Dynamics of polymer molecules: a comparison of strongly coupled correlated (internal viscosity) and non-correlated (local mode) models for molecular weight independent conformational relaxation

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Two models have been examined for the dynamics of the molecular weight independent high frequency relaxation process in dilute polymer solutions. One is based on uncorrelated local motions of some undefined chain segments. The other is associated with cooperative motions of the whole chain. Both models have similar origins in molecular bond rotational potentials, and have a strong similarity in the broad features of their predictions or applicability to experimental observations. However the model of cooperative motions involves fewer independent assumptions, and provides a more quantitative framework for self-consistent explanation and prediction of relaxation parameters. In this way it seems to provide the more satisfactory description, at least in the case of polystyrene solutions.

INTRODUCTION

A number of different ultrasonic (u.r.), dielectric (d.r.) and nuclear magnetic (n.m.r.) relaxation observations of dilute polymer solutions have indicated the existence of a process which is associated with a change in the shape (conformation) of the polymer chain, and which is characterized by a molecular weight independent relaxation time. In general, it has been customary to assign this process to some movement of a localized segment of the polymer chain, and to refer to the motion as a segmental or local mode. This has been done because the observed relaxation times are much shorter than those characterizing the cooperative motions of large sections of the chain (such as the Rouse–Zimm normal modes) and do not exhibit the characteristic molecular weight dependence of such modes.

The implication in such a description has been that the movement of any small section of the macromolecule is independent (at least in phase) of the movement of any other similar section, and so is uncorrelated along the whole chain length. Such a mode of motion has usually been seen as different from, although compatible with[1], the correlated long wavelength modes.

However this model of uncorrelated or independent motions is not the only interpretation of the experimental observations. Recently it has been shown[2] that a consideration of polymer chain dynamics based upon strongly coupled (cooperative) modes of motion[3] can result in a viscoelastic relaxation spectrum containing both low frequency molecular weight dependent modes and also modes associated with a molecular weight independent peak in the relaxation time spectrum. An important aspect of this model is the role of internal viscosity[4–6] in opposing changes in chain conformation and in providing the inter-segment coupling.

The predictions of this internal viscosity model for viscoelastic relaxation bear a strong qualitative resemblance to the other relaxation observations referred to above, and raise the question as to whether the high frequency molecular weight-independent process is better described as an uncooperative localized movement of some segment or rotor (the uncoupled local mode or *LM* model), or as a cooperative motion of short wavelength (the internal viscosity or *IV* model). Since the dimensions of the 'segment' and the 'wavelength' may be comparable, the difference in the models relates to questions of phase and coupling, rather than to the distances involved in the movement.

Since both models predict relaxation spectra with broadly similar features, and have a common basis in conformational rearrangement opposed by covalent bond rotation potentials, it is difficult to distinguish which might be more realistic. However there are differences in detail. With this in mind we have examined critically the ability of each model to describe the details of the high frequency process in much studied[7–9] dilute solutions of styrene polymers.

UNSATISFACTORY FEATURES OF THE 'LOCAL MODE' MODEL

In general terms, the *LM* model avoids the difficulty of formulating a molecular or mathematical description of the detailed movement involved by ascribing it to some undefined segmental process. This is simply assumed to have any characteristics necessary for the interpretation of

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molecular relaxation processes (e.g. rotation of a reference dipole interacting weakly with a small number of neighbouring dipoles in dielectric relaxation or interchange between two states of different enthalpy, entropy and volume in ultrasonic relaxation). In this way a large variety of requirements are accommodated within the scope of imprecise definition.

Coexistence with the Rouse–Zimm model

A significant unsatisfactory feature of the *LM* model is that the observed relaxation occurs at frequencies below those corresponding to the lowest wavelength Rouse–Zimm modes. Thus for polystyrene of molecular weight 2.5×10^5 at 303K, the Rouse–Zimm spectrum extends[10] from a first mode at about 50 kHz to a mode (for a Gaussian equivalent segment of 10 styrene units) at 3 GHz, whereas the observed molecular weight independent mode occurs at 20 MHz. The use of Occam's razor would find a single explanation encompassing a smooth transition from the low to the high frequency behaviour, and so describing the way in which the Rouse-Zimm model becomes inapplicable at high frequencies. In this context we note that an internal viscosity large enough to give the narrowing[11] of the Rouse–Zimm spectrum required in the *LM* model, would also be large enough to give a peak[3,6] in the high frequency relaxation time spectrum as described in the *IV* model.

