Linear Viscoelasticity Revisited: The Relaxation Function of Monodisperse Polymer Melts

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ABSTRACT: The linear viscoelastic properties of linear polymers may be calculated from the models of molecular dynamics derived from the reptation concept. The paper presents an analytical form of the complex shear modulus integrating the various relaxation processes of linear flexible chains over a wide range of time or frequencies covering the terminal relaxation region up to the glassy behavior. The model may be easily translated from one polymer species to another, and model predictions are compared with the experimental data for various polymers: polystyrene, polybutadiene, and poly(methyl methacrylate).

1. Introduction

The understanding of the relationship between the rheological properties of polymers and their molecular structure has considerably improved in the past few years with the interest of physicists in the matter and particularly with the development of molecular dynamics theories. The reptation concept may be used to derive precisely the main features of the peculiar viscoelastic behavior of long and flexible chains. Besides the academic interest of molecular theories relating molecular dynamics to the macroscopic viscoelastic behavior, the fine description of the structure/property relationships is of the upmost importance for the polymer industry, as the processing as well as final properties of polymers are directly governed by their rheological behavior. Besides, rheological measurements (and especially mechanical spectroscopy) are used now as an analytical tool of polymer characterization, and a lot of effort is spent for example to derive the molecular weight distribution of polymers from their linear viscoelastic properties. The basic de Gennes/Doi–Edwards reptation model and its various improvements (fluctuations of tube length, constraint release, etc.) give a reasonable picture of the main trends of viscoelastic properties as a function of chain length for monodisperse species. Furthermore, the concept of tube renewal (or constraint release) gives a reasonable picture of the effects of polydispersity, and we are now to the point where it is possible to calculate the linear viscoelastic properties of a linear commercial polymer from its molecular weight distribution with a reasonable accuracy. Furthermore, the kernel of constitutive equations of nonlinear viscoelasticity is generally made of one material function of linear viscoelasticity: relaxation function, memory function, or distribution of relaxation times.

However, the basic information needed for these calculations (viscoelastic functions of polydisperse samples, nonlinear behavior) is the knowledge of one linear viscoelastic function (in the widest range possible of times or frequencies) as a function of molecular weight and temperature; in most cases, the "monodisperse behavior" is introduced either as experimental data or in a phenomenological way, the molecular dynamics features being introduced only at the level of some characteristic viscoelastic parameters (i.e., zero-shear viscosity, limiting compliance or plateau modulus) and their respective scaling laws with chain length. We present in this paper a general model integrating in a formal way the various relaxation processes of reptation, plus the transition region to the glassy behavior. The model integrates a distribution of relaxation times for each relaxation process, leading to a complete analytical form of the relaxation function and the complex shear modulus covering a very broad range of times (respectively frequencies) from the glassy region to the terminal relaxation region.

2. Theory

De Gennes[1] presented in 1971 the concept of reptation to describe the diffusion process of a macromolecule in the network formed by the surrounding molecules. Starting from that idea, Doi and Edwards[2] developed in 1978 a theory relating the dynamics of polymer melts to their viscoelastic properties. That model describes the relaxation of a polymeric chain in a highly entangled medium as a sequence of three relaxation processes with a specific time scale:

(i) The first relaxation process A is the Rouse-like relaxation of segments between entanglement points. As the characteristic time τ_A of that relaxation process is quite small compared with the maximum relaxation time, the entanglement points may be considered as fixed in that time scale. The time τ_A is independent of chain length.

(ii) The second relaxation process B corresponds to a retraction of the chain along its tube to recover the equilibrium length; its characteristic time τ_B scales as M^2, M being the chain length (or molecular weight). Hence τ_B is proportional to the Rouse time of the chain.

(iii) The third relaxation process C corresponds to the reptation process itself, and τ_C is proportional to M^3.

If the model does not give the whole story, it certainly pictures the essential of the dynamics of concentrated entangled chains. For example, Tassin and Monnerie[3] have shown a good agreement between the experimental and theoretical exponents related to each relaxation process by infrared dichroism measurements performed on hydrogenated and deuterated polystyrene samples.

As far as the spacing of relaxation times for the A process is concerned, the various authors do agree with a Rouse distribution,[4] τ_A being the maximum time.

There is more concern about the second B process. Ylitalo et al.[5] have shown by birefringence and infrared dichroism measurements that the relaxation of chain ends is faster than the relaxation of segments within the chain. This observation questions the Doi and Edwards hypothesis[2] of uniform retraction within the tube. The fact that this retraction within the tube is a unidimensional process

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may *a priori* reject a Rouse-like distribution.[4] Kavassalis and Noolandi[6] have extended the Rouse model, initially derived for nonentangled polymers, to the case of entangled chains. They show that the relaxation of a polymer chain may be associated with a Rouse model, but their model diverges from the Doi–Edwards model at large times.

The distribution of relaxation times in the terminal region corresponds to the de Gennes/Doi–Edwards model modified by other processes like the fluctuations of tube length proposed by Doi.[7]

One of the first authors who tried to calculate an accurate relaxation function in a large time scale was Lin.[8] So, after giving the complete analytical form of our relaxation function, we will compare it with Lin's model. We will then show that our model allows one to derive with a good accuracy the linear viscoelastic behavior of narrowly distributed chains without any adjustment in a very large frequency (or time) domain, whatever the chemical structure of the polymer.

To build our model, we will use the Doi–Edwards approach that starts from the calculation of the stress tensor $\sigma_{\alpha\beta}$ after a sudden homogeneous deformation E (step strain). We will follow the various relaxation processes and give the distribution of relaxation times (hence the relaxation function $G(t)$) associated with each domain.

