eq 3 by e^{iqk} and summing over all k's, we get the general normal mode equation ($\bar{\tau}_0 \rightarrow \tau_0$)

$$2(1 - \cos q)x'(q,t) + \tfrac{4}{3}i \sin q \int_{-\infty}^{t} \dot{x}'(q,\tau)e^{-(t-\tau)/\tau_0}\, \mathrm{d}\tau = 0 \tag{10}$$

It should be noted that eq 10 would be obtained without the ringwise assumption through the following steps: (i) express eq 3 in terms of bond projections $l_x(k,t) = x(k + 1,t) - x(k,t)$, defining a virtual bond projection $l_x(0,t) \equiv l_x(N,t)$ (periodic condition); (ii) multiply by e^{iqk}; (iii) sum over all k's and use the following definition for $x'(q,t)$:

$$\begin{aligned} \sum_{k=1}^{N} l_x(k,t)e^{iqk} &= x'(q,t)(e^{-iq} - 1) \qquad (q \neq 0) \\ \sum_{k=1}^{N} l_x(k,t) &= x(N,t) - x(0,t) \end{aligned} \tag{11}$$

The above procedure leads to eq 10, although the connection between $x'(q,t)$ and $x(k,t)$ is not established yet. Antitransforming eq 11, we now easily prove that ($0 \leq r$, $s \leq N$)

$$x(r,t) - x(s,t) = \sum_{k=s}^{r-1} l_x(k,t) = N^{-1} \sum_{\{q\}(\neq 0)} x'(q,t)(e^{-iqr} - e^{-iqs}) + \frac{r-s}{N}[x(N,t) - x(0,t)] \tag{12}$$

For unperturbed configurations, the left-hand side is of order $|r - s|^{1/2}$, while the last term on the right-hand side is of order $|r - s|/N^{1/2}$. Consequently, for $|r - s|/N \ll 1$ the latter term may be neglected and the relationships given in eq 9 between $x'(q,t)$ and $x(k,t)$ are valid for the noncyclic chain as well. In conclusion, the periodic assumption rigorously leads to eq 10, although eq 9 turns out to be only valid for atom pairs separated by a small number of bonds in comparison with the full chain length.

So far both the external friction and the Brownian forces have been neglected. The corresponding equation when both these forces are considered but the internal viscosity is not may be expressed as (cf. eq 31 of ref 18)

$$\begin{aligned} 2\alpha(q)(1 - \cos q)x'(q,t) + \zeta\dot{x}'(q,t) &= X'(q,t) \\ \alpha(q) &= 3k_BT/C(q)l^2 \end{aligned} \tag{13}$$

where l is the C–C bond length, ζ is the friction coefficient per skeletal atom, $X'(q,t)$ is the transform of the Brownian forces $X(k,t)$ acting on the chain atoms (see by analogy eq 9), and $C(q)$ is the generalized characteristic ratio, containing full information on the geometrical averages of the unperturbed chain.[18] This function is sharply peaked around $q = 0$, and for polyethylene ($q < 2\pi/10$, $T \simeq 100$ °C) it is approximately given by

$$C(q) = 0.11/(1 - 0.984 \cos q) \tag{14}$$

while for $q = 0$ it coincides with the usual C_∞ characteristic ratio.[19] The problem of incorporating eq 10 into eq 13 is straightforward, in view of the linear nature of the problem:

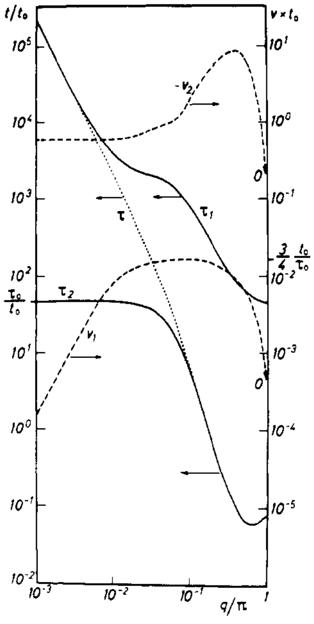

Figure 1. Plots of the relaxation times (τ_1 and τ_2) and of the velocities of propagation (v_1 and $-v_2$) vs. q for the general normal mode amplitude $x'(q,t)$ (see eq 19–23; $t_0 = \zeta l^2/k_BT$). The ratio τ_0/t_0 is 46.7. The dotted line shows the relaxation time τ in the absence of internal viscosity (i.e., for $\tau_0 = 0$).

it merely requires multiplying eq 10 by $\alpha(q)$ and adding the terms containing ζ and X':

$$2\alpha(q)(1 - \cos q)x'(q,t) + \tfrac{4}{3}i\alpha(q) \sin q \int_{-\infty}^{t} \dot{x}'(q,\tau)e^{-(t-\tau)/\tau_0}\, d\tau + \zeta\dot{x}'(q,t) = X'(q,t) \tag{15}$$

It is possible to prove that $x'(q,t)$ represents a wave perturbation with $2\pi/q$ chain atoms per wavelength, traveling at a speed that is smaller than $3/(4\tau_0)$ atoms/s (cf. eq 6 and Figure 1), the larger are ζ and/or q. Except for the sign the term containing the time integral is obviously to be identified with the transform of the internal viscosity force $\Phi'(q,t)$. In the particular case that τ_0 may be regarded as vanishingly small compared with the overall relaxation time of $x'(q,t)$, we get

$$\lim_{\tau_0 \to 0} \Phi'(q,t) = -\tfrac{4}{3}i\alpha(q) \sin q\ \tau_0\dot{x}'(q,t) \tag{16}$$

This limiting form of the internal viscosity has two important analogies with other currently proposed expressions (see ref 5, for example); namely, it is proportional both to the strain rate $\dot{x}'(q,t)$ and to q (for $q \ll 1$), apart from the sign. However, a very important difference must be stressed: unlike other expressions, it contains the out-phasing imaginary unit. This feature is clearly related with the damped-wave relaxation, as we shall see again when discussing the spectrum of the relaxation times. Also, we will come back to compare the internal viscosity relaxation effect predicted by our approach with that of other theories (see discussion after eq 45).

