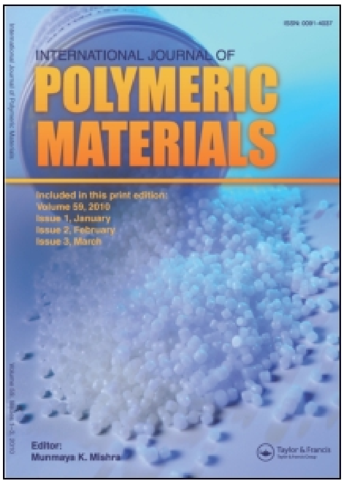

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

New Approach to the Relaxation Phenomena Theory of the Amorphous Linear Entangled Polymers

Yu. K. Kokorin[a]; V. N. Pokrovskii[a]
[a] Research Institute, Altay, Béésk-city, Russia

To cite this Article Kokorin, Yu. K. and Pokrovskii, V. N.(1993) 'New Approach to the Relaxation Phenomena Theory of the Amorphous Linear Entangled Polymers', International Journal of Polymeric Materials, 20: 3, 223 — 237
To link to this Article: DOI: 10.1080/00914039308048364
URL: http://dx.doi.org/10.1080/00914039308048364

Intern. J. Polymeric Mater., 1993, Vol. 20, pp. 223–237
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

New Approach to the Relaxation Phenomena Theory of the Amorphous Linear Entangled Polymers

YU. K. KOKORIN and V. N. POKROVSKII
Research Institute, Altay, Béésk-city, Russia

(Received June 26, 1992)

Approach based on polymer chain dynamics in the "tube" is highlighted and its weaknesses presented. A new approach is proposed and its results discussed.

KEY WORDS Relaxation phenomena, chain entanglements, chain dynamics.

Both theoretical and experimental investigations of the undilute solutions and entangled polymer melts present substantial difficulties. As for the theory, the greatest success has been achieved within the scope of the uni-molecular approach.

The approach based on the polymer chain dynamics in the "tube"[1,2] will be highlighted below. However, subsequent investigations have shown that the "tube" model fails to explain the whole set of the experimental factors,[3-12] including the superslow relaxation processes, that play an important role in many phenomena.

The results obtained on the basis of an essentially different and alternative approach[3,13] are presented below.

THE MACROMOLECULE DYNAMICS EQUATION

The Gaussian subchains model is used to describe the dynamics of the long macromolecules at the system slow motion. The surroundings of the macromolecule is regarded as a continuous viscoelastic medium whose influence on the polymer chain movement has a relaxational (retarding) character. Assuming linear approximation at the medium velocity gradient, the polymer chain motion equation in the normal coordinates $\rho_i^\alpha(t)$ is written as

$$m\,\ddot{\rho}_i^\alpha(t) = -\int_0^\infty \beta_\alpha(s)[\dot{\rho}_i^\alpha - \nu_{ij}\rho_j^\alpha]_{t-s}\,\mathrm{d}s - \int_0^\infty \varphi_\alpha(s)[\dot{\rho}_i^\alpha - \omega_{ij}\rho_j^\alpha]_{t-s}\,\mathrm{d}s$$

$$- 2T\mu\lambda_\alpha\rho_i^\alpha(t) + R_{\alpha\beta}^{-1}\Phi_i^\beta(t); \qquad (s \geqslant 0) \quad (1)$$

$$\alpha, \beta = 0, 1, \ldots, N; \qquad i, j = 1, 2, 3$$

Here m is subchain (Brownian particle) mass, $\nu_{ij} = \partial v_i/\partial x_j$ = unperturbed medium velocity gradients tensor, $\omega_{ij} = (\nu_{ij} - \nu_{ji})/2$.

The first term on the right in Equation (1) describes the drag force of α-th bead when it moves relative to the medium and other chain particles. The eigenvalues $\beta_\alpha(s)$ of the external friction kernel are chosen in a form of the pure viscous and viscoelastic or aftereffecting terms:

$$\beta_\alpha(s) = \beta(s) = 2\zeta\delta(s) + \frac{\zeta B}{\tau}\exp(-s/\tau), \qquad (\alpha = \overline{0, N}) \tag{2}$$

where **B** is the factor of the subchain friction coefficient ζ increasing because of entanglements. The postulated relaxation time τ agrees, as has been shown,[3] with the calculated macroscopic relaxation time $\tau' = \eta/G_e'$, where η = viscosity and G_e' = plateau shear modulus.

The second term on the right in Equation (1) represents the forces of the "internal" viscosity. However, in a customary understanding, the internal viscosity forces are caused by the potential barrier of the internal rotation. For undilute systems, they are negligible in comparison with the forces affecting the deformation of the entangled macromolecule. Accordingly, the eigenvalues of the "internal" friction kernel is selected in a form:

$$\varphi_\alpha(s) = \varphi(s) = \begin{cases} 0, & \alpha = 0 \\ \dfrac{\zeta E}{\tau}\exp(-s/\tau), & \alpha = \overline{1, N} \end{cases} \tag{3}$$

where the component taking into account the proper internal viscosity (unconnected with the entanglements), is neglected: **E** is coefficient of the internal viscosity increasing due to the entanglements.

