Entanglement behaviour in dynamic bulk and shear properties as studied by acoustic methods

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The effect of entanglements has been shown to contribute to dynamic bulk properties as well as to dynamic shear properties. The dynamic volume viscosity η'_v has been estimated from measurements of longitudinal and shear waves by acoustic methods. The measurements have been performed in a frequency range from 10^3 to 10^8 Hz in solutions of polybutadiene and poly(ethylene glycols) of different molecular masses. The shape of the relaxation spectrum of the volume viscoelasticity conforms to that found by Doi and Edwards for shear properties. The relaxational bulk modulus has been calculated in the framework of Doi–Edwards theory. The ratio η'_v/η'_s does not coincide with the theoretical value but appears to remain constant over a wide frequency range including that of entanglements.

(Keywords: entanglement; dynamic bulk properties; dynamic shear properties; acoustic methods; polybutadiene; poly(ethylene glycol))

INTRODUCTION

The influence of so-called entanglements on the *shear* viscoelasticity of polymeric melts and concentrated solutions has been studied extensively both experimentally and theoretically[1–9]. Substantial additional insight into polymer dynamics can be provided by studies of *volume* viscoelasticity (see e.g. refs. 10–13). However, no sufficiently definite evidence of the effects of *entanglements* on the volume viscoelasticity has been established up to now.

Theoretical work dealing with the effects of entanglements does not consider the volume deformation—the polymer is regarded as incompressible. This is understandable since in that way some subtle points calling for non-trivial assumptions are avoided. We shall suggest here a tentative generalization of the Doi–Edwards' theory[9], assuming that any change in the dimensions of polymeric coils, including isotropic expansion, will contribute to the stress tensor. A similar treatment applied rigorously to the bead–spring model of polymers in dilute solution is known to lead to the universal relation $\eta^*_v/\eta^*_s = 2/3$ between complex volume ($\eta^*_v = \eta'_v - i\eta''_v$) and shear ($\eta^*_s = \eta'_s - i\eta''_s$) viscosities at all frequencies[14]. Experimentally, the ratio is usually several times larger and depends on concentration and nature of the solvent[15,16]; some possible explanations of this fact have been discussed elsewhere[14,15].

Indications of the entanglement effects in volume viscosity have been found in some earlier papers[15,17–19], but those systems did not encourage a quantitative analysis. Only in ref. 15 was Edwards and Grant's theory[20] as extended by Berger and Straube[21] tentatively applied. Here, on the contrary, we are going to show by a more quantitative analysis that the theory of Doi and Edwards[9] can satisfactorily describe the entanglement behaviour even at molecular masses M not much in excess of the critical value M_c corresponding to the change in the steady flow shear viscosity $\eta_{s,0}$ dependence from $\eta_{s,0} \sim M$ to $\eta_{s,0} \sim M^{3.4}$ (ref. 1).

THEORETICAL

We shall assume here, following Lamb *et al.*[5], that the relaxation spectrum of a polymer can be divided into two main ranges. The high-frequency range embraces all scales of normal motional modes up to chain length corresponding to molecular mass $N_e = M_c/2M_0$, where M_0 is the molecular mass of the statistical segment. The nature of the relaxation spectrum in this range has no generally accepted explanation. The Rouse model is very popular but requires somewhat doubtful changes to account for the experimentally observed shape of the spectrum; the problem is discussed in more detail elsewhere[15]. Here we shall treat the shape of this portion of the spectrum semiempirically (see below).