Deferring to a following section the problem of hydrodynamic interaction, we will now proceed within the free-draining approximation. A convenient approach to solving eq 15 involves the substitution of $x'(q,t)$ and $X'(q,t)$ with their time Fourier transforms, i.e.

$$x'(q,t) = \int_{-\infty}^{\infty} x''(q,\omega)e^{-i\omega t}\, d\omega$$
$$x''(q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} x'(q,t)e^{i\omega t}\, dt \tag{17}$$

(analogously for $X'(q,t)$ and $X''(q,\omega)$), obtaining

$$x''(q,\omega) = X''(q,\omega)(1 - i\omega\tau_0)/\{2\alpha(q)(1 - \cos q)(1 - i\omega\tau_0) + \tfrac{4}{3}\alpha(q)\omega\tau_0 \sin q - i\omega\zeta(1 - i\omega\tau_0)\} = X''(q,\omega)\psi''(q,\omega) \tag{18}$$

where the last equality is to be taken as a definition of $\psi''(q,\omega)$. Back-transformation of $x''(q,\omega)$ gives, in view of the convolution and Cauchy's theorems

$$x'(q,t) = \frac{1}{2\pi}\int_{-\infty}^{t} X'(q,\tau)\psi'(q,t - \tau)\, d\tau \tag{19}$$

where

$$\begin{aligned}\psi'(q,t) &= \int_{-\infty}^{\infty} \psi''(q,\omega)e^{-i\omega t}\, d\omega \\ &= \frac{2\pi i}{\zeta\tau_0(\omega_1 - \omega_2)}[(1 - i\omega_1\tau_0)e^{-i\omega_1 t} - (1 - i\omega_2\tau_0)e^{-i\omega_2 t}] \quad (\text{for } t \geq 0) \\ &= 0 \quad (\text{for } t < 0)\end{aligned} \tag{20}$$

$$\omega_1 = \frac{A(q) - \sqrt{A^2(q) + B(q)}}{2\zeta\tau_0} \tag{20a'}$$

$$\omega_2 = \frac{A(q) + \sqrt{A^2(q) + B(q)}}{2\zeta\tau_0} \tag{20b'}$$

$$A(q) = -i[2\alpha(q)\tau_0(1 - \cos q) + \zeta] + \tfrac{4}{3}\alpha(q)\tau_0 \sin q$$
$$B(q) = 8\alpha(q)\zeta\tau_0(1 - \cos q)$$

If we write

$$\omega_n = -\frac{2\pi}{T_n} - \frac{i}{\tau_n} \qquad (n = 1, 2) \tag{21}$$

where T_n and τ_n are an oscillation period and a relaxation time, respectively ($\tau_n > 0$), we see that the chain relaxation proceeds through damped propagating waves. In fact, considering eq 9, 19, and 20, we have

$$x(k,t) = \int_{-\infty}^{t} d\tau\ X'(q,\tau)\sum_{\{q\}}[U(q) \exp(-i\omega_1(t - \tau) - iqk) + V(q) \exp(-i\omega_2(t - \tau) - iqk)] \tag{22}$$

where $U(q)$ and $V(q)$ are suitable functions of q. In view of eq 21 the argument of the exponentials is of the form $i[(t - \tau)2\pi/T_n - qk] - (t - \tau)/\tau_n$, the real and the imaginary components representing the damped and the propagating terms, respectively. The associated velocities are

$$v_n = 2\pi/qT_n \qquad (n = 1, 2) \tag{23}$$

It may be of interest to evaluate the expressions of τ_n and v_n in the two limits of $\tau_0/\zeta \to 0$ and $\zeta/\tau_0 \to 0$.

Using in both cases the series development

$$(A^2(q) + B(q))^{1/2} = A(q)\left(1 + \frac{1}{2}\frac{B(q)}{A^2(q)} + ...\right)$$

we have

$$\begin{aligned}\tau_1 &= \tau(q) = \zeta/[2\alpha(q)(1 - \cos q)] \\ v_1 &= 8\alpha^2(q)\tau_0 \sin q(1 - \cos q)/(q\zeta^2)\end{aligned} \tag{24a}$$

$$\tau_2 = \tau_0 \qquad v_2 = -4\alpha(q) \sin q/(3q\zeta) \tag{24b}$$
$$(\tau_0/\zeta \to 0)$$

and

$$\tau_1 = \tau_0\left[\frac{5}{9} + \frac{8}{9(1-\cos q)}\right] \qquad v_1 = \frac{1}{\tau_0}\,\frac{6\sin q}{q(13-5\cos q)} \tag{25a}$$

$$\tau_2 = \zeta/[2\alpha(q)(1-\cos q)] \qquad (=\tau(q)) \qquad v_2 = -4\alpha(q)\sin q/(3q\zeta) \qquad (=\text{as above}) \tag{25b}$$

$$(\zeta/\tau_0 \rightarrow 0)$$

Equations 24a and 24b indicate that, when the internal viscosity tends to vanish, in addition to the usual spectrum $\tau(q)$ (cf. ref 18, eq 33), a rotational relaxation τ_0 still exists with no coupling among chain bonds. In the alternative limit of vanishing external friction, we see that $\tau(q)$ is still present; however, now the internal viscosity also produces a spectrum of its own (i.e., τ_1) with coupling among skeletal rotations as indicated by the q^{-2} dependence as $q \rightarrow 0$. The corresponding velocity of propagation, v_1, is largest for $q = 0$ and equal to $3/(4\tau_0)$, in agreement with eq 6, as expected.

Figure 1 shows the plots of τ_n and v_n ($n = 1, 2$) vs. q for a specific, nonlimiting case. The time unit is conveniently chosen as[19]

$$t_0 = \zeta l^2/k_B T \tag{26}$$

so that $\alpha(q) = 3\zeta/[C(q)t_0]$ (see eq 13). The generalized characteristic ratio $C(q)$ is taken from ref 18, while $\tau_0/t_0 = 46.7$ was chosen to obtain the best agreement with the experimental results for the complex modulus of polystyrene (see following). It should be remarked that in so doing we are unduly extending to polystyrene the configurational properties of polyethylene; although this arbitrariness should not be too serious, in view of the basically exploratory purpose of the present paper, it must be clearly stressed that all the numerical results reported in this paper depend on the above choice of τ_0 and therefore should be attributed to polystyrene. Needless to say, the basic qualitative features of Figure 1 should not depend on this particular choice.