As the zero mode describes translational motion of the chain as a whole when it doesn't undergo deformations, the eigenvalue $\varphi_0 = 0$. While generally speaking the parameters **B** and **E** depend on the mode number α, here these parameters are taken as constant. As can be shown, taking into account these parameters' dependence on α only leads to working out the molecule dynamics in detail without really changing its essential features.

Integration of Equation (1) for all times s preceding the present time t takes account of the whole macromolecule history in the system.

The third term on the right of Equation (1) represents the elastic pairwise interaction of the neighboring chain particles. The elastic constant is written in a form $2T\mu$, where T is the system temperature, and $\mu = 3N/2R^2$. For the case in question of an ideal chain, the mean square end-to-end distance $R^2 = Nb^2$. The eigenvalues of the elastic pairwise interaction matrix $\lambda_\alpha = 4 \times \sin^2[\alpha\pi/2(N + 1)]$.

Finally, the last term on the right in Equation (1) expresses the random Brownian force distributed according to the Gaussian law with the mean equal zero and the correlation function

$$K_{ij}^{\alpha\beta}(s) = T\zeta\delta_{ij}\delta_{\alpha\beta}\left[2\delta(s) + \frac{B + E}{\tau}\exp(-s/\tau)\right];$$

$R_{\alpha\beta}$ = the orthogonal matrix of the transformation to the normal coordinates.

Thus, in the approximation under consideration the macromolecule dynamics is defined by the Rouse longest relaxation time $\tau^* \equiv \tau_1^R = \alpha^2\tau_2^R \sim \mathbf{C}^0\mathbf{M}^2$ and the quantities **B**, **E** and $\chi = /2\mathbf{B}\tau^*$, are universal functions of the parameter $\mathbf{Z} \sim \mathbf{C}^1\mathbf{M}^{0.5}$, where **C** = concentration and **M** = polymer molecular weight[13,14]:

$$\mathbf{B} \sim \mathbf{C}^{4.8}\mathbf{M}^{2.4}, \qquad \mathbf{E} \sim \mathbf{C}^{4.8}\mathbf{M}^{2.4}, \qquad \chi \sim \mathbf{C}^{-2}\mathbf{M}^{-1}$$

The polymer chemical nature is incorporated into the theory through the friction coefficient ζ.

DIFFUSION OF THE CENTER OF MASS OF THE MACROMOLECULE AND SUBCHAIN

The r.m.s. center of mass displacement (q^2) and α-th subchain (X_α^2) in the polymer liquid at rest, calculated[14,15] on the basis of the dynamics Equation (1) including the postulates (2) and (3) are

$$q^2(t) = \frac{6T\tau}{\zeta(N + 1)(B + 1)}\left[\frac{t}{\tau} + \frac{B}{B + 1}\left(1 - e^{[-t/\tau(B+1)]}\right)\right] \tag{4}$$

$$\mathbf{X}_\alpha^2(t) = q^2(t) + \frac{6T\tau}{\zeta(N + 1)} \times \sum_{\gamma=1}^{N} \frac{4\tau_\gamma^R}{\tau}\left[P_\gamma^+\left(1 - e^{-(t/2\tau_\gamma^+)}\right) + P_\gamma^-\left(1 - e^{-(t/2\tau_\gamma^-)}\right)\cos^2\frac{(2\alpha + 1)\gamma\pi}{2(N + 1)}\right] \tag{5}$$

$$P_\gamma^\pm = \frac{2\tau_\gamma^\pm - \tau}{2(\tau_\gamma^+ - \tau_\gamma^-)}; \qquad \begin{aligned} 2\tau_\gamma^\pm &= \tau_\gamma \pm \sqrt{\tau_\gamma^2 - 2\tau\tau_\gamma^R} \\ 2\tau_\gamma &= \tau + 2\tau_\gamma^R(1 + B + E) \end{aligned} \tag{6}$$

Here, $\tau_\gamma^\pm$ = two sets of the relaxation times arising when macromolecule introducing in the viscoelastic liquid, $P_\gamma^\pm$ = corresponding weights.

The dependences (4) and (5), investigated in detail in References 14 and 15, are shown in Figure 1. The characteristic times in the t-units and the scales in the X^2 units are shown at the axis. Here only the most significant results should be highlighted.