2.1. The A Relaxation Process: Rouse Diffusion between Entanglement Points. This relaxation process may be defined as a Rouse diffusion between entanglement points. The characteristic relaxation time of the A process is

$$\tau_{\mathrm{A}} = \frac{1}{6\pi^2}\frac{\zeta_0 b^2}{kT}N_{\mathrm{e}}^{\,2} \tag{1}$$

where N_{e} is the number of monomers between entanglement points, k is Boltzmann's constant, T is the absolute temperature, b is the monomer length, and ζ_0 is the monomeric friction coefficient. The relaxation function associated with the A process is

$$\mu_{\mathrm{A}}(t) = \sum_{p=1}^{n_1} \exp\left(-\frac{tp^2}{\tau_{\mathrm{A}}}\right) \tag{2}$$

where n_1 may be equated to the number of monomers N_{e}; more reasonably, n_1 corresponds to the number of Kuhn segments between entanglements. Hence $n_1 \le N_{\mathrm{e}}$. To define completely the relaxation modulus, we have to determine the initial modulus G'_{N}, so

$$G(t) = G'_{\mathrm{N}}\mu_{\mathrm{A}}(t) \tag{3}$$

G'_{N} is a function of strain and may be written as

$$G'_{\mathrm{N}} = \frac{\rho RT}{M_{\mathrm{e}}}\frac{1}{\langle|Eu|\rangle} \tag{4}$$

where E is the strain tensor, u is a unit vector corresponding to the vector linking two entanglement points (slip-link segment); the $1/\langle|Eu|\rangle$ term expresses the fact that the molecule is outside its equilibrium configuration: from Doi–Edwards $G'_{\mathrm{N}} = (4/5)(\rho RT/M_{\mathrm{e}})$.

We may then write the relaxation modulus corresponding to the A relaxation process (short times) as

$$G(t) = \frac{\rho RT}{M_{\mathrm{e}}}\frac{1}{\langle|Eu|\rangle}\sum_{p=1}^{n_1} \exp\left(-\frac{tp^2}{\tau_{\mathrm{A}}}\right) \tag{5}$$

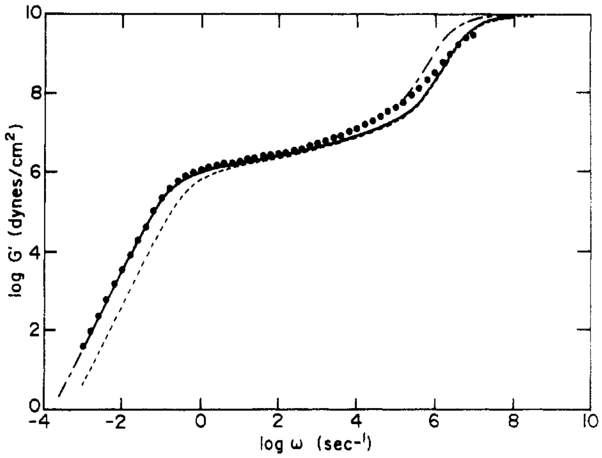

Figure 1. Elastic modulus of polystyrene sample PS 200 at 200 °C: (●) experimental; (—) model (eq 22) including parameter P; (- - -) model with $\tau_0 = 2 \times 10^{-7}$ s; (-·-) model with $\tau_0 = 5.6 \times 10^{-7}$ s.

2.2. The B Relaxation Process. Doi and Edwards postulate that the chain recovers its equilibrium monomer density along its contour by a retraction motion of the chain within the tube. That motion, induced by the chain ends, leads to a relaxation function

$$\mu_{\mathrm{B}}(t) = \sum_{p\ \mathrm{odd}} \frac{8}{p^2\pi^2}\exp\left(-\frac{p^2t}{\tau_{\mathrm{B}}}\right) \tag{6}$$

with

$$\tau_{\mathrm{B}} = \frac{\zeta_0 b^2 N^2 N_{\mathrm{e}}^{\,2}}{3\pi^2 kT} \tag{7}$$

and N the number of entanglements along the chain or the number of segments of the primitive chain.

We found that this function does not fit the experimental data.

Viovy[9] describes that reequilibration process as an exchange of monomers between neighboring segments: he calls that process "reequilibration across slip-links", and the corresponding relaxation function may be written as

$$\mu_{\mathrm{B}}(t) = \sum_{p=1}^{N} \frac{1}{N}\exp\left(-\frac{p^2t}{\tau_{\mathrm{B}}}\right) \tag{8}$$

That function corresponds to a Rouse spacing of relaxation times and gives a better fit of the experimental data. This function has also been used by Cloizeaux[10–12] and Rahalkar[13] to calculate the complex shear modulus $G^*(\omega)$. Hence the relaxation function of the B process may be written as

$$G(t) = \frac{\rho RT}{M_{\mathrm{e}}}\sum_{p=1}^{N} \frac{1}{N}\exp\left(-\frac{p^2t}{\tau_{\mathrm{B}}}\right) \tag{9}$$

2.3. Reptation: Relaxation Process C. In the final relaxation process the molecule recovers its final isotropic configuration by a reptation (snakelike) motion. The characteristic time for the reptation process is

$$\tau_{\mathrm{C}} = \frac{1}{\pi^2}\frac{\zeta_0 a^2 N_{\mathrm{e}}}{kT}N^3 \tag{10}$$

where a is the tube diameter ($a^2 = N_{\mathrm{e}}b^2$).