The two branches of the relaxation times τ_n do not overlap (see Figure 1); while they have the same value (i.e., τ_0) at one of their extremes, at the other end they coincide with the curve giving the relaxation time in the absence of internal viscosity (τ in the figure). For $q \rightarrow 0$ the relative weight of the internal viscosity tends to vanish, as may be inferred from analysis of eq 20′, and the behavior of τ_n and v_n is closely described by eq 24. For larger q ($\gtrsim 0.1\pi$) the reverse limit is approached; i.e., the external friction effect tends to vanish and the curves are in excellent agreement with eq 25. In particular, the velocity v_1 of the slowly decaying branch approaches rather closely its upper limit, $3/(4\tau_0)$. The other velocity, v_2, is accurately given by the (identical) expressions reported in eq 24 and 25, and it is notable insofar as (i) it is much larger than v_1 and (ii) it goes backward (cf. the negative sign). Both features may seem strange at first, but they may be explained by considering that the algebraic expression of v_2 does not contain the internal viscosity; consequently, as long as the velocity of this satellite wave is only controlled by the external friction, it need not be limited either by the upper bound $3/(4\tau_0)$ or by the direction of the major wave as given by the sign of v_1.

Complex Modulus

In this section we will introduce the effect of hydrodynamic interaction, as it appears to be required by the experimental results for the complex modulus of long chains in dilute solution.[6-8] We will follow the preaveraging treatment given by Ronca[25] and reported in Appendix I, which fits very conveniently the Langevin approach. The hydrodynamic interaction effect is merely reflected in the replacement of the friction coefficient ζ by the following q-dependent quantity ($N \rightarrow \infty$)

$$\zeta \rightarrow \zeta(q) = \frac{\zeta}{1 + h_0 N^{1/2}\pi\cos(qN/2)J_0(qN/2)} = \frac{\zeta}{1 + h_0 f(q,N)} \tag{27}$$

where h_0 is the coefficient of hydrodynamic interaction (see eq I-7) and $J_0(x)$ is the Bessel function of order zero.

Let us now consider the viscosity effect due to a chain in dilute solution while the chain experiences an alternate shear stress produced by a velocity gradient in the solvent. The fluid velocity goes along x and its gradient is along z; the applied frequency is ω. We shall denote by $f_x(k,t)$ the component along x of the force exerted by the kth chain atom upon the solvent at time t and by $z(k,t)$ the z coordinate of the same atom. The solvent velocity at the position occupied by the kth atom with the chain absent is

$$v_x^{(0)}(k,t) = \gamma e^{i\omega t} z(k,t) \tag{28}$$

while the velocity of the kth chain atom relative to the solvent is

$$\dot{x}_{\text{rel}}(k,t) = \dot{x}(k,t) - v_x^{(0)}(k,t) \tag{29}$$

and its Fourier transform is, in view of eq 28

$$\dot{x}'_{\text{rel}}(q,t) = \dot{x}'(q,t) - \gamma e^{i\omega t} z'(q,t) \tag{30}$$

The complex viscosity is[26]

$$\eta^* = \eta_s + \frac{c}{\gamma e^{i\omega t}} N \langle f_x(k,t) z(k,t) \rangle_k \tag{31}$$

where c is the polymer concentration expressed as (number of chains)/volume. It will be useful to decompose both $f_x(k,t)$ and $z(k,t)$ into normal mode components, according to eq 9, so that

$$\langle f_x(k,t) z(k,t) \rangle_k = N^{-1} \sum_k \langle f_x(k,t) z(k,t) \rangle = N^{-2} \sum_{\{q\}} \langle f_x'(q,t) z'(-q,t) \rangle \tag{32}$$

From its definition, $f_x(k,t)$ is the sum of the Brownian force $X(k,t)$ and of the viscous drag $-\zeta\cdot\dot{x}(k,t)$, and its normal mode transform is conveniently given by the first two terms of eq 15; i.e.

$$f_x'(q,t) = 2\alpha(q)(1-\cos q)x'(q,t) + {}^4\!/_3 i\alpha(q)\sin q \int_{-\infty}^{t} \dot{x}'(q,\tau) e^{-(t-\tau)/\tau_0}\,\mathrm{d}\tau \tag{33}$$

where $x'(q,t)$ obeys eq 15, provided we replace the friction force component $\zeta(q)\dot{x}'(q,t)$ by $\zeta(q)\dot{x}'_{\text{rel}}(q,t)$ (see eq 27 and 30).

Introducing now the time Fourier transforms for both $x'(q,t)$ and $z'(q,t)$ and using the fluctuation–dissipation theorem (Appendix II, eq II-5), on the assumption that the Brownian forces along x and z are uncorrelated, we get with the aid of Cauchy's theorem

$$\eta^* = \eta_s - ck_B T \sum_{\{q\}} \left\{ \frac{1}{\tau_0(\omega_1^* - \omega_2^*)(2\alpha(q)\tau_0(1-\cos q) + \zeta(q))} \times \left[\frac{N(q,\omega_1^* - \omega)P(q,\omega_1^*)}{M(q,\omega_1^* - \omega)\omega_1^*} - \frac{N(q,\omega_2^* - \omega)P(q,\omega_2^*)}{M(q,\omega_2^* - \omega)\omega_2^*} \right] \right\} \tag{34}$$

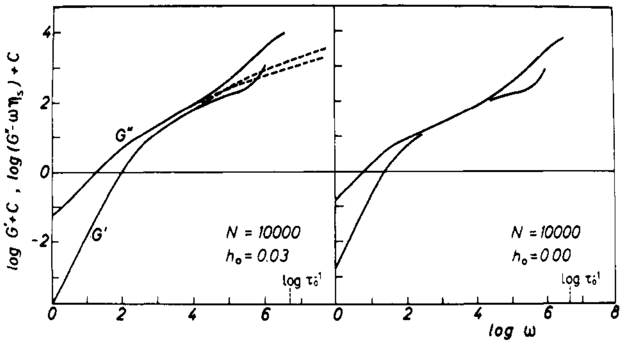

Figure 2. Logarithmic plots of G' and of $G'' - \omega\eta_s$ (η_s = solvent viscosity) vs. ω. The complex modulus $G^* = i\omega\eta^* = G' + iG''$ is calculated from eq 34 and 36. C is a proper constant. The friction coefficient ζ is 10^{-6} g s^{-1} per skeletal C atom; that should approximately correspond to a solvent viscosity $\eta_s \simeq 1$ P. $T = 400$ K, l (the C–C bond length) = 1.54 Å, and t_0 ($=\zeta l^2/k_BT$) = 4.3×10^{-9} s. The rotational relaxation time is $\tau_0 = 46.7t_0$ (as in Figure 1) = 2×10^{-7} s. The value of h_0 is chosen arbitrarily. N is the number of C atoms per chain. On the left-hand side, the dashed lines correspond to an absence of internal viscosity (i.e., $\tau_0 = 0$). On the right-hand side the hydrodynamic interaction is suppressed; in the middle ω range the curves belonging to G' and G'' are virtually superimposed.