1) Relaxation spectrum (6) contains the Rouse relaxation times τ_α^R. Actually,

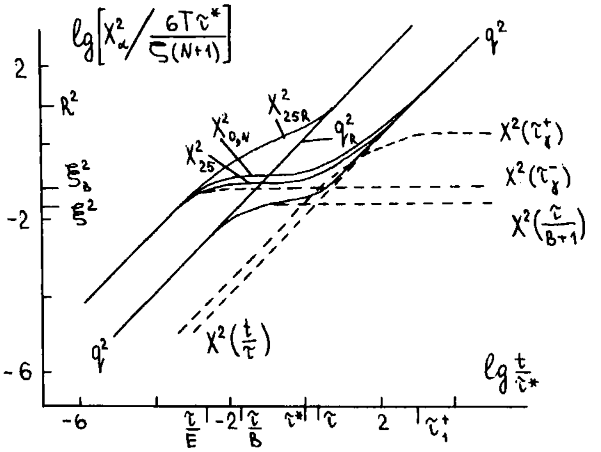

FIGURE 1 $N = 50$, $E = 10^3$, $B = 10^2$, $\chi = 10^{-2}$.

the limit transition to the viscous medium case without memory and entanglements (τ, B, $E \rightarrow 0$) results in the Rouse spectrum $\tau_\alpha^R = \zeta/4T\mu\lambda_\alpha$. Equations (4) and (5) are in this case transformed into the corresponding results for the Rouse model (a single macromolecule in the viscous fluid without entanglements), marked in Figure 1 and in the text with the index R.

2) For the other limiting case (many entanglements, B, $E >> 1$), the superslow relaxation times $\tau_\alpha^+ > \tau$ appear in the system. The longest one of these, the time τ_1^+ ($\sim C^{4.8}M^{4.4}$), corresponds to the rearrangement (relaxation) in the polymer chain (stresses) segments which size is in the order of a macromolecule mean size R. From this follows that τ_1^+ is the stress relaxation time in the system as a whole—on the scales equal to the total polymer sample sizes; this time is the longest one of the relaxation times in the system. The superslow relaxation processes mechanism is defined at the microscopic level.

3) The dynamics Equation (1) results in the inherent length

$$\xi = \frac{6T\tau}{\zeta(N + 1)(B + 1)} \sim C^{-1}M^0$$

in the system occurrence (plateau in the curve $q^2(t)$ in Figure 1). Its physical significance is the mean distance between entanglements.

4) The postulated relaxation time $\tau(\sim C^{2.8}M^{3.4})$ corresponds to the relaxation of the macromolecule parts on the scale ξ.

5) One physical meaning of the theory parameter χ is the value reciprocal to the entanglements number per macromolecule N_e: $\chi = \pi^2/2N_e$. Another interpretation of χ is a mean macromolecule size to mean entanglement distance ratio: $\chi = \xi^2\pi^2/2R^2$.

6) The relation with the viscoelasticity is established:

$$G_e' = \frac{1}{6} nT \frac{R^2}{\xi^2},$$

where n is the number of macromolecules per unit volume.

7) The mobility anisotropy for the polymer chain is established[14] from the dynamics Equation (1). The dynamics model (1)–(3) also leads to[14] the fluctuations of the "tube" length and diameter, and macromolecule "leakage" through "tube walls," effects that are artificially introduced into the "tube" approach.

8) Contrary to Doi and Edwards' conclusion[2] it is shown that the macromolecule ends do not play an essential role in the dense system.

In addition it should be noted that sigmoidal curves similar to the ones in Figure 1 were obtained[16–20] through simulation of the molecule dynamics.

QUASI-ELASTIC LIGHT AND NEUTRON SCATTERING

Calculated on the basis of results (4)–(6) the incoherent scattering functions from one macromolecule

$$S_{\text{in}}(q, t) = \frac{1}{N+1} \sum_{\alpha=0}^{N} \exp\left[-\frac{q^2}{6} X_\alpha^2(t)\right]$$

are shown in Figure 2. Here $q = (4\pi/\lambda)\sin \theta/2)$ is the wave vector; $\lambda =$ the incident radiation wave length, $\theta =$ the scattering angle. All the characteristic features of the $X_\alpha^2(t)$ relaxation behavior, discussed above, have an effect on the scattering processes.

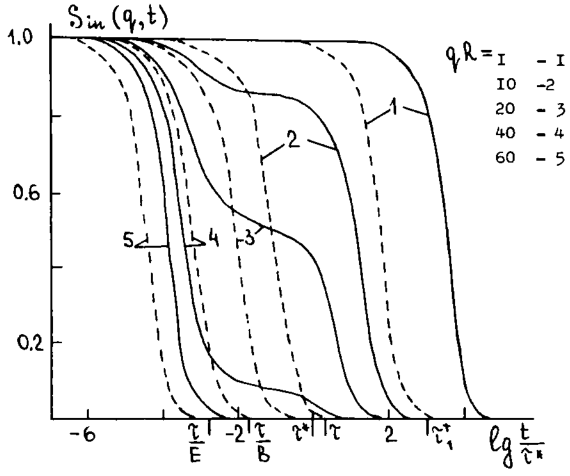

FIGURE 2 $N = 10^2$, $E = 10^3$, $B = 10^2$, $\chi = 10^{-2}$, - - - = Rouse model.