The rest of the spectrum will be considered in the frame of Doi–Edwards' theory[9] to consist of two parts: rapid and slow ones. Consequently the total shear modulus G_e of all normal modes larger than N_e in scale is subdivided into two parts, G_r and $G_{sl} = G_{\mathrm{plateau}}$. The rapid part G_r relaxes via redistribution on Kuhn's segments among the

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portions of the chain between the 'slip links'. The slow part G_{sl} relaxes via the diffusion of a 'primitive chain' along its tube, which leads to its disengagement from the links. According to refs. 9 and 22:

$$G_e = (c/M)NRT \qquad G_{sl} = G_e - G_r = \tfrac{4}{5}G_e \tag{1}$$

where c is the mass concentration, M is the molecular mass of the polymer and N is the number of primitive chain segments per molecule. For the corresponding parts of the relaxational bulk modulus K we have, according to the Appendix:

$$K_e = G_e \nu \qquad K_{sl} = K_e - K_r = \tfrac{1}{2}\mathrm{K}_e \tag{2}$$

where ν is found as the ratio η'_v/η'_s for high frequencies (i.e. for subchain motions).

For the part of the complex shear viscosity connected with the slow relaxation, Doi and Edwards obtain the expression:

$$\eta_s^* = G_{sl}\frac{\pi^2}{8}\sum_{p=1,3,\ldots}\frac{1}{p^4}\frac{\tau_p}{1+\mathrm{i}\omega\tau_p} \tag{3}$$

Here $\tau_p = \tau_e/p^2$ is the relaxation time of the p-node normal mode and τ_e is the characteristic disengagement time:

$$\tau_e = \frac{N_0^3 l^4}{D_c d_e^2 \pi^2} \tag{4}$$

where l is the length of a subchain, N_0 is the number of subchains in a molecule, D_c is the diffusion coefficient of a Kuhn's segment and d_e is the length of the primitive chain segment (the distance between slip links). The same spectrum with K_{sl} is expected for the corresponding part of η_v^*.

The spectrum connected with G_r has not been considered explicitly by Doi and Edwards, who only noted that its characteristic time should be small. As a lower-limit estimation we can assume a Rouse-like spectrum with relaxation times extrapolated for the modes of corresponding scales from the high-frequency data, i.e. unrestricted by entanglements. On the other hand, the motions leading to redistribution of the chain between slip links involve diffusion of portions of the chain along the tube. This would mean that, for chains that are not very long compared to N_e, the longest of its characteristic times can be rather slow—actually not much faster than τ_e; thus one can assign to G_r a spectrum similar to (4) as an upper-limit estimation. This means in effect assuming that $G_{sl} = G_e$ and $G_r = 0$.

Actually only if the last assumption were valid could the relation $\eta_v^*/\eta_s^* = \mathrm{const}$ hold exactly for all frequencies. Otherwise there should be some deviation caused by the different values of K_{sl}/K_e and G_{sl}/G_e. It seems, however, that this deviation cannot be detected under existing experimental conditions.

EXPERIMENTAL

The methods we have used for measuring dynamic shear and volume viscoelastic properties have been described elsewhere (see Alig *et al.*[15] and references therein). Basically, shear acoustic impedance is measured, from which complex shear viscosity η_s^* or complex shear modulus $G^* = \mathrm{i}\omega\eta_s^*$ is calculated:

$$\eta_s^* = \eta'_s - \mathrm{i}\eta''_s = \eta'_s - \mathrm{i}\frac{G'}{\omega} = \frac{1}{\mathrm{i}\omega}(G' + \mathrm{i}G'') \tag{5}$$

The measurements cover the frequency ranges $f = \omega/2\pi =$ 23–1300 kHz at 190–320 K and 7–100 MHz at 293 K. The steady-state viscosities $\eta_{s,0}$ have also been measured.

The volume properties are expressed by the real part of the complex volume viscosity, and extracted from the attenuation of the longitudinal ultrasonic waves given by:

$$\alpha = \frac{\omega^2}{2\rho v^3}\frac{4}{3}\eta_{\mathrm{eff}} \tag{6}$$

where ρ is the density, v is the velocity of sound and the 'effective viscosity' is:

$$\eta_{\mathrm{eff}} = \eta'_s + \tfrac{3}{4}\eta'_v \tag{7}$$

The ultrasonic absorption α has been measured in the range 80 kHz–100 MHz mostly at a single temperature.