where ω_n^* are the complex conjugates of ω_n (n = 1, 2; see eq 20′), with substitution of ζ with $\zeta(q)$ (eq 27), while M, N, and P are given by

$$M(q,\omega) = N(q,\omega) - i\omega\zeta(q)(1 - i\omega\tau_0) \qquad (35)$$

$$N(q,\omega) = 2\alpha(q)(1 - \cos q)(1 - i\omega\tau_0) + {}^4\!/_3\alpha(q)\omega\tau_0 \sin q$$

$$P(q,\omega) = [\zeta(q)(1 + \omega^2\tau_0^2) - {}^4\!/_3\alpha(q)\omega\tau_0^2 \sin q]/2\pi$$

Although the above result was obtained by considering only one of the two possible propagation directions (cf. eq 1 and 10), it correctly represents the overall average because it is invariant upon changing the sign of q. The complex modulus is related to the complex viscosity by[26]

$$G^* = G' + iG'' = i\omega\eta^* \qquad (36)$$

Figure 2 shows double-logarithmic plots of G' and $G'' - \omega\eta_s$ vs. the applied frequency ω for given values of t_0 ($=\zeta l^2/k_BT$) and τ_0 ($\simeq 47t_0$, as in Figure 1) and for a relatively large molecular weight. On the left-hand side the value chosen for the coefficient of hydrodynamic interaction, h_0 (see eq 27), appears to fit several experimental results on polystyrene reasonably well;[6-8] its effect may be seen by comparison with the right-hand side, where $h_0 = 0$. It should be remarked that in this context we are treating h_0 as an adjustable parameter, without recourse to eq I-7, in view of both the uncertainties in the application of Stoke's law (i.e., the ratio ζ/η_s) and the several assumptions involved in the preaveraging treatment of the hydrodynamic interaction. On the other hand, the value chosen by us for h_0 (=0.03, see Figure 2) is in rough agreement with that assumed by Osaki and Schrag ($h^*_{av} = 0.2$ for a chain segment of $\nu \simeq 23$ skeletal atoms), considering the equivalence $h_0\nu^{1/2} = h^*$. As to τ_0, the dashed lines obtained for $\tau_0 = 0$ may illustrate its influence on the results.

Figure 3 shows some experimental data obtained from polystyrene solutions by the Wisconsin group[7] together with the best-fitting curves from eq 34–36; on the left-hand side, calculated plots obtained by taking τ_0 3 times more and 3 times less than $\simeq 47t_0$ are also reported, showing that this optimum value cannot be changed very much. The most serious disagreement between observed and calculated values occurs for G' toward the high-frequency limit; in this region it would be very interesting to obtain additional measurements, but experimental difficulties appear to arise, strongly affecting their precision.[6,7] For ω values close to τ_0^{-1} the G' and G'' calculated curves would intersect each other, as already observed in the preliminary less accurate results previously reported by one of us.[13] However, this theoretical prediction and the general behavior of the curves in this frequency range are certainly influenced by our assumption of a single, noncooperative rotational relaxation around chain bonds. Another discrepancy concerns the theoretical chain length that is 30–40% longer than the experimental one, in terms of backbone atoms, which might be more or less directly ascribed to our extrapolation to polystyrene of the configurational properties of polyethylene.

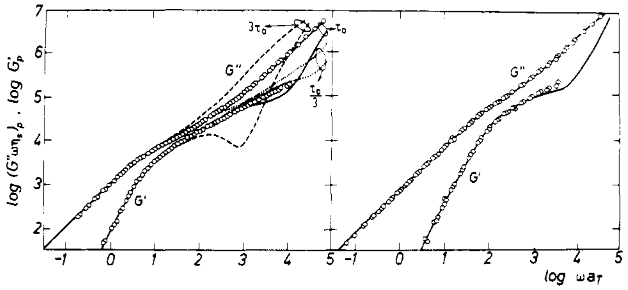

Figure 3. Experimental values (circles) of the reduced complex modulus of the polystyrene solutions.[7] The molecular length is equal to 5100 and 981 C atoms on the left- and right-hand sides, respectively. The best-fitting calculated curves (solid lines) were obtained from eq 34 and 36, with N (number of C atoms in the backbone) equal to 8000 and 1300 (left- and right-hand sides, respectively) and all other parameters as in Figure 2. The dashed and dotted lines on the left-hand side correspond to a τ_0 value multiplied, respectively, by 3 and by $^1/_3$ compared with the solid lines. (The pairs of G' and G'' calculated curves were superimposed on the experimental points after a rigid, parallel shift.)

If $\omega\tau_0 \ll 1$ the approximation indicated in eq 16 may be used. Then the above approach may be followed with no need of introducing the time Fourier transforms, and the complex viscosity reduces to, after averaging the terms with opposite q

$$\eta^* = \eta_s + ck_BT\sum_{\{q\}}\frac{\zeta(q)}{4\alpha(q)(1 - \cos q)}\;\frac{1 + i\omega[8\alpha(q)\tau_0^2/9\zeta(q)](1 + \cos q)}{1 + i\omega\bar{\tau}(q)/2} \qquad (37)$$

where

$$\bar{\tau}(q) = \frac{\zeta^2(q) + ({}^4\!/_3\tau_0\alpha(q)\sin q)^2}{2\alpha(q)\zeta(q)(1 - \cos q)} \qquad (37')$$

is the effective mode relaxation time.[27] If τ_0 is zero it reduces to the usual relaxation time $\tau(q)$ in the absence of internal viscosity, see eq 24. Extrapolation of eq 37 to large ω values (provided $\omega \ll \tau_0^{-1}$) gives a real, positive contribution for each q, in agreement with the usual semiempirical forms incorporating the internal viscosity into the Rouse–Zimm theory.