Like in the diffusion case there are three observed time ranges of essentially different behavior:

$$S_{\text{in}}(q, t) = \exp \begin{cases} -a(N+1)\dfrac{t}{\tau^*} & 0 < t < \dfrac{t}{E} \\ -a2\pi\left(\dfrac{B\chi}{1+B+E}\right)^{1/2} \equiv \xi_s & \dfrac{\tau}{E} < t < \tau \\ -a\dfrac{1}{B+1}\dfrac{t}{\tau^*} & \tau_1^+ < t < \infty \end{cases}$$

where $a = q^2R^2/6\pi^2$. At the large and small times $S_{\text{in}}(q, t)$ decreases at two different exponential rates (nowadays there are indirect evidences confirming this fact for the real polymers). The plateau ξ_s which has a length equal to τ, as in Figure 1 ($E \gg B \gg 1$), is observed in the intermediate range. This plateau's presence is here marked apparently for the first time.

The incoherent scattering intensity from one macromolecule at the frequency ω in interval $\omega + d\omega$ is proportional to dynamic form-factor

$$S_{\text{in}}(q, \omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} S_{\text{in}}(q, t)e^{i\omega t}\, dt$$

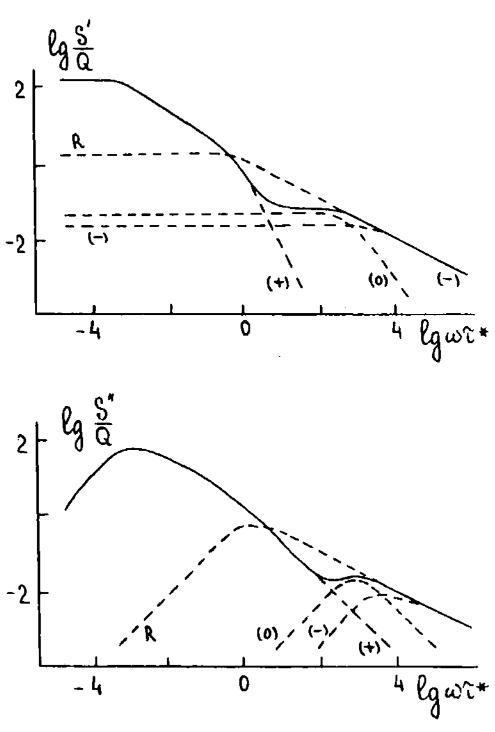

FIGURE 3 $N = 10^3$, $E = 10^3$, $B = 10^2$, $\chi = 10^{-2}$.

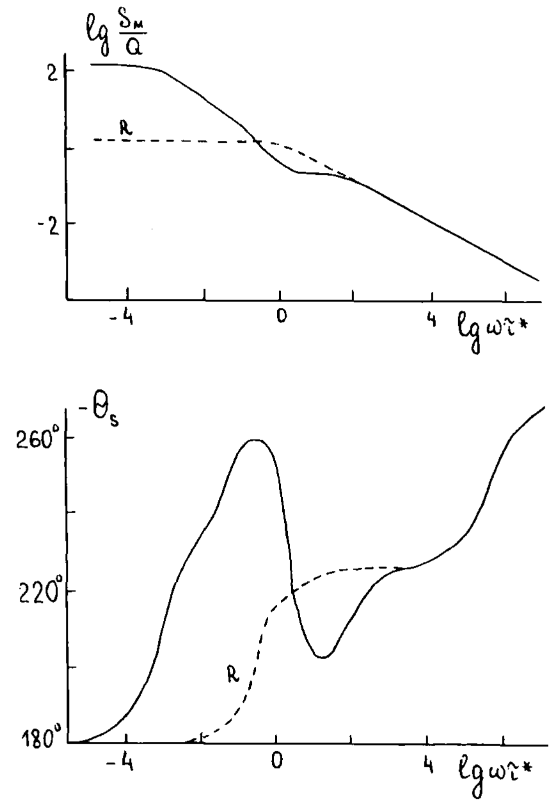

FIGURE 4 $N = 10^3$, $E = 10^3$, $B = 10^2$, $\chi = 10^{-1}$.

The experimentally measured quantity is the peak half-width $\Delta\omega_q$ for dependence $I_{\text{in}}(q, \omega) = S_{\text{in}}(q, \omega)/S_{\text{in}}(q, 0)$ at fixed q, which is obtained in the following form

$$\Delta\omega_q = \frac{q^2R^2}{\sigma\pi^2\tau^*}(B + 1) = \Delta\omega_q(B + 1) \sim C^{4.8}M^{1.4}$$

where $\Delta\omega_q$ is the half-width for the Rouse model. Thus, at the transition from a dilute to undilute solution, the half-width increases by **B** times. The macromolecule mobility decreases **B** times when this transition occurs.