The frequency–temperature superposition (reduced variables) method has been used to enlarge the frequency range of shear measurements.

The values of $\eta_{s,0}$ have been used to calculate the frequency and viscosity shift factors[1]. It is to be noted that the applicability of this method to the total frequency range, including long-range (entanglement-effected) and short-range (local) motions, is in itself an important fact not explicitly assumed by the existing theories. The volume viscosity data refer to the experimental temperature.

In choosing the systems for studying the influence of entanglements on η'_v, one must fulfil two requirements. First, M must exceed M_c sufficiently for entanglement effects to be noticeable. At the same time, τ_e must be low enough for the frequencies $f \approx 1/(2\pi\tau_e)$ to be accessible for ultrasonic methods. This requires that the polymer should have a very flexible chain. Also there should be no side-groups capable of contributing to the high-frequency rotational-isomeric volume viscosity.

Two polymeric systems have been studied. The first is a polybutadiene (PB) of rather complex isomeric composition and not very narrow molecular mass distribution (*MMD*) ($M_n = 8600$, $M_w = 13\,000$) in solution in methylbutylbenzene (MBB) and toluene as solvents. More information on this system and experimental data on the shear and volume viscoelastic properties of MBB solutions and melt have been published[15].

The other system is a series of poly(ethylene glycols) (PEGs) with a rather narrow *MMD* ($M_w/M_n = 1.06$–1.14) produced by Merck-Schuchardt*; a physicochemical description of these can be found in ref. 23. Actual values of M have been measured viscosimetrically in water solutions (using $[\eta] = M^{0.76} \times 2.4 \times 10^{-4}\,\mathrm{dl\,g^{-1}}$; the constants are averaged literature data[23]).

Only longitudinal ultrasonic properties have been studied in this system since our shear apparatus does not work with electroconductive media. Though rich shear data exist in the literature[24], directly combining them with our data is not possible because no points were obtained in ref. 24 for the frequency range of interest here.

RESULTS AND DISCUSSION

As discussed elsewhere[15], the PB high-concentration solutions in MBB showed the relation $\eta'_v/\eta'_s = \mathrm{const}$ to hold over a wide frequency range, including the part

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* Except PEG-3000 (produced by 'LOBA') and PEG-5000 (a laboratory product)

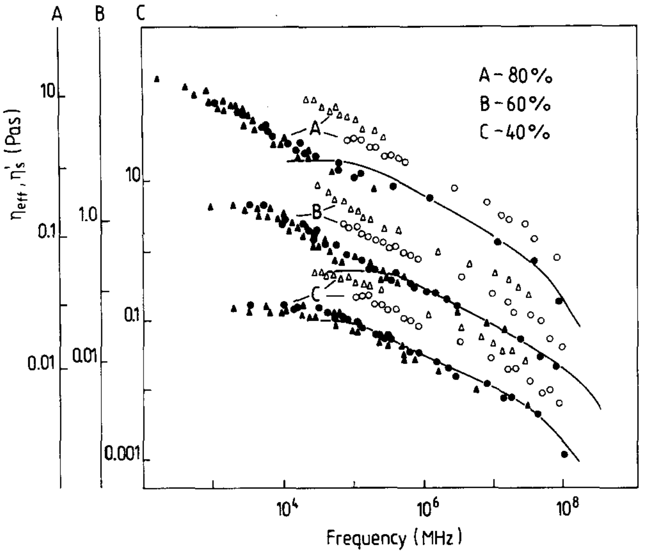

Figure 1 Frequency dependence of the effective (△, ○) and dynamic shear (▲, ●) viscosity for different volume fractions ϕ of polybutadiene in methylbutylbenzene (○, ●) and toluene (△, ▲) at $T = 293$ K. The data reduction is described in the text

where entanglement effects were quite prominent. To make this conclusion more certain we have added more measurements with toluene as solvent: owing to lower viscosity of toluene the spectra are shifted to higher frequencies and the experimental 'window' probes somewhat deeper into the entanglement range.