Dynamic Structure Factor

We will limit our attention to the scattering range

$$0.1 \le Q \le 0.4\ \text{Å}^{-1} \qquad Q = 4\pi \sin(\theta/2)/\lambda \qquad (38)$$

where the experimental results should reflect the actual stereochemical structure of the polymer, although the precise location of the scattering centers within each methylene unit is irrelevant. For a discussion of the degree

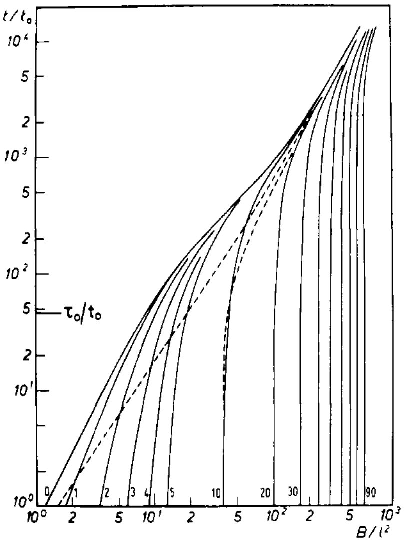

Figure 4. t vs. correlation function $B(k,t)$ (from eq 41), with respective units of t_0 and l^2. The k integers are reported on the curves. The ratio τ_0/t_0 is the same as in Figures 1 and 2. The dashed lines correspond to $B(0,t)$ and $B(10,t)$ in the absence of internal viscosity.[19]

of approximation obtainable from the following calculations, see ref 19; here it should suffice to remind that it appears to be adequate for $t/t_0 > 6$–10. In particular, the hydrodynamic interaction will be neglected henceforth, so that $\zeta(q) \equiv \zeta$.

For a chain with N ($\rightarrow\infty$) scattering atoms the dynamic structure factor in the assumption of coherent and incoherent scattering, respectively, is[21]

$$S(Q,t) = N^{-1}\{\exp[-\tfrac{1}{6}Q^2B(0,t)] + 2\sum_{k=1}^{\infty}\exp[-\tfrac{1}{6}Q^2B(k,t)]\} \tag{39}$$

$$S_{\mathrm{incoh}}(Q,t) = \exp[-\tfrac{1}{6}Q^2B(0,t)] \tag{40}$$

where $B(k,t)$ is the correlation function at time t between two atoms separated by k bonds and is given by eq 8. The square averages involved may be evaluated from a joint application of eq 9, 17, 18, and II-5 of Appendix II and by using Cauchy's theorem. The result is

$$B(k,t) = \frac{12k_BT}{\zeta^2\tau_0^2}\int_0^{2\pi}\mathrm{d}q\ \mathrm{Re}\left\{\frac{i}{\omega_1-\omega_2}\left[\frac{P(q,\omega_2)[1-e^{-i\omega_2t}\cos(qk)]}{(\omega_2-\omega_1^*)(\omega_2-\omega_2^*)} - \frac{P(q,\omega_1^*)[1-e^{-i\omega_1t}\cos(qk)]}{(\omega_1-\omega_1^*)(\omega_1-\omega_2^*)}\right]\right\} \tag{41}$$

where Re means "real part of", ω_1 and ω_2 are given by eq 20′, and $P(q,\omega)$ is given by eq 35. As a particular case we have verified that for $t = 0$ the above expression reduces to the equilibrium value, i.e., $\langle[\mathbf{r}(k,0) - \mathbf{r}(0,0)]^2\rangle$, as expected. If the observation time is $\gg\tau_0$, the approximation shown in eq 16 may still be adopted, and we get

$$B(k,t) = \frac{l^2}{2\pi}\int_0^{2\pi}C(q) \times \frac{1 - e^{-t/\bar{\tau}(q)}\cos(qk)\cos\left(\dfrac{4}{3}\dfrac{\tau_0\alpha(q)\sin q}{\zeta}\dfrac{t}{\bar{\tau}(q)}\right)}{1-\cos q}\,\mathrm{d}q \tag{42}$$

where $\bar{\tau}(q)$ is given in eq 37′. It is apparent that the internal viscosity contributes both by increasing the relaxation time $\bar{\tau}(q)$ and by introducing a time oscillation factor. Plots of t vs. $B(k,t)$ calculated according to eq 41 are reported in Figure 4 in the respective units t_0 and l^2 ($=l_{\mathrm{C-C}}^2 = (1.54\ \text{Å})^2$) (see eq 26); the characteristic time τ_0 of the internal viscosity has been kept at the value used for Figure 1–3. For comparison, plots of $B(k,t)$ for $k = 0$ and $k = 10$ calculated in the absence of internal viscosity (i.e., with $\tau_0 = 0$) are also also reported with dashed lines. The effect of internal viscosity is particularly noticeable as a decrease of the time rate of $B(k,t)$ at small k (up to 6–7), especially for $t \simeq \tau_0$. As a result, the cooperativity of the motion of atoms adjacent along the chain sequence is enhanced. In fact, the internal viscosity reduces the rate at which any conformational difference between adjacent parts of the chain sets in (cf. eq 1), producing the same effect as additional chain rigidity. In the two extremes of very large and very small times the internal viscosity appears to have no effect. In the former case, Figure 4 shows that the corresponding dashed and solid lines merge at large t/t_0. As for $t \rightarrow 0$, it is possible to show that $B(k,0)$ is always zero except for $k = 0$, in which case it is given by $6k_BT/\zeta$ (cf. eq 31 of ref 19). This result implies that the initial decay time

$$\tau_Q = -\left(\frac{\partial \ln S(Q,t)}{\partial t}\right)^{-1}_{t=0} \tag{43}$$

is also insensitive to internal viscosity in the case of both coherent and incoherent scattering. This is not the case for the half-peak time width $t_{1/2}$, which is reported in Figure 5 for the two cases. (We have used eq 39 even for $t = 0$, after verifying that adoption of Yoon and Flory's Monte Carlo results for $S(Q,0)$[28] leads to very modest differences in $t_{1/2}$, as also observed in the first paper of this series.[19]) For the sake of comparison plots of τ_Q are also reported in Figure 5, although they coincide with those obtained with $\tau_0 = 0$ for the reasons stated above. It is apparent from the figure that both characteristic times, $t_{1/2}$ and τ_Q, obey the simple power law

$$\text{time} \times Q^{\beta} = \text{constant} \tag{44}$$

as was also the case in the absence of internal viscosity.[19] The numerical values of β for $t_{1/2}$ and τ_Q are reported in Table I for both the coherent and the incoherent cases; the values obtained for $\tau_0 = 0$[19] are also given for comparison. A decrease of roughly 0.5 unit in the exponent for $t_{1/2}$ is