THE OPTICAL ANISOTROPY

At the oscillatory shear flow $\gamma(t, \omega) \sim e^{-i\omega t}$, the complex birefringence Δn is related to the velocity gradient γ by the relation

$$\Delta n(t, \omega) = n_1(t, \omega) - n_2(t, \omega) = S(\omega)\gamma(t, \omega)$$

that determines the mechano-optic coefficient

$$S(\omega) = S'(\omega) + iS''(\omega) = S_M(\omega)e^{i\theta_s(\omega)}$$

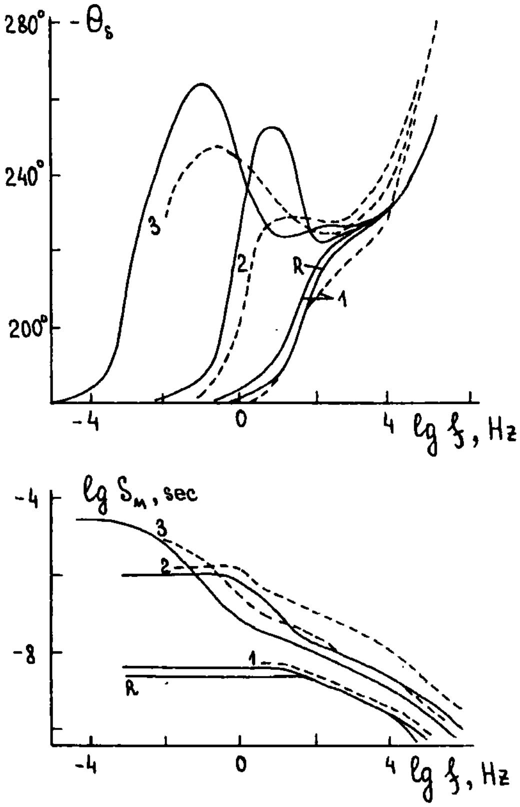

FIGURE 5 - - - = experimental data.[5]

The phase angle, θ_S, specifies the phasing Δn with respect to γ; $S_M = (S'^2 + S''^2)^{1/2}$ is the modulus of the mechano-optic coefficient.

The calculations on the dynamics Equation (1) result in the expression[21]:

$$
\begin{aligned}
S'(\omega) &= Q \sum_{\alpha=1}^{N} \left[\frac{P_\alpha^+}{1 + (\omega\tau_\alpha^+)^2} + \frac{P_\alpha^-}{1 + (\omega\tau_\alpha^-)^2} + \frac{P_\alpha^0}{1 + (\omega\tau_\alpha^0)^2} \right] \\
S''(\omega) &= Q\omega \sum_{\alpha=1}^{N} \left[\frac{P_\alpha^+\tau_\alpha^+}{1 + (\omega\tau_\alpha^+)^2} + \frac{P_\alpha^-\tau_\alpha^-}{1 + (\omega\tau_\alpha^-)^2} + \frac{P_\alpha^0\tau_\alpha^0}{1 + (\omega\tau_\alpha^0)^2} \right]
\end{aligned}
\qquad (7)
$$

The coefficient $Q \sim C^1M^1$ and is independent of chain subdivision. Relaxation time $\tau_\alpha^0 = 2\tau_\alpha^+\tau_\alpha^-/(\tau_\alpha^+ - \tau_\alpha^-) \approx 2\tau_\alpha^-$. Quantities P with indices are the weights by means of which every relaxation time contributes to the S' and S''; they are dependent only on $\tau_\alpha^\pm$ and τ_α^R.

The dependences (7) are represented in Figure 3. Characteristically, there are three sets of relaxation times, plateau occurrence and extrema at intermediate frequencies. These particularities reflect on the S_M and θ_S behavior (Figure 4).

The obtained results provide for the first time explanation[21] of the experimental

TABLE I

Characteristics of poly-α-methylstyrene solutions in Aroclor-1248 at $T = 25°C$ and theoretical quantities

System	N_e	$M \cdot 10^{-5}$	$C \cdot 10^3$, g/sm^3	$\tau^* \cdot 10^3$, s	τ, s	τ_1^+, s	N	E	B	χ	C/C^*	$C[\eta]$
1	0.25	4	9.1	2	—	—	50	0	0.6	4.85	1	1
2	2.94	4	105	2	0.08	0.17	50	12	50	0.42	11	12
3	14.1	50	41.1	300	12.6	99	625	70	238	0.088	21	23