The relaxation function is given in the original Doi–Edwards picture[2] by the equation

$$\mu_{\mathrm{C}}(t) = \sum_{p\ \mathrm{odd}} \frac{8}{p^2\pi^2}\exp\left(-\frac{p^2t}{\tau_{\mathrm{C}}}\right) \tag{11}$$

The plateau modulus of that relaxation domain is

$$G_{\mathrm{N}} = \frac{\rho RT}{M_{\mathrm{e}}} \tag{12}$$

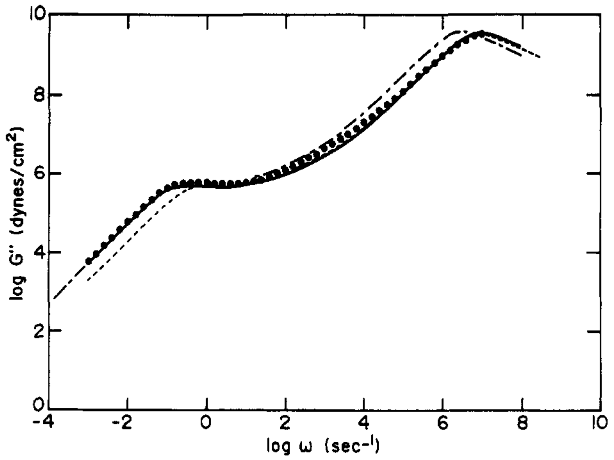

Figure 2. Loss modulus of polystyrene sample PS 200 at 200 °C: (●) experimental; (—) model (eq 22) including parameter *P*; (- - -) model with $\tau_0 = 2 \times 10^{-7}$ s; (-·-) model with $\tau_0 = 5.6 \times 10^{-7}$ s.

Hence the relaxation modulus is

$$G(t) = \frac{\rho RT}{M_e} \sum_{p\ \mathrm{odd}} \frac{8}{p^2\pi^2} \exp\left(-\frac{p^2 t}{\tau_C}\right) \tag{13}$$

The refinement introduced by Doi,[7] who considers tube length fluctuations, is more relevant to experimental scaling laws as far as the viscosity/molecular weight dependence is concerned. Following that concept, $G(t)$ can be cast into the integral form

$$G(t) = \frac{\rho RT}{M_e}\left(\int_0^{2N^{1/2}} \exp\left(-\frac{t}{\tau\xi(1)}\right) \mathrm{d}\xi + \int_{2/N^{1/2}}^{1} \exp\left(-\frac{t}{\tau\xi(2)}\right) \mathrm{d}\xi\right) \tag{14}$$

where

$$\tau\xi(1) = \frac{N\xi^4}{16}\tau_C \qquad \xi < 2/N^{1/2} \tag{15}$$

$$\tau\xi(2) = \left(\xi - \frac{1}{N^{1/2}}\right)^2 \tau_C \qquad 1 > \xi > 2/N^{1/2} \tag{16}$$

2.4. High-Frequency Relaxation Domain: The Transition Region between the Rubbery and Glassy Behaviors. Glöcke and Nonnenmacher[14] have recently proposed an analytical form of the complex shear modulus $G^*_{\mathrm{HF}}(\omega)$ at very high frequencies as

$$G^*_{\mathrm{HF}}(\omega) = \frac{G_{\mathrm{inf}} + G_N[\mathrm{i}\omega\tau_0]^{-\mu}}{1 + [\mathrm{i}\omega\tau_0]^{-q}} \tag{17}$$

where μ and q are adjustable parameters and G_N and G_{inf} are respectively the plateau and glassy moduli. We found that a Cole–Cole or Davidson–Cole equation gives a much better fit in the transition region; we used in the present case a Davidson–Cole equation, which presents the advantages to be truncated at large times and to give analytical forms in both the time and frequency domains:

$$G^*_{\mathrm{HF}}(\omega) = G_{\mathrm{inf}} - \frac{G_{\mathrm{inf}}}{[1 + \mathrm{i}\omega\tau_0]^{1/2}} \tag{18}$$

with

$$\tau_0 = \frac{\zeta_0 b^2}{\pi^2 kT} \tag{19}$$

(i.e., there is no adjustable parameter).

The inverse Fourier transform of that equation gives the relaxation function:

$$G_{\mathrm{HF}}(t) = G_{\mathrm{inf}}[1 - \mathrm{erf}((t/\tau_0)^{1/2})] \tag{20}$$

2.5. Relaxation Modulus in the Whole Time Scale. Hence the relaxation modulus may be calculated from a very limited number of physical parameters (G_N, G_{inf}, and τ_0), with no "ad-hoc" parameters, in a time range covering the initial glassy behavior ($t \to 0$) to the terminal relaxation region. For a typical polymer, this range exceeds ten decades of time; the complete expression of the relaxation modulus is

$$G(t) = G_N\left[\int_0^{2/N^{1/2}} \exp\left(-\frac{t}{\tau\xi(1)}\right) \mathrm{d}\xi + \int_{2/N^{1/2}}^{1} \exp\left(-\frac{t}{\tau\xi(2)}\right) \mathrm{d}\xi\right] + G'_N\left[\sum_{p=1}^{n_1} \exp\left(-\frac{tp^2}{\tau_A}\right) + \sum_{p=1}^{N} \frac{1}{N} \exp\left(-\frac{p^2 t}{\tau_B}\right)\right] + G_{\mathrm{inf}}[1 - \mathrm{erf}((t/\tau_0)^{1/2})] \tag{21}$$