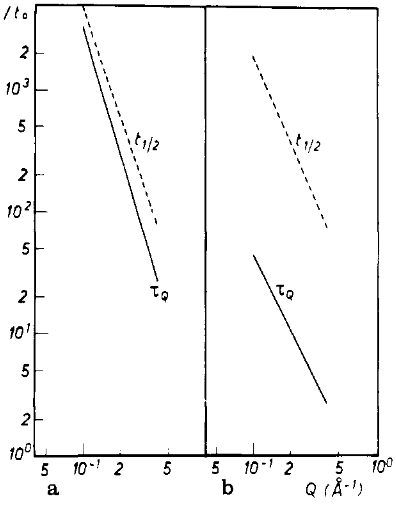

Figure 5. Half-peak time widths ($t_{1/2}$) and incipient decay times (τ_Q; see eq 43) plotted vs. Q for (a) the coherent and (b) the incoherent dynamic structure factors.

Table I
Values of β for the Characteristic Times (See Eq 44, $0.1 \leqslant Q \leqslant 0.4$ Å^{-1}) with and without Internal Viscosity (See Also Ref 19)

	$\tau_0 = 0$	$\tau_0 = 46.7t_0$
$t_{1/2}$ (coherent scattering)	3.2	2.8
τ_Q (coherent scattering)	3.6	3.6
$t_{1/2}$ (incoherent scattering)	3.1	2.4
τ_Q (incoherent scattering)	2.0	2.0

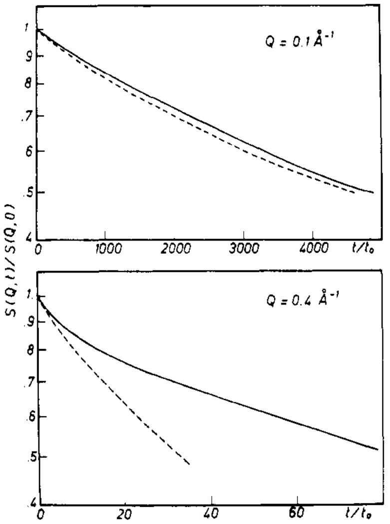

Figure 6. Coherent dynamic structure factor (see eq 39) vs. t for the two extremes of the Q range under investigation (i.e., $0.1 \le Q \le 0.4$ Å^{-1}; continuous lines with $\tau_0 = 46.7t_0$, dashed lines with $\tau_0 = 0$).

induced by the internal viscosity, the average value being 2.6. It may be worth recalling that a value of 2.67 (=8/3) was predicted by us for a very rigid chain (incoherent case[19]), which further illustrates at a qualitative level that the internal viscosity effect is similar to that expected for an increased elastic stiffness. (Values of β between 2.4 and 2.8, obtained in a Q range partially overlapping with that considered here, have indeed been recently obtained for poly(tetrahydrofuran) and polystyrene, and the decrease from the value of 3 observed for poly(dimethylsiloxane) was attributed to chain stiffness.[29]) However, it is important to recall that the ratio τ_0/t_0 adopted by us was derived from the experimental results obtained by Schrag, Ferry, and co-workers on polystyrene solutions[6,7] and that the corresponding ratio for polyethylene should be smaller. In fact, the decrease of τ_0 due to the absence of steric interference between phenyl groups should be much larger than the decrease in ζ (and therefore in t_0; see eq 26) due to the reduction in the linear size of the monomer units; as a consequence, the ratio τ_0/t_0 should diminish. In conclusion, the actual effect of internal viscosity on polyethylene chains should be smaller than that evidenced by the present exploratory results, and β should be closer to 3. Therefore the basic conclusion arrived at in our earlier paper[19] is confirmed "a fortiori"; i.e., there is no need to invoke the hydrodynamic interaction effect to explain an experimental value of β equal to, or even lower than, 3.

The deviation of $S(Q,t)$ from a simple time exponential is further enhanced by internal viscosity, as illustrated in the plots reported in Figure 6. (The initial slope $-S(Q,0)/\tau_Q$ is insensitive to internal viscosity; cf. comments to eq 43.) The effect is largest when $t_{1/2}$ is close to τ_0. As an example, for $Q = 0.4$ the ratio $t_{1/2}/\tau_Q$ is 6.4 instead of 2.5 for $\tau_0 = 0$ (the ratio should be 0.7 for a simple exponential). Even larger ratios are observed in the case of incoherent scattering; see Figure 5b. These results are obviously related to the existence of the two branches of relaxation times reported in Figure 1. The lower branch essentially coincides over a large q range with the shortest relaxation times to be expected for $\tau_0 = 0$, which explains why the initial relaxation is independent of internal viscosity. On the other hand, around τ_0 there is a particularly high density of the normal mode relaxation times, which explains why the internal viscosity effect is especially strong when the time of observation is close to τ_0.

Concluding Remarks

The message of this work is that there can be no instantaneous long-range transmission of tensile force in a soft system like a coiled polymer chain. As a consequence, conformational diffusion along the chain comes into play, and this is where the internal viscosity originates.