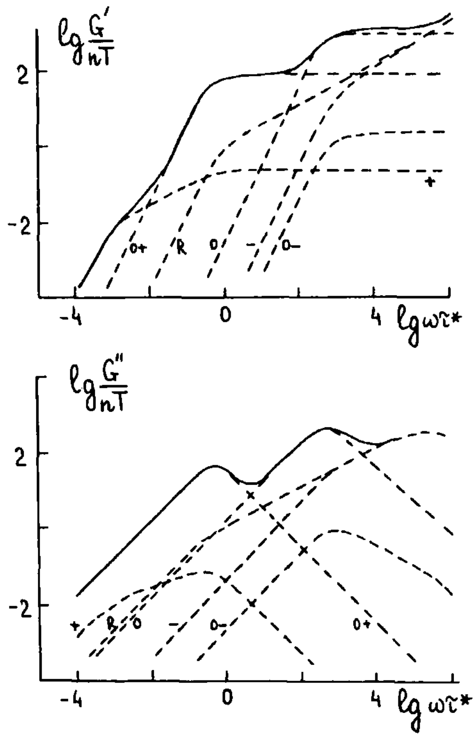

FIGURE 6 $N = 10^3$, $E = 10^3$, $B = 10^2$, $\chi = 10^{-2}$.

data[5] for narrow fractions of poly-α-methylstyrene solutions represented in Figure 5 and Table I, where C^* is critical concentration for the coils overlapping, $[\eta]$ is intrinsic viscosity. Above-mentioned particularities are very prominent for the system 3 (undilute solution) and even for the system 2 (semi-dilute solution).

LINEAR VISCOELASTICITY

Calculations[3,12,13] using the dynamics Equation (1) led to the following expressions for the elastic modulus G' and loss modulus G''

$$G'(\omega) =$$

$$nT\omega^2 \sum_{\alpha=1}^{N} \left[\frac{A_\alpha^+ \tau_\alpha^{+2}}{1 + (\omega\tau_\alpha^+)^2} + \frac{A_\alpha^- \tau_\alpha^{-2}}{1 + (\omega\tau_\alpha^-)^2} + \frac{A_\alpha^0 \tau_\alpha^{02}}{1 + (\omega\tau_\alpha^0)^2} + \frac{A_\alpha^0 \tau_\alpha^{0+2}}{1 + (\omega\tau_\alpha^{0+})^2} + \frac{A_\alpha^0 \tau_\alpha^{0-2}}{1 + (\omega\tau_\alpha^-)^2} \right] \tag{8}$$

$$G''(\omega) =$$

$$nT\omega \sum_{\alpha=1}^{N} \left[\frac{A_\alpha^+ \tau_\alpha^+}{1 + (\omega\tau_\alpha^+)^2} + \frac{A_\alpha^- \tau_\alpha^-}{1 + (\omega\tau_\alpha^-)^2} + \frac{A_\alpha^0 \tau_\alpha^0}{1 + (\omega\tau_\alpha^0)^2} + \frac{A_\alpha^0 \tau_\alpha^{0+}}{1 + (\omega\tau_\alpha^{0+})^2} + \frac{A_\alpha^{0-} \tau_\alpha^{0-}}{1 + (\omega\tau_\alpha^{0-})^2} \right]$$

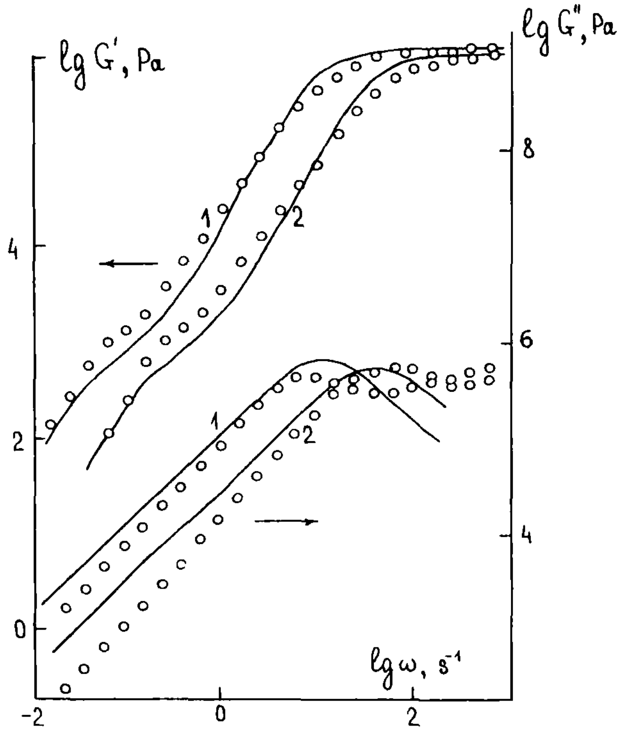

FIGURE 7 ○ = experimental data,[12] $N = 10^2$.

represented in Figure 6. Here the quantities A with indices are the weights, depending, as above, on $\tau_\alpha^\pm$ and τ_α^R; $\tau_\alpha^{0\pm} = 2\tau\tau_\alpha^\pm/(\tau + 2\tau_\alpha^\pm)$ are two new sets of relaxation times exhibited in this phenomenon. It is easy to check that i) $\tau_\alpha^{0-} \approx 2\tau_\alpha^-$ and ii) the set of the relaxation times τ_α^{0+} are reduced, in fact, to a single time: $\tau_\alpha^{0+} \approx \tau$.