In *Figure 1* the results for the shear η_s' and effective η_{eff} viscosities for PB solutions in MBB and toluene are presented in reduced form, as $a_{ST}(\eta - \eta_\infty)$ vs. $a_{ST}f$. Here η_∞ is the asymptotic value for $f \rightarrow \infty$: it accounts for relaxation processes much faster than those represented in the observed spectra. The shift factor a_{ST} is chosen as $\eta_{s,0}T_{ref}\rho_{ref}/\eta_{ref}T_\rho$, where η_{ref} and ρ_{ref} are $\eta_{s,0}$ and ρ for the corresponding MBB solution at $T = T_{ref} = 293$ K. The way the η_s' data fall on a common curve illustrates the applicability of temperature- and solvent-frequency superposition laws; constant ratios η_{eff}/η_s' are clearly seen in the total frequency range where η_{eff} data are available.

To show that this range extends into the entanglement region we have drawn curves for η_s' in *Figure 1* calculated on the basis of the data found from the infinite-dilution measurements described in ref. 15. They represent the expected spectra involving motions on scales smaller than the separation of entanglement points. It is important for our present purpose that the assumptions in ref. 15 tend to estimate the widths of those spectra on a frequency scale closer to the upper possible limit. Thus the elevation of points over the left horizontal portions of the curves is almost certainly due to to entanglement effects. One more indication of this is the increase of the slope of experimental curves towards the low-frequency portion of the graphs: no other mechanism is known to lead to such an increase. As already mentioned, the wide *MMD* of our PB does not encourage a more quantitative analysis.

In *Figure 2* the effective viscosities of PEG melts at 338 K are shown (the data published in ref. 19 plus new results for $M = 6000$ and 20000). All curves coincide in the high-frequency range $f > 3$ MHz. The sequence of curves for $M = 1000$ and 2000 is natural for polymers without entanglements, though the latter curve already shows some steepening before levelling off at low frequencies. Other curves show clear effects of entanglements. The curves in *Figure 2* should be compared with those for η_s' in ref. 24. The latter are incomplete, being drawn partly by interpolation just in the range important for our discussion. But constancy of η_v'/η_s' over the entire f and M ranges can be implied by the following fact. At low frequencies, whenever η_{eff} curves flatten off to make possible a fair estimation of the limiting value $\eta_{eff,0}$, then $\eta_{eff,0}/\eta_s' = 3.5$ (that is $\eta_v'/\eta_s' = 3.3$) is found. As to the high-frequency range where the curves for all $M \geqslant 1000$ coincide, the ratio η_v'/η_s' should be constant as suggested by the results for other systems[15–17]. Its value must be equal to $\eta_{v,0}'/\eta_{s,0}'$ for $M = 1000$. Thus it is quite natural to assume that the curves in *Figure 2* also represent $\frac{3}{4}\eta_v'/(1 - 1/3.5) = 1.05\eta_v'$. It is important to note that the low-frequency ascent of the η_{eff} curves cannot be explained away as entirely due to the corresponding behaviour of the η_s' contribution. Whatever interpolation through the gap in the data of König *et al.*[24] is used to subtract η_s' from η_{eff}, the curves for $1.05\eta_v'$ would not drastically differ from those shown in *Figure 2* and used for further analysis.