2.6. Complex Shear Modulus in the Whole Frequency Range. The complex shear modulus is the Fourier transform of eq 21:

$$G^*(\omega) = G_N\left[\int_0^{2/N^{1/2}} \frac{\omega^2(\tau_\xi(1))^2 + \mathrm{i}\omega\tau_\xi(1)}{1 + \omega^2(\tau_\xi(1))^2} \mathrm{d}\xi + \int_{2/N^{1/2}}^{1} \frac{\omega^2(\tau_\xi(2))^2 + \mathrm{i}\omega\tau_\xi(2)}{1 + \omega^2(\tau_\xi(2))^2} \mathrm{d}\xi\right] + G'_N\left[\frac{1}{N}\sum_{p=1}^{N} \frac{\omega^2\left[\frac{\tau_B}{p^2}\right]^2 + \mathrm{i}\omega\frac{\tau_B}{p^2}}{1 + \omega^2\left[\frac{\tau_B}{p^2}\right]^2} + \sum_{p=1}^{n_1} \frac{\omega^2\left[\frac{\tau_A}{p^2}\right]^2 + \mathrm{i}\omega\frac{\tau_A}{p^2}}{1 + \omega^2\left[\frac{\tau_A}{p^2}\right]^2}\right] + G_{\mathrm{inf}}\left[1 - \frac{1}{[1 + \mathrm{i}\omega\tau_0]^{1/2}}\right] \tag{22}$$

3. Comparison between Model Predictions and Mechanical Spectroscopy Data for Various Polymer Species

We have compared our model to the experimental data presented in the literature for three different polymer species: polystyrene, poly(methyl methacrylate), and polybutadiene. All samples have been obtained by anionic polymerization and have a narrow molecular weight distribution. At last we will present a comparison between our model and Lin's model which covers also a wide range of times or frequencies.

3.1. Polystyrene. 3.1.1. Sample. The data on polystyrene we used have been obtained by Montfort[15] in a comprehensive study of the relation between linear viscoelasticity and molecular dynamics of monodisperse homopolymers and blends. PS 200 (M_w = 200000) is a sample from Pressure Chemical Co. with a polydispersity index $M_w/M_n < 1.06$. The $G^*(\omega)$ master curves in Figures 1 and 2 (reference temperature T = 160 °C) have been obtained using time–temperature equivalence in the temperature range: 140–210 °C. The corresponding WLF parameters are given in Table I.

3.1.2. Comparison with Model Predictions. We have used the values obtained by Montfort[16] for the physical parameters needed by the model to calculate $G^*(\omega)$ in the whole frequency range (eq 22). The plateau modulus G_N

Table I. WLF Parameters

polymer	T_0 (K)	C_1	C_2 (K)
PS	433	6.3	111.4
PB	298	3.48	163
PMMA	493	11	80

Table II. Characteristic Parameters for Polymers

polymer	G_N (Pa)	G_{inf} (Pa)	τ_0 (s)	P
PS	2.0×10^5	1×10^9	5×10^{-8}	0.5
PB	1.5×10^6	4×10^8	0.023×10^{-8}	0.44
PMMA	5.6×10^5	5×10^7	2.9×10^{-8}	0.71

and the molecular weight between entanglements are those given by Montfort[16] and Cassagnau:[17] $G_N = 2 \times 10^5$ Pa and $M_e = 18500$. The glassy modulus G_{inf} is given in the literature (Ferry[18]); for polystyrene $G_{inf} = 10^9$ Pa. The value of τ_0 is derived from the experimental terminal relaxation time $T_d = \eta_0 J_0^e$,[17,18] which, according to Doi,[7] is related to τ_C by

$$\tau_C = \frac{T_d}{[1 - 1/N^{1/2}]^2} \tag{23}$$

Then, from eqs 10 and 29, we calculate the value of τ_0 ($\tau_0 = 5.6 \times 10^{-7}$ s at 160 °C). Figures 1 and 2 show a reasonable agreement between eq 22 and the experimental data, especially in the terminal zone. Agreement is poor in the high-frequency region because the time τ_0 is overestimated. If τ_0 is adjusted in the high-frequency region ($\tau'_0 = 2 \times 10^{-7}$ s), the discrepancy occurs in the low-frequency domain (Figures 1 and 2). Therefore, we obtain a good fit in the low- and high-frequency regions using the following set of relaxation times:

$$\begin{aligned} \tau'_0 &= 2 \times 10^{-7}\ \text{s} \\ \tau_A &= {}^1/_6 \tau_0 N_e^{\,2} \\ \tau_B &= {}^1/_3 \tau_0 N_e^{\,2} N^2 \\ \tau_C &= \tau_0 N_e^{\,2} N^3 \\ \tau_0 &= 5.6 \times 10^{-7}\ \text{s} \end{aligned} \tag{24}$$

To explain the small difference between the kinetic units at low and high frequencies, one may assume that the statistical segment lengths in the terminal and glassy relaxation regions are different. We may define a parameter P to characterize the length variation of the segment such as $\tau'_0 = P^2\tau_0$, leading to $b' = Pb$. For polystyrene we get $P = 0.5$.

This experimental fact may be interpreted either as (i) a variation in the length of the statistical segment or (ii) a slight difference in the friction coefficients of local and overall chain motions. This last assumption has been discussed by Plazek et al.,[19] who have shown that the WLF parameters (that reflect the thermal variations of the friction coefficient ζ_0) are slightly different in the terminal and glassy regions. Lin[20] links that discrepancy to the dependence of the glass transition temperature on molecular weight (hence molecular weight distribution). To test that hypothesis, we have selected four different polystyrene samples of molecular weights $M = 90000$, 200000, 400000, and 900000 (the polydispersity indices are respectively 1.04, 1.06, 1.06, and 1.12). The variations of the complex shear modulus of the four samples may be fitted with a single set of parameters (τ'_0, P, G_N, G_{inf}), so the P parameter does not depend on chain length, contrary to Lin's assumption. The physical parameters for polystyrene are reported in Table II. The experimental data and theoretical curves of the four samples have been reported in Figures 3 and 4.