The basic effects produced by internal viscosity upon the relaxation mechanism are as follows: (i) each normal mode contains two different relaxation times; (ii) each relaxation term contains an oscillatory factor producing a damped traveling wave (see eq 21 and Figure 1); (iii) the internal viscosity contributes to the longer relaxation times by an amount that increases with q. Point iii may be illustrated with reference to Figure 1, where the internal viscosity effect is roughly identifiable with the difference $\tau_1(q) - \tau(q)$. For small q values ($\lesssim 3 \times 10^{-2}\pi$), $\tau_1(q)$ is virtually coincident with $\bar{\tau}(q)$ (see eq 37, 37′, and 42) and we may write

$$\tau_1(q) - \tau(q) \simeq \bar{\tau}(q) - \tau(q) = \frac{8}{9}\alpha(q)\frac{\tau_0^2}{\zeta(q)}(1 + \cos q) \qquad (45)$$

The above result, assumed to be proportional to q in the classical Cerf–Peterlin theory,[4,5] is rapidly increasing with q with the present theory as well, at least referring to the free-draining case (i.e., $\zeta(q)$ = constant); in fact, for our polyethylene chain $\alpha(q)$ changes as $1 - 0.984 \cos q$ (see eq 13 and 14). (It is possible to show that there would be an increase with the hydrodynamic interaction as well, provided $q \gtrsim 3 \times 10^{-2}\pi$.) It is apparent from Figure 1 that even for $q > 3 \times 10^{-2}\pi$ the difference $\tau_1(q) - \tau(q)$ is still increasing; the *relative* effect of the internal viscosity may be expressed as $[\tau_1(q)/\tau(q)] - 1$, which is at a maximum for $q = \pi/2$, changing with an approximately linear law in the range $0.1 \le q \le 0.35$. This result is analogous to that found by Adelman and Freed,[15] although the linear angular range is about twice as large in their case and their maximum is at $q = \pi$.

Even in the ideal case where the external friction vanishes, the internal viscosity provides a Rouse-like spectrum of the relaxation times proportional to τ_0 (see eq 25a). Although for a complete discussion of chain dynamics in the gas state the inertia terms should also be taken into account explicitly, we believe the above conclusion is basically in agreement with the Monte Carlo results obtained by Verdier and Stockmayer.[30] These authors show that the relaxation of a linear chain occurring via a series of stochastic conformational jumps must essentially conform to the Rouse predictions. On the other hand, these conclusions should not be modified, whether these jumps are triggered by the Brownian forces exerted by the solvent or by force oscillations induced by the chain thermal motion itself. In contrast, the simpler molecular model proposed by Van Beek and Hermans,[31] Bazua and Williams,[12] and MacInnes[11] leads to a flat spectrum of relaxation times for $\zeta \to 0$. Vanishing relaxation times are found in this limit within the mode–mode coupling approach,[15] although here the dynamic effects related to the rotations around skeletal bonds are explicitly disregarded.

In conclusion, although we do not exclude that the mode coupling which results from anharmonicity of the intramolecular potentials may be relevant for a complete description of chain dynamics, we believe that hindrance to skeletal rotations is the major source of those experimental facts usually ascribed to internal viscosity. It is not clear whether its effect, as accounted for within our approach, is fully encompassed by the Kirkwood diffusion equation.[32] However, it is worth pointing out that we also predict the independence of the incipient relaxation mechanism from internal viscosity, in agreement with Fixman's results from computer dynamical simulation of chains with rotational barriers, performed according to the above equation.[17] Incidentally, Fixman finds an activation-type dependence of the rate constant from the barrier height (see eq 2) and confirms the relatively small effect of chain connectivity on the rotational transitions, in agreement with Helfand's theoretical investigations.[33] This demonstrates that the assumption of crankshaft-like rotations previously made by one of us[13] is probably incorrect.

Approximately extending to (atactic) polystyrene the configurational properties of polyethylene, we have reproduced some basic features of its complex modulus in dilute solution for $\omega < \tau_0^{-1}$. Since it turns out that the curves reported in Figures 2 and 3 depend quadratically on τ_0/t_0 (see eq 37), our choice for this ratio ($\sim$50) should be relatively accurate. (In fact, relatively small changes entail big differences, as shown by the dashed and dotted line curves reported in Figure 3.) For a solvent viscosity $\eta_s = 1$ P, the friction constant per skeletal atom should be[5] around $\sim 10^{-6}$ g s^{-1}; then t_0 (eq 26) is $\sim 0.4 \times 10^{-8}$ s and $\tau_0 \sim 2 \times 10^{-7}$ s. It is interesting that Matsuo et al., from nuclear relaxation experiments on polystyrene in benzene and $CHCl_3$ ($\eta_s \sim 10^{-2}$ P), found a distribution of relaxation times around 10^{-9} s.[34] This value agrees with the τ_0 value if the proportionality between τ_0 and η_s is assumed,[32] in agreement with Kramers's kinetic theory in the diffusive limit[35] and also with the experimental conclusions of the Wisconsin group,[6-8] which undoubtedly apply to the present approach as well. The existence of a range of rotational relaxation times, instead of a unique value, as assumed by us, might explain the discrepancies from calculations and experiments observable in Figure 3 as ω approaches τ_0^{-1}.

Acknowledgment. We gratefully acknowledge many helpful discussions with Dr. Giorgio Ronca. We are entirely indebted to him for the analytical treatment of hydrodynamic interaction. We also warmly thank one anonymous Referee for useful suggestions. This work was supported by the Research Contribution of Consiglio Nazionale delle Ricerche (Grant No. CT 78.00939.03).

Appendix I. Hydrodynamic Interaction—Ronca's Treatment[25]

Let us denote by $\mathbf{F}(k,t)$ the hydrodynamic force exerted by the solvent on the kth skeletal atom. From Oseen's formula[26] we obtain

$$\mathbf{F}(k,t) = -\zeta[\dot{\mathbf{r}}(k,t) - \mathbf{v}^{(0)}(k,t)] - \zeta \sum_{m=1}^{N}{}' \mathbf{T}(k,m,t)\mathbf{F}(m,t) \tag{I-1}$$

where $\sum'$ means that $m = k$ must be excluded from the summation. $\dot{\mathbf{r}}(k,t)$ is the velocity of the kth atom, $\mathbf{v}^{(0)}(k,t)$ gives the solvent velocity in the position occupied by the kth atom *if the chain were absent*, while $\mathbf{T}$ is the usual Oseen tensor. If the chain motion is slow enough, or if its amplitude is small, this tensor can be preaveraged over the chain unperturbed configurations[26] to obtain

$$\langle \mathbf{T}(k,m) \rangle = T_0(k - m)\cdot\mathbf{E} \tag{I-2}$$

where $\mathbf{E}$ is the unit matrix and $T_0(k - m) = (6\pi\eta_s)^{-1}\langle r_{km}^{-1}\rangle$, η_s being the solvent viscosity and r_{km} the distance between the kth and mth atoms. Consequently, in eq I-1 $\mathbf{T}(k,m,t)$ will be substituted by the average given by (I-2). Then, multiplying both sides of (I-1) by e^{iqk} and summing over k from 1 to N (cf. eq 9), we get