Near-ideality of the molecular weight independent process

Careful analysis of dilute solution dielectric and ultrasonic relaxation data[7,8,12] reveals that the absorption is nearly ideal. It is difficult to see why a series of independent arbitrary rotors should not give rise to a spectrum of relaxation times rather than to phenomena capable of interpretation as two state (ultrasonic) or single dipole (dielectric) processes.

High frequency viscoelastic relaxation

There is now considerable evidence that the dynamic viscosity of dilute polystyrene solutions shows a relaxation in the same high frequency region as the dielectric and ultrasonic relaxations. The viscosity effect can be explained[2] by the introduction of a mode dependent friction constant derived[5,6] in a logical fashion from the concept of internal viscosity. However the simple motions implied in the *LM* model do not contain any comparable built-in common origin for viscous and other relaxation losses.

The role of solvent viscosity

The ultrasonic relaxation time appears[13,14] to change from being dependent on, to being independent of solvent viscosity over a certain viscosity range. An explanation[14] in terms of the *LM* model has involved the coexistence of two types of local mode (solvent viscosity dependent and solvent viscosity independent) which have differing activities in the ultrasonic and viscoelastic phenomena.

Residual molecular weight dependence

For molecular weights below a critical value the relaxation times decrease as molecular weight decreases[7,8]. The *LM* model provides no satisfactory means of predicting either the critical molecular weight or the observed time–molecular weight dependence. The qualitative explanations of whole molecule rotation in the dielectric case and enhanced end-group flexibility in the ultrasonic case seem too disparate to match comfortably the remarkably similar experimental findings.

POSSIBLE IMPROVEMENTS OFFERED BY THE INTERNAL VISCOSITY MODEL

The mathematical derivation of this model, and the significance of internal viscosity within it, have been published previously[2,3,6]. The basic equation governing the rate of conformational arrangements of a single chain is:

$$\zeta_s \dot{\mathbf{R}}(s, t) - \zeta_I \frac{\partial^2}{\partial s^2} \dot{\mathbf{R}}(s, t) - \epsilon \frac{\partial^2}{\partial s^2} \dot{\mathbf{R}}(s, t) = \phi(s, t) \qquad (1)$$

where ζ_s, ζ_I and ϵ are constants, $\mathbf{R}(s, t)$ is the position vector at time t, of an element of chain labelled s, and $\phi(s, t)$ is the Langevin 'random' force. Throughout hydrodynamic and excluded volumes are ignored. Equation (1) gives rise to the relaxation spectrum:

$$\tau_j = [\zeta_s + \zeta_I(\pi^2 j^2/N^2)]/\epsilon(\pi^2 j^2/N^2) \qquad (2)$$

where N is the number of repeat units in the chain. Clearly if there exists a value of $j = j_0$ ($\ll N$) such that:

$$\zeta_I(\pi^2 j^2/N^2) \gg \zeta_s \text{ for } j > j_0$$

τ_j will be roughly independent of j for this range of j and will satisfy:

$$\tau_j = \zeta_I/\epsilon; \quad j > j_0 \qquad (3)$$

This implies that a number of polymer modes will have relaxation times clustered around $\tau = \zeta_I/\epsilon$ which constitutes a peak in the relaxation time spectrum.

When the relaxation times are spaced sufficiently closely to be treated as a continuous function of mode number, the density of states (corrected for an earlier[3] error) is given by:

$$n(\omega) = \left(\frac{\epsilon L}{\pi}\right)\left(\frac{\zeta_s}{\omega}\right)^{1/2}(\epsilon - \omega\zeta_I)^{-3/2} \qquad (4)$$

Here $n(\omega)$ is the number of modes with inverse relaxation time ω. As ω increases from a small value $n(\omega)$ clearly decreases, passes though a minimum (at $\omega = \epsilon/2\zeta_I$, as can easily be verified by differentiation) and then has a peak at $\omega = \epsilon/\zeta_I$. It is this peak in the density of states that provides the alternative explanation to the high frequency relaxation.

Coexistence with the Rouse–Zimm model

Since both the low and the high frequency modes are derived on the same mathematical model, there is no 'discontinuity' in the explanations offered for the different extremities of the relaxation spectrum, and there is no artificial compression of one spectrum to avoid overlap with another. Despite the considerable work[13,14] relating the Rouse–Zimm model with internal viscosity to a superposition of local transitions, the actual derivation of a mode dependent friction constant is still missing in the *LM* model, whereas the *IV* model establishes the derivation on more general considerations[5,6].