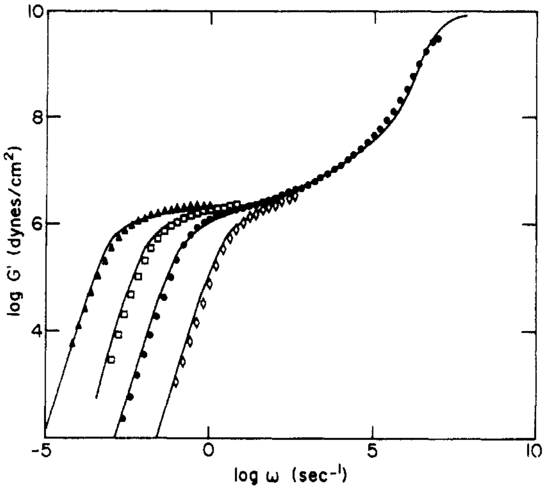

Figure 3. Elastic modulus of polystyrene samples at 160 °C: (—) model (eq 22); (▲) $M = 900000$; (□) $M = 400000$; (●) $M = 200000$; (◇) $M = 90000$.

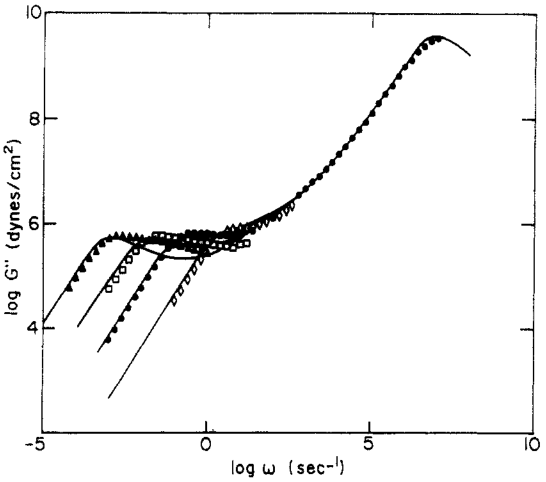

Figure 4. Loss modulus of polystyrene samples at 160 °C: (—) model (eq 22); (▲) $M = 900000$; (□) $M = 400000$; (●) 200000; (◇) $M = 90000$.

As a partial conclusion, we may say that eqs 10 and 19 give only an approximate relation between τ_0 and τ_C: this implies that the usual picture of long-scale motions simply generated by short-scale motions with the same characteristic lengths and times is certainly oversimplified.

3.2. Polybutadiene. 3.2.1. Samples. We have tested our model on the rheological data obtained by Colby et al.[21] on an anionic polybutadiene sample called "B2" ($M_w = 130000$, $M_w/M_n < 1.1$; the sample microstructure was 35.5% 1,4-cis/54.5% 1,4-trans/10% 1,2-vinyl). We have selected this paper of Colby et al. among other papers on the rheology of polybutadiene because the authors derived also all the parameters needed in our simulation (i.e., G_N, G_{inf}, ζ_0, molecular weight dependence at 25 °C, etc.), and we wish, whenever possible with the literature data, not to derive ourselves the physical parameters involved in the model.

3.2.2. Comparison with Model Predictions. Hence we may readily calculate the $G^*(\omega)$ curves for samples of the same microstructure. The master curve of sample B2 is presented in Figures 5 and 6 along with the lines calculated from our model. With Colby's[21] parameters, in particular $\zeta_0 = 2.61 \times 10^{-7}$ g/s at 25 °C, the agreement is poor at low frequencies (dashed lines). Agreement is better with Roovers'[22] value of $\zeta_0 = 1.1 \times 10^{-7}$ g/s (dot-

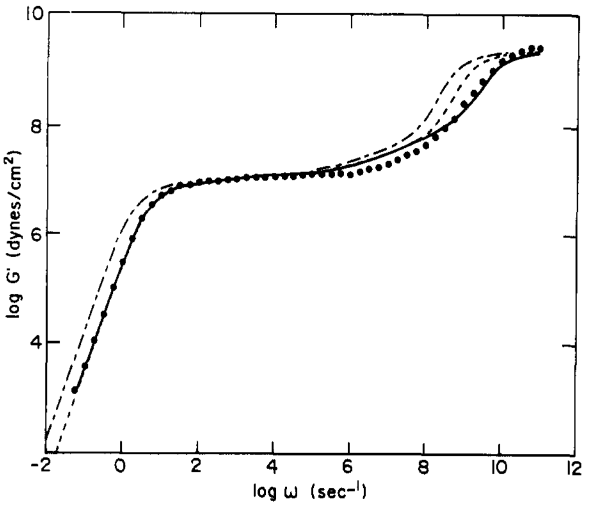

Figure 5. Elastic modulus of polybutadiene sample B2 at 25 °C: (●) experimental; (—) model (eq 22) including parameter P; (- - -) model with $\zeta_0 = 1.1 \times 10^{-7}$ g/s; (-·-) model with $\zeta_0 = 2.6 \times 10^{-7}$ g/s.