$$\mathbf{F}'(q,t) = -\frac{\zeta}{1 + \zeta T_0'(q)}[\dot{\mathbf{r}}'(q,t) - \mathbf{v}^{(0)\prime}(q,t)] \tag{I-3}$$

where

$$\begin{aligned} \mathbf{r}'(q,t) &= \sum_{k=1}^{N} \mathbf{r}(k,t)e^{iqk} \\ T_0'(q) &= \frac{1}{6\pi\eta_s} \sum_{k=1}^{N} \cos(qk)\left\langle \frac{1}{r_k} \right\rangle \end{aligned} \tag{I-4}$$

and r_k denotes the distance between two atoms separated by k chain bonds. We will assume the following: (i) the chain may be considered as infinitely long and connected ringwise; (ii) the probability distribution for r_k is Gaussian with a mean-square value $\langle r_k^2\rangle_c = C(0)l^2k(N - k)/N$ (the subscript c stands for "connected ringwise"), which is correct only for both k and $N - k$ very large. Under these assumptions we have

$$\left\langle \frac{1}{r_k} \right\rangle = \frac{6^{1/2}}{[\pi C(0)]^{1/2} l |k(1 - k/N)|^{1/2}} \tag{I-5}$$

and according to Bloomfield and Zimm[36] we have from (I-4)

$$T_0'(q) = (h_0/\zeta)N^{1/2} \cos(qN/2) J_0(qN/2) \tag{I-6}$$

where $J_0(x)$ is the Bessel function of order zero, while h_0 is the coefficient of hydrodynamic interaction defined as

$$h_0 = \zeta/\{[6C(0)]^{1/2}\pi^{3/2}\eta_s l\} \tag{I-7}$$

We may now write (I-3) in the following form:

$$\mathbf{F}'(q,t) = -\zeta(q)\cdot[\dot{\mathbf{r}}'(q,t) - \mathbf{v}^{(0)\prime}(q,t)] \tag{I-8}$$

where (see I-6)

$$\zeta(q) = \frac{\zeta}{1 + \zeta T_0'(q)} = \frac{\zeta}{1 + h_0 N^{1/2}\pi \cos(qN/2) J_0(qN/2)} \tag{I-9}$$

In conclusion, we obtain the remarkable result that the effect of hydrodynamic interaction may be simply accounted for by substituting ζ with $\zeta(q)$ in all the normal mode equations valid for the free-draining model.[25]

Appendix II. Fluctuation–Dissipation Theorem

Let us first write eq 15 in the form

$$2\alpha(q)(1 - \cos q)x'(q,t) + \zeta\dot{x}'(q,t) + \int_{-\infty}^{t} \eta'(q,t - \tau)\dot{x}'(q,\tau)\,\mathrm{d}\tau = X'(q,t) \tag{II-1}$$

where

$$\eta'(q,t) = +\tfrac{4}{3}i\alpha(q) \sin q e^{-t/\tau_0} \quad (t \geq 0) \tag{II-2}$$

$$(\eta'(q,t) \equiv 0 \text{ for } t < 0)$$

The random force $X'(q,t)$ is related with the terms containing $\dot{x}'(q,t)$ by the fluctuation–dissipation theorem,[24]

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which will be conveniently written in the following form:

$$\langle X'(q,t)X^{*\prime}(q',0)\rangle = \langle X'(q,t+t')X^{*\prime}(q',t')\rangle = Nk_BT\{2\zeta\delta(t) + \eta'(q,t) + \eta^{*\prime}(q,-t)\}\Delta(q-q') \quad \text{(II-3)}$$

where δ and Δ stand for the Dirac delta function and for the Kronecker delta, respectively. The above representation differs from the currently employed only in view of the term $\eta^{*\prime}(q,-t)$. This contribution was added to fulfil the symmetry property

$$g(q,t) = \langle X'(q,t)X^{*\prime}(q,0)\rangle = \langle X'(q,0)X^{*\prime}(q,-t)\rangle = g^*(q,-t) \quad \text{(II-4)}$$

otherwise no substantial change is implied, since $\eta^{*\prime}(q,-t) \equiv 0$ for $t > 0$ (see eq II-2). Multiplying the second and third members of eq II-3 by $\exp[+i\omega(t+t') - i\omega'(t')]$ and integrating over both t and t', we get

$$\langle X''(q,\omega)X^{*\prime\prime}(q',\omega')\rangle = \frac{Nk_BT}{\pi}\left(\zeta - {}^4\!/_3\alpha(q)\sin q\frac{\omega\tau_0^{\,2}}{1+\omega^2\tau_0^{\,2}}\right)\Delta(q-q')\delta(\omega-\omega')$$

$$(X^{*\prime\prime}(q,\omega) = X''(-q,-\omega)) \quad \text{(II-5)}$$

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Polystyrene Dynamics in Dilute Solution: A Further Investigation by Electron Spin Resonance. Comparison with Other Techniques

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ABSTRACT: ESR relaxation measurements were carried out on dilute solutions of in-chain spin-labeled polystyrene in toluene in the temperature range 0–90 °C. There was some evidence for two different relaxation processes, in agreement with the "phase transition" observed at about 50 °C by several authors using different experimental techniques. Energy barriers to rotation were obtained after allowance was made for the viscous drag of the solvent, and the number of monomer units involved in each relaxation process was calculated by employing Kramers' rate constant for the crankshaft rotation and a three-state model. From comparison with results reported in the literature for local motion in polystyrene, differences have been shown to arise through both the internal barrier to rotation and the preexponential term.

Introduction

Studies of intramolecular motion of polystyrene in dilute solution have been carried out by several groups using ^{1}H,[1-4] ^{2}H,[2,5] and ^{13}C[3,6-15] nuclear magnetic relaxation, fluorescence depolarization,[16,17] Rayleigh scattering depolarization,[18-20] Raman line shape analysis,[21,22] and ultrasonic relaxation.[23-27] These measurements have clearly demonstrated the local character of the motions involved in the relaxation processes whose correlation time is independent of the molecular weight above a critical value of 10 000.

The single isotropic correlation theory was found inadequate to interpret the NMR[3,4,14] and fluorescence depolarization[16,17] data. On the other hand, the three-bond jump model for diamond lattice chains[28] has been proven to be successful in the description of the segmental reorientation of the chain backbone in terms of two correlation times. Ultrasonic absorption experiments have also