As Figure 6 shows, the superslow relaxation times are exhibited at the lowest frequencies as a "shoulder" on the dependence $G'(\omega)$. At the same time the loss modulus is less sensitive to the superslow relaxation processes. These two observations are corroborated by experimental data[12] represented in Figure 7 and in Table II (where M_e = molecular weight between the entanglements, ρ = polymer density), and also by other results.[4] Tables I and II show that τ_1^+ exceeds τ by one to two or more orders.

Separating the viscosity coefficient η and the elasticity coefficient ν from the expansion $G(\omega) = -i\eta\omega + \nu\omega^2$ at low frequencies gives the following results[3]:

$$\eta = \frac{\pi^2}{6} nT(B + 1)\tau^* \sim C^{5.8}M^{3.4}, \qquad \nu = \frac{\pi^2}{3} nT[(B + 1)\tau^*]^2\chi \sim C^{8.6}M^{6.8} \qquad (9)$$

Similarly, at high frequencies the plateau modulus value is found[3]:

$$G'_e = \frac{\pi^2}{12} nT\chi^{-1} \sim C^3M^0 \qquad (10)$$

TABLE II

Characteristics of 1,4-polybutadiene melts at $T = 60°C$ and theoretical quantities

System	$M \cdot 10^{-5}$	$M_e \cdot 10^{-3}$	$n \cdot 10^{-18}$, sm^{-3}	ρ, g/sm^3	$B \cdot 10^{-2}$	$E \cdot 10^{-3}$	$\chi \cdot 10^2$	$\tau^* \cdot 10^3$, s	τ, s	τ_1^+, s	N_e
1	1	1.9	5.4	0.9	4.3	2.2	1.2	2.5	0.03	6.58	52.6
2	1.42	1.9	3.8	0.9	10	5	0.9	6.3	0.11	37.8	74.7

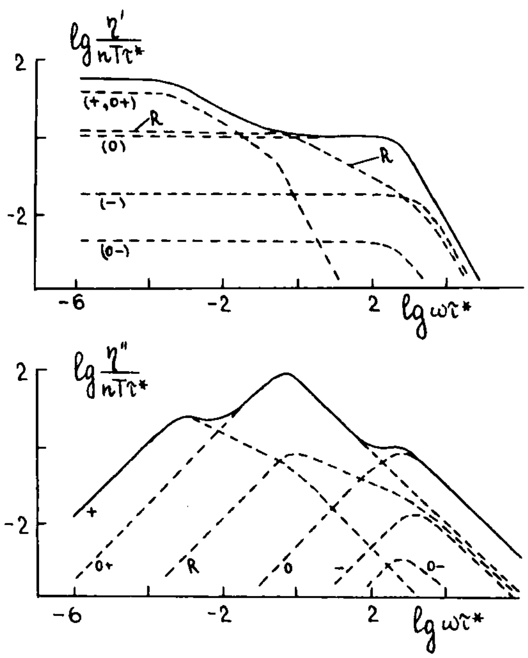

FIGURE 8 $N = 10^2$, $E = 10^3$, $B = 10^2$, $\chi = 10^{-2}$.

The dependences (9) and (10) are typical for the real polymers. They also produce useful relation: $\nu = \tau^2 G'_e = \tau\eta$.

For the intrinsic quantities (in the case of the dilute blends of two narrow fractions of one and the same polymer)

$$[\eta] = \lim_{c\to 0} \frac{\eta - \eta_0}{c\eta_0}, \qquad [\nu] = \lim_{c\to 0} \frac{\nu - \nu_0}{c\nu_0},$$

where zero index refers to the matrix properties, the following relations are obtained[22]

$$[\eta] \sim M^1 M_0^{-1}, \qquad [\nu] \sim M^1 M_0^{-1}$$

By contrast, the "tube" model gives[23] $[\eta] \sim M^3 M_0^{-3}$. According to the experimental data for the polybutadienes[24]

$$[\eta] \sim M^{0.5} M_0^{-0.8}, \qquad [\nu] \sim M^{1.3 \div 3.0} M_0^{-(1.8 \div 2.2)}$$

and for the polystyrenes[25] $[\eta] \sim M^{0.6-0.7} M_0^{-(0.3 \div 0.4)}$.