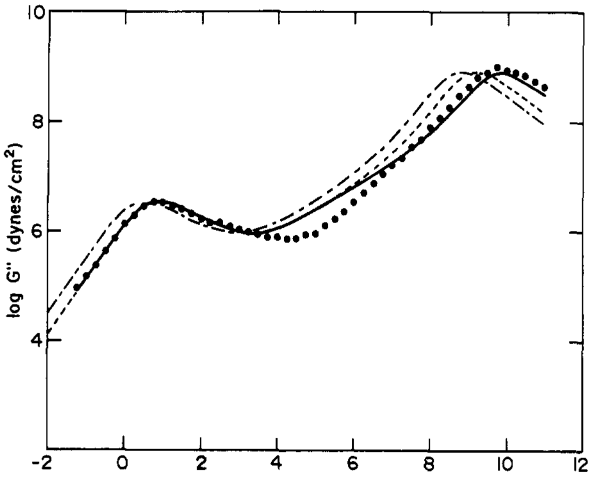

Figure 6. Loss modulus of polybutadiene sample B2 at 25 °C: (●) experimental; (—) model (eq 22) including parameter P; (- - -) model with $\zeta_0 = 1.1 \times 10^{-7}$ g/s; (-·-) model with $\zeta_0 = 2.6 \times 10^{-7}$ g/s.

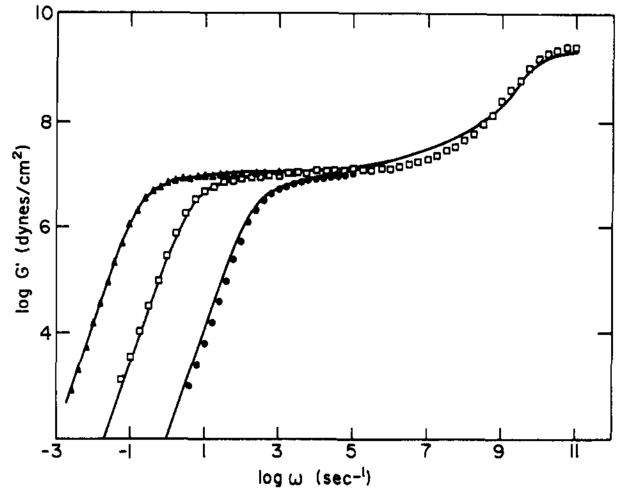

Figure 7. Elastic modulus of polybutadiene samples at 25 °C: (—) model (eq 22); (▲) $M = 361000$; (□) $M = 130000$; (●) $M = 39400$.

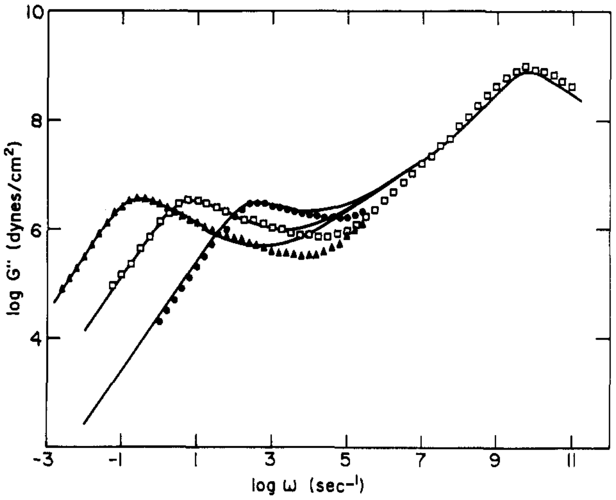

Figure 8. Loss modulus of polybutadiene samples at 25 °C: (—) model (eq 22); (▲) $M = 361000$; (□) $M = 130000$; (●) $M = 39400$.

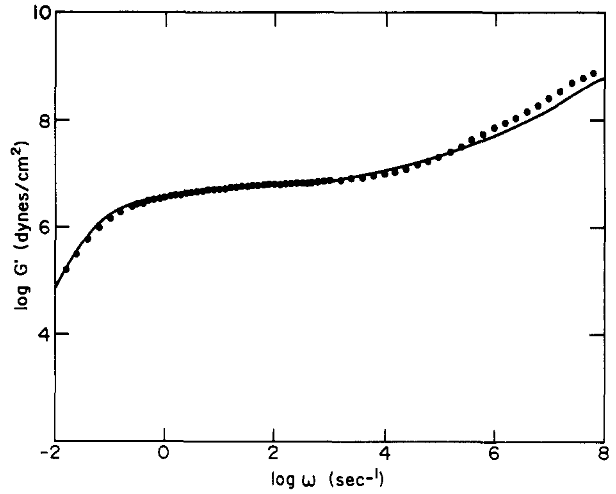

Figure 9. Elastic modulus of poly(methyl methacrylate) sample at 220 °C: (●) experimental; (—) model (eq 22).

dashed lines) but still poor at high frequencies. The final adjustment is obtained with a modified value of ζ_0 in the high-frequency domain (eq 18), which amounts to introducing the parameter P depicting the change of statistical segment lengths or mobilities involved in the terminal and glassy relaxation mechanisms, as already observed for polystyrene. The value of P for polybutadiene ($P = 0.44$) is very close to that of polystyrene. The effects of molecular weight may be readily taken into account by the model, using a single set of parameters (τ'_0, P, G_N, G_{inf}). We have reported in Figures 7 and 8 the experimental variations of the complex shear modulus of three anionic polybutadiene samples[22] compared with the model predictions (molecular weights are 39400, 130000, and 361000 and polydispersity indices are <1.1).