Near-ideality of the relaxation process

Whereas in the *LM* model it is not at all possible to predict any form of distribution function, in the *IV* model this is described in the distribution of modes around the peak in the density of states function. Unfortunately complete quantitative description requires knowledge of both the number of modes within the peak and the weighting factors for mode activity in the phenomenon involved. Since, at the present time, these can be introduced only as empirical parameters, we have replaced the *'a posteriori'* empiricalism of one model by a framework which allows *'a priori'* evaluation in principle but not in practice.

High frequency viscoelastic relaxation

The fundamental basis of the *IV* model results in a natural coincidence of the high frequency relaxation modes in the dielectric, ultrasonic and viscoelastic phenomena. It must be stressed that, while the *IV* model produces this coincidence in the time/frequency dimension, the relative absorption amplitudes still remain a function of the undetermined mode weighting factors.

The role of solvent viscosity

The complex dependence on solvent viscosity follows automatically from the relative importance of internal and solvent-derived friction factors. For low solvent viscosity the internal viscosity is independent of solvent viscosity, but increases linearly at high solvent viscosity[5,6,14,15]. Since the relaxation time of the peak is ζ_I/ϵ, ϵ is an elastic constant (independent of solvent viscosity) and ζ_I is the internal viscosity friction coefficient, the viscosity dependence of any observed relaxation can be described quantitatively in terms of well established parameters.

Residual molecular weight dependence

The *IV* model can describe, in a self-consistent but semi-quantitative manner, the observed molecular weight dependence. The description is not yet fully quantitative because, to produce a complete theory of dielectric or ultrasonic relaxation the response (or mode weighting) part of the problem must be superimposed on the frequency part. Selecting ultrasonic relaxation as an example, we write for the absorption:

$$\frac{A(f)}{f^2} = \rho \sum_{j=1}^{N} A_j\tau_j/(1 + f^2\tau_j^2) \tag{5}$$

where $A(f)$ is absorption at frequency f, A_j is the weighting factor of the jth mode and ρ is the number density of polymer molecules. Following an earlier paper[2] we introduce the upper critical length (*ucl*) and lower critical level (*lcl*) for a given polymer fluid. The *ucl* is defined as the number of units in a polymer for which the first normal mode has a relaxation time $2\zeta_I/\epsilon$. This essentially defines the critical length above which the peak region is fully formed and the corresponding relaxation frequency is molecular weight independent. The *lcl* is defined as the minimum polymer size such that equation (1) does not provide an accurate description of even the first normal mode (i.e. the *lcl* corresponds in concept to the Gaussian subunit). The quantities j_{ucl} and j_{lcl} correspond to the mode numbers with half wavelengths corresponding to these critical lengths. As before we rewrite equation (5) as:

$$\frac{A(f)}{f^2} = \rho \left[\sum_{j=1}^{j=j_{ucl}} A_j\tau_j/(1 + f^2\tau_j^2) + \sum_{j=j_{ucl}}^{j=j_{lcl}} A_j\tau_j/(1 + f^2\tau_j^2) + \sum_{j=j_{lcl}}^{j=N} A_j\tau_j/(1 + f^2\tau_j^2) \right] \tag{6}$$

This gives the acoustic absorption of all modes. We are primarily interested in that absorption associated with the peak, so:

$$\frac{A_{\text{u.r.}}(f)}{f^2} = \rho \sum_{j=j_{ucl}}^{j=j_{lcl}} A_j\tau_j/(1 + f^2\tau_j^2) \tag{7}$$

We neglect as before[2], the third term on the r.h.s. of equation (6). Its inclusion makes little difference to the analysis. For chains sufficiently long that $j_{ucl} \gg 1$, $\tau_j(j_{ucl} \leqslant j \leqslant j_{lcl})$ will be independent of molecular weight and we expect $A_j(j_{ucl} \leqslant j \leqslant j_{lcl})$ to be similarly independent of M (this is immediately true[2] for viscoelastic absorption since $A_j \equiv 1$ for all $j < j_{lcl}$). The number of modes with mode number between j_{ucl} and j_{lcl} increases and, at constant concentrations, ρ decreases linearly with increasing molecular weight. Thus, for such molecular weight that $j_{ucl} \gg 1$, we expect $A_{\text{u.r.}}(f)/f^2$ and its relaxation time to be independent of molecular weight. However if the chain length is sufficiently small that $\tau_1 < 2\zeta_I/\epsilon$ then the longest relaxation time in the peak region, (i.e. those with relaxation times $\simeq 2\zeta_I/\epsilon$) will have been removed from the peak. Since the observed relaxation time will be the weighted average over the peak region, removing the longest relaxation times from this average may be expected to decrease its value.