On the basis of the results (8) the dynamic viscosity $\eta(\omega) = -G(\omega)/i\omega = \eta'(\omega) - i\eta''(\omega)$ is calculated

$$\eta'(\omega) =$$

$$nT \sum_{\alpha=1}^{N} \left[\frac{A_\alpha^+ \tau_\alpha^+}{1 + (\omega\tau_\alpha^+)^2} + \frac{A_\alpha^- \tau_\alpha^-}{1 + (\omega\tau_\alpha^-)^2} + \frac{A_\alpha^0 \tau_\alpha^0}{1 + (\omega\tau_\alpha^0)^2} + \frac{A_\alpha^{0+} \tau_\alpha^{0+}}{1 + (\omega\tau_\alpha^{0+})^2} + \frac{A_\alpha^{0-} \tau_\alpha^{0-}}{1 + (\omega\tau_\alpha^{0-})^2} \right]$$

$$\eta''(\omega) =$$

$$nT\omega \sum_{\alpha=1}^{N} \left[\frac{A_\alpha^+ \tau_\alpha^{+2}}{1 + (\omega\tau_\alpha^+)^2} + \frac{A_\alpha^- \tau_\alpha^{-2}}{1 + (\omega\tau_\alpha^-)^2} + \frac{A_\alpha^0 \tau_\alpha^{02}}{1 + (\omega\tau_\alpha^0)^2} + \frac{A_\alpha^{0+} \tau_\alpha^{0+2}}{1 + (\omega\tau_\alpha^{0+})^2} + \frac{A_\alpha^{0-} \tau_\alpha^{0-2}}{1 + (\omega\tau_\alpha^{0-})^2} \right]$$

These dependences are shown in Figure 8, representing the relaxation properties of the dynamic modulus in a full measure.

CONCLUSION

The observable characteristic features of the undilute linear polymers' relaxation behavior can be understood on the basis of the current approach without using such conceptions as the labile knots network or "tube."

The environment properties in the "tube" model are represented by a single parameter—the "tube" diameter, which itself provides no information on the medium dynamic properties. This is from our point of view the main disadvantage of de Gennes, Doi and Edwards, of the approach with whose theory it is impossible to describe the complex hierarchical relaxation behavior observable for the inequilibrium phenomena.

Note also that the majority of the features *postulated* in the "tube" model, are *consequences* of the dynamics model (1)–(3).

There is a simpler, but as is easily seen, deficient variant[26] of the present approach.

References

1. P.-G. De Gennes, *J. Chem. Phys.*, **55**, 572 (1971).
2. M. Doi and S. F. Edwards, *J. Chem. Faraday Trans. II*, **74**, 1789; 1802; 1818 (1978).
3. V. N. Pokrovskii and Yu. K. Kokorin, Int. Rubber Conf., Moscow, 1984, Sept. 4–8, Preprint A64.
4. V. R. Raju, H. Rachapudy and W. W. Graessley, *J. Polym. Sci.: Polym. Phys. Ed.*, **17**, 1223 (1979).
5. T. P. Lodge and J. L. Schrag, *Macromolecules*, **15**, 1376 (1982).
6. W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1 (1974).
7. E. D. Von Meerwall, *Rubber Chem. & Technol.*, **57**, 523 (1985).
8. D. E. Kranbuehl and P. H. Verdier, *Macromolecules*, **18**, 1638 (1985).
9. M. F. Marmonier and L. Leger, *Phys. Rev. Lett.*, **55**, 1078 (1985).
10. H. Kim, T. Chang, J. M. Yohanan, L. Wang and H. Yu, *Macromolecules*, **19**, 2737 (1986).
11. J. Des Cloiseaux, *J. Phys. Lett.*, **45**, 17 (1984).
12. Yu. G. Yanovsky, V. N. Pokrovskii, Yu. K. Kokorin, Yu. N. Karnet and L. V. Titkova, *Vysokomol. Soedin.*, **30A**, 1009 (1988).
13. V. N. Pokrovskii and V. S. Volkov, *Polym. Sci. USSR* (Engl. Transl.) **20A**, 255; 2700 (1978).
14, Yu. K. Kokorin and V. N. Pokrovskii, *Vysokomol. Soedin.*, **32A**, (1990). In Print.
15. V. N. Pokrovskii and Yu. K. Kokorin, *Vysokomol. Soedin.*, **27B**, 794 (1985).
16. K. Kremer, *Macromolecules*, **16**, 1632 (1983).

17. K. Kremer and K. Binder, *J. Chem. Phys.*, **81**, 6381 (1984).
18. A. Baumgartner, *Ann. Rev. Phys. Chem.*, **35**, 419 (1984).
19. J. M. Deutsch, *Phys. Rev. Lett.*, **54**, 56 (1985).
20. A. Baumgartner and K. Binder, *J. Chem. Phys.*, **75**, 2994 (1981).
21. V. N. Pokrovskii and Yu. K. Kokorin, *Vysokomol. Soedin.*, **29A**, 2173 (1987).
22. V. N. Pokrovskii and Yu. K. Kokorin, *Vysokomol. Soedin.*, **26B**, 573 (1984).
23. M. Daoud and P.-G. de Gennes, *J. Polym. Sci.: Polym. Phys. Ed.*, **17**, 1971 (1979).
24. G. V. Vinogradov, Yu. G. Yanovsky and L. I. Ivanova, *Intern. J. Polym. Mater.*, **9**, 257 (1982).
25. H. Watanabe and T. Kotaka, *Macromolecules*, **17**, 2316 (1984).
26. G. Ronca, *J. Chem. Phys.*, **79**, 1031 (1983).