3.3. Poly(methyl methacrylate). 3.3.1. Samples. The rheological properties of anionic poly(methyl methacrylate) samples (from Pressure Chemical Co.) have been studied by Cassagnau.[17] The model predictions have been compared with the data obtained on the sample referenced as PMMA400 ($M_w = 400000$, $M_w/M_n = 1.14$) in Cassagnau's work. The reference temperature for the master curve is 200 °C, and the corresponding WLF parameters are reported in Table I. The rheological data (G', G'') have been obtained using an Instron 3250 rotary rheometer in cone–plate geometry. Experimental procedures and sample preparation have been described earlier.[17]

3.3.2. Comparison with Model Predictions. The physical parameters used to derive G' and G'' from eq 22 are given in Table II. The agreement between calculated and experimental values is quite reasonable in the terminal and glassy regions, but there is a noticeable difference in the coupling region (Figures 9 and 10). That may be due to the sample polydispersity; another explanation could

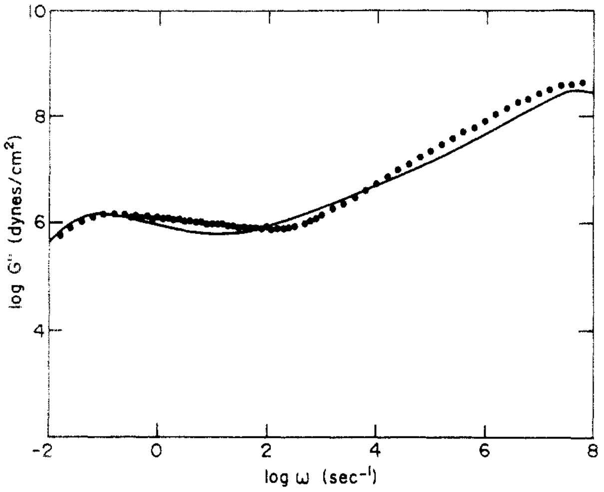

Figure 10. Loss modulus of poly(methyl methacrylate) sample at 220 °C: (●) experimental; (—) model (eq 22).

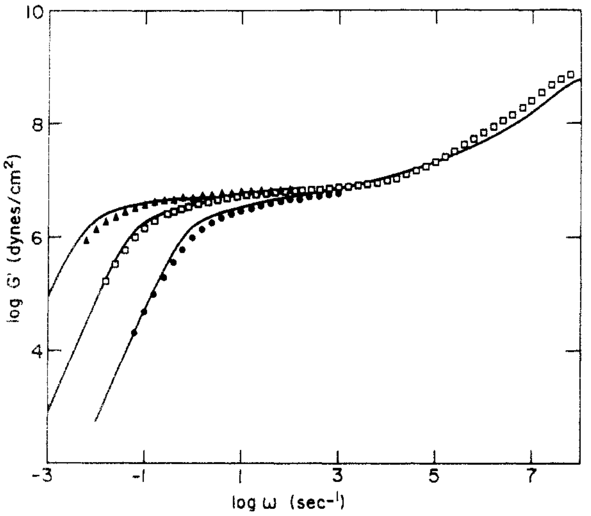

Figure 11. Elastic modulus of PMMA samples at 22 °C: (—) model (eq 22); (▲) $M = 840000$; (□) $M = 400000$; (●) $M = 188200$.

be a difference in the broadness of the distribution of relaxation times in the transition region, which might differ from one polymer to another: this may be simply taken into account by changing the exponent of the Davidson–Cole relaxation function, adding an adjustable parameter at the expense of the model's simplicity and generality. Once again, the molecular weight effects are reasonably taken into account by the model: we have selected three different poly(methyl methacrylate) samples[17] of molecular weights M_w = 188200, 400000, and 840000 and polydispersity indices 1.02, 1.14, and 1.12, respectively, from Pressure Chemical Co. The variations of the complex shear modulus of the samples are reasonably predicted by the model from the same set of basic parameters (τ'_0, P, G_N, G_{inf}) (see Figures 11 and 12).

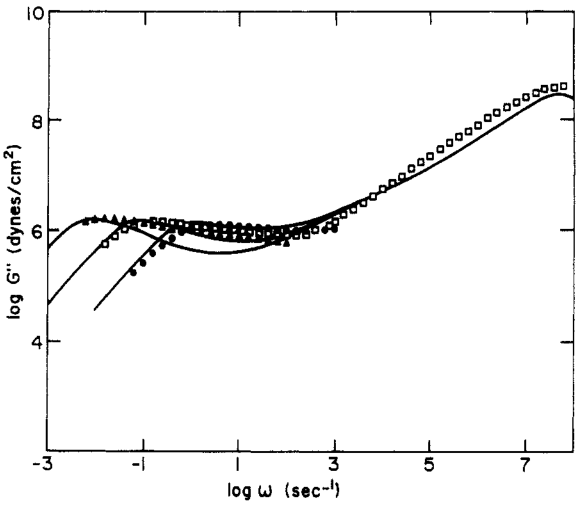

Figure 12. Loss modulus of PMMA samples at 220 °C: (—) model (eq 22); (▲) $M = 840000$; (□) $M = 400000$; (●) 188200.

Table III. Characteristic Lengths for Polymers

polymer	b (Å)[a]	l_0 (Å)[b]	C_∞[b]	l (Å)	b' (Å)
PS	7.4	1.54	10.3	15.86	3.7
PB	6	1.47	5.4	7.94	2.6
PMMA	6.9	1.54	8.7	13.40	4.9

[a] Reference 18. [b] Reference 26.

As a conclusion of the experimental section, we would like to emphasize the fact that the three processes described by Doi and Edwards and their respective relaxation times τ_A, τ_B, and τ_C reflect diffusion mechanisms involving the same statistical unit of length b. But the glassy behavior seems to be related to a different characteristic length b'. We have reported in Table III the values of b, defined as the average monomer unit length (Ferry[18]), and b', derived from the relation $b' = Pb$. Their respective values indicate that the unit lengths involved in glassy relaxations are about half those concerning the terminal and plateau domains. The monomer length is itself lower than the Kuhn segment length l, defined from the characteristic ratio C_∞[23]

$$C_\infty = \langle R^2 \rangle / (n l_0^2) \tag{25}$$

where l_0 is the average length of the main-chain bonds and $\langle R^2 \rangle$ is the unperturbed radius of gyration, such that $l = C_\infty l_0$. Hence the glassy transition involves submonomeric units of length b' that can be approximated by a mean square average length l' given by $l'^2 = C_\infty l_0^2$.