It is interesting to note, and is characteristic of the similarity of the concepts underlying both models, that the molecular weight dependence in both arises from essentially the same source, i.e. the macromolecule being sufficiently short that the longest relaxation time becomes comparable with the high frequency process relaxation time.

The *IV* model then makes the simple but important prediction that the critical chain length, L_c, (molecular weight M_c) at which the high frequency relaxation parameters become molecular weight independent is that value when the *first* normal mode has a relaxation time, $2\zeta_I/\epsilon$. We take $\tau_p = \zeta_I/\epsilon$ to be the observed acoustic relaxation time. Thus:

$$\left(\zeta_s + \zeta_I \frac{\pi^2}{L_c^2}\right) \Big/ \epsilon \frac{\pi^2}{L_c^2} = 2\zeta_I/\epsilon = 2\tau_p$$

so

$$\tau_p = \zeta_s \Big/ \left(\frac{\epsilon\pi^2}{L_c^2}\right) \tag{8}$$

where L_c is also the length corresponding to the *ucl*. If we choose a molecule sufficiently long that $\zeta_s \gg \zeta_I(\pi^2/L^2)$ then its first normal mode will have a relaxation time τ_1 such that:

$$\tau_1' = \zeta_s \Bigg/ \left(\frac{\epsilon\pi^2}{L^2}\right) \tag{9}$$

where L is the length of this polymer. Combining equations (8) and (9) gives:

$$L_c = L(\tau_p/\tau_1')^{1/2}$$

or

$$M_c = M(\tau_p/\tau_1')^{1/2} \tag{10}$$

Thus M_c can easily be found if we know the acoustic relaxation time (for $M > M_c$) and the first normal mode relaxation time for a polymer with $M \gg M_c$.

This represents a very significant advance over the *LM* model, since it offers a new prediction which can be tested against experimental observation. For polystyrene in toluene at 303K, $M = 2.5 \times 10^5$, $M \gg M_c$, so $\zeta_I(\pi^2/L^2) \ll \zeta_s$. The reciprocal first normal mode relaxation time is 50 kHz, the reciprocal high frequency acoustic relaxation time is 20 MHz, and so equation (10) gives directly and simply:

$$M_c \simeq 12\,500$$

The observed value of ~15 000 must be regarded as strong justification of the model, and its assumption that the low frequency normal mode and high frequency acoustic processes have a common origin. The *LM* model, by expressly severing any connection between the two frequency regions, cannot predict a quantitative relationship between them (compare with equation 10).

Physical basis of the IV *model*

The assumptions on which the *IV* model is based are as follows: (a) There exists in the chain an entropic spring restoring force. This concept is well tested in polymer science, and holds as well in solution as in rubber-like solids. (b) The molecular interactions, other than those rigid bond forces giving rise to the entropic force above, can be represented by dissipative forces. It is an accepted idea in statistical physics that a fluctuating force, which has no correlations after a time short on a molecular scale, gives rise to a dissipative resistance. This is the basis of the Langevin equation and other stochastic models of molecular dynamics.

In the polymer case there are two types of fluctuating force – one deriving from polymer–solvent interactions and the other from intrachain bond rotational potentials. The *IV* model represents both of these as dissipative mechanisms, the principal difference being that the polymer–solvent dissipation is isotropic, whereas the bond rotational forces dissipate energy linearly along the chain, and so give rise to a force opposing changes in the curvature of the chain.

This basis is to be compared with the specific assumption of the *LM* model that the motion of a polymer is a superposition of independent local conformational transitions, in which the high frequency absorption process is attributed to a particular transition.

CONCLUSION

We have discussed two models for the dynamics of the high frequency molecular weight independent relaxations observed in polymer solutions. Both start from a consideration of bond rotations hindered by interatomic potentials. However in one case all conceptual difficulties are swept aside into a hypothetical segment having all required properties and moving as an independent entity, whereas in the other a formal treatment through internal viscosity establishes a description of correlated high frequency normal modes. In general the *IV* model involves fewer unrelated assumptions, is more clearly self consistent between different relaxation phenomena, and offers quantitative predictions (such as the critical molecular weight) in a way that the *LM* model does not. Despite the fact that the problem of the mode response weighting factor remains unsolved, and that the mathematics of the model contain certain assumptions (which do appear reasonable), at the present time the *IV* model of correlated motions appears to offer a more consistent picture of molecular chain dynamics than the more qualitative model involving undefined correlated chain segments. Clearly a final decision on the importance of correlation in high frequency chain movements awaits study of other polymer systems, and the relating of response functions to known bond rotational potentials.

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