The agreement is qualitatively good (see Table III), and l' can be associated with some local conformational changes such as damped vibrational motions as mentioned by Kanaya et al.[24] in a study of quasielastic neutron scattering on polybutadiene.

Taking that effect into account, the calculation of the overall relaxation modulus $G(t)$ from our model needs only four parameters: G_N, G_{inf}, τ_0, and P.

3.4. Comparison with Lin's Model. Starting also from the Doi–Edwards model, Lin[8] has proposed an equation for the relaxation function, in which four relaxation processes are taken into account: besides the basic three relaxation domains described above, Lin adds an additional relaxation function $\mu_x(t)$ with a characteristic time τ_x. Lin attributes this process to a chain sliding motion through entanglements (slip-link). This fourth diffusion process allows for the chain to reequilibrate the monomer density after a sudden deformation. Lin's $\mu_x(t)$ function is given as

$$\mu_x(t) = \frac{1}{4}\exp\left(-\frac{t}{t_x}\right) \tag{26}$$

with

$$\tau_x = 0.55\frac{\zeta_0 b^2 N_e^{\,2} N}{\pi^2 kT} \tag{27}$$

Taking into account tube length fluctuations, the relaxation function at large times becomes

$$G(t) = \frac{4G_N}{5}[B\mu_B(t) + C\mu'_C(t)] \tag{28}$$

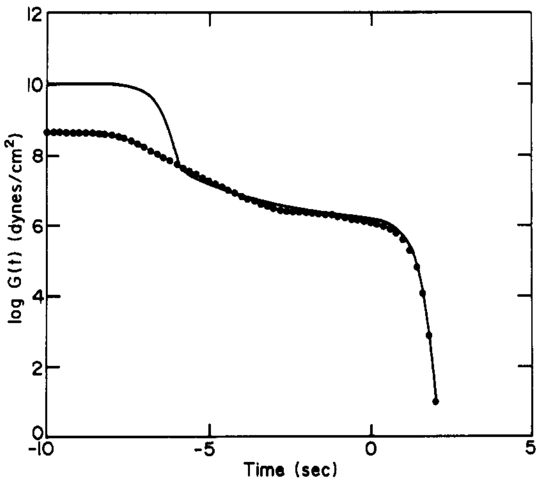

Figure 13. Relaxation modulus of polystyrene sample F20. Comparison between Lin's model and the present model: (●) Lin's model; (—) present model (eq 22).

with

$$B = 1/N^{1/2} \tag{29}$$

$$C = 1 - B \tag{30}$$

$$\mu_B(t) = \sum_{p\ \mathrm{odd}} \exp\left(-\frac{tp^2}{\tau_B}\right) \tag{31}$$

and

$$\mu'_C(t) = \sum_{p\ \mathrm{odd}} \exp\left(-\frac{tp^2}{\tau'_C}\right) \tag{32}$$

where

$$\tau'_C = \tau_C\left[1 - \frac{1}{N^{1/2}}\right]^2 \tag{33}$$

Introducing the $\mu_x(t)$ and $\mu_A(t)$ functions in eq 28, Lin's general relaxation function becomes

$$G(t) = \frac{4G_N}{5}[B\mu_B(t) + C\mu'_C(t)][1 + \mu_A(t)][1 + \mu_x(t)] \tag{34}$$

We have compared the predictions of Lin's model and our model with the experimental data reported by Lin[8] on a narrow molecular weight distribution polystyrene sample from Toyo Soda Co. referenced as F20 (M_w = 186000, M_w/M_n = 1.07). The reference temperature is 135 °C. The values of the physical parameters are $G_N = 2.05 \times 10^5$ Pa, $\tau_0 = 1.95 \times 10^{-7}$ s, and $G_{\mathrm{inf}} = 10^9$ Pa.

In Figure 13, we see that there is a good agreement between the two models in the time scale studied by Lin (10^{-4}–10^2 s), but then a discrepancy occurs at short times, mainly because Lin's model does not take into account the transition and glassy regions.

4. Conclusion

We tried to provide a formal framework to derive the linear viscoelastic properties of linear polymers, whatever their chemical structure: our work is based on the principles of the dynamics of flexible chains developed in the past few years (basically reptation), and the general features of these concepts are confirmed here: as a first approximation only a few physical microscopic parameters are sufficient to describe the overall relaxation of macromolecular chains in a very large range of times (or frequencies), as the scaling laws of the viscoelastic parameters with chain length are independent of the chemical nature of the chain. The model is basically simple, relevant to any linear polymer, and it is easy to "translate" the model from one polymeric species to another. The model has been tested on three polymers: polystyrene, polybutadiene, and poly(methyl methacrylate): the general model predictions are quite reasonable, and this model (monodisperse case) is presently integrated in a more general framework including polydispersity (constraint release) effects in order to derive numerically the linear visoelastic behavior of a commercial linear polymer from its molecular weight distribution.

We have interpreted the elementary relaxation time change between the terminal and the glassy zones in terms of different characteristic lengths. However, some evidence of nonuniformity of the friction coefficient has been shown experimentally that could have some impact on the relaxation time rescaling process. Obviously, there is a need for refining the model with new ideas about the relaxation processes involved in the transition region (i.e., what happens "between entanglements") in order to explain the slight differences between the WLF parameters in the transition and terminal regions already mentioned by experimentalists.[25]

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