It is interesting to note that the steepening of the low-frequency part of the curves already starts at $M = 2000$, which is more than twice as low as M_c. We think this is the first indication of an (underdeveloped) effect of entanglements, which seems more prominent in the shape of the spectrum than in $\eta_{s,0}$ behaviour. A question can then arise why $\eta_{s,0}$ behaves like $\eta_{s,0} \sim M$ as far as M_c. This can be understood if one takes into account that the Rouse-like contribution to $\eta_{s,0}$ does not increase with M beyond M_e whereas the Doi–Edwards contribution increases very rapidly; thus the $\eta_{s,0} \sim M$ law between M_e and M_c may be simply the effect of compensation of these two tendencies. One should mention, by the way, that the diffusion curve for PEG switches from $D \sim M^{-1}$ to $D \sim M^{-2}$ behaviour at $M = 2000$[25]. Another explanation for the underdeveloped entanglements in PEG below M_c is the assumption of a special entanglement between transient intermolecular structures formed by hydrogen bonds and having effective molecular masses above the critical values as discussed for poly(propylene glycol)[26,27].

To compare the results with the Doi–Edwards theory we must first eliminate other contributions. *Figure 3*

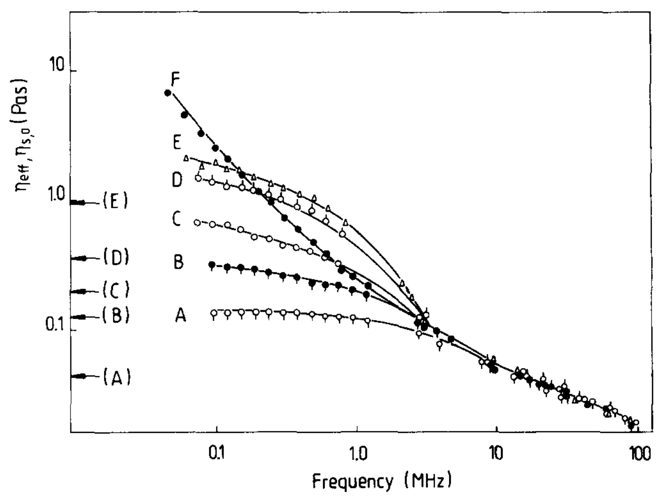

Figure 2 Effective viscosities of PEGs vs. frequency: A, $M = 1.0 \times 10^3$; B, $M = 2.0 \times 10^3$; C, $M = 3.0 \times 10^3$; D, $M = 5.0 \times 10^3$; E, $M = 6.0 \times 10^3$; F, $M = 20 \times 10^3$. Arrows on the left indicate the levels of $\eta_{s,0}$

shows the method of elimination. Curve A for $M = 1000$ was used to find (as in ref. 15) the parameters of the theory of Gaussian subchains with intrachain hydrodynamic interaction[28]. Curves B and B′ are obtained as extrapolations of this theory to $M = M_e = 2250$ and actual M ($= 6000$) respectively. Curve C is drawn as $\eta'_{v,B} + (\eta'_{v,B'} - \eta'_{v,B})K_r/K_e$ (here and later the second subscript refers to the curve). Values $\eta'_{v,D} - \eta'_{v,C}$ are those to be compared with Doi–Edwards theory. The theoretical value $K_r/K_e = 1/2$ was used in *Figure 3*.

Another way corresponding to the assumption that 'rapid' and 'slow' processes have actually the same kinetics would be subtracting curve B from D. This has also been tried and led to essentially the same estimations for τ_e.

Figure 4 shows the results of the described treatment for $M = 6000$ and 20 000. The broken curves are theoretical ones, obtained by averaging equation (3) with *MMD* found in refs. 23 and 29 for similar M_w/M_n values. (The method of averaging is described at length elsewhere[5].) The positioning of the curves along the f axis gives the values of τ_e as 0.25×10^{-6} s and 1.5×10^{-5} s for $M = 6000$ and 20 000 respectively (τ_e values refer to the monodisperse polymer with $M = M_w$). From the vertical positioning of the curves the value K_{sl} is found: $K_{sl} = 1.0 \times 10^7$ Pa (with 20% difference between values for $M = 6000$ and 20 000). Whether this value is to be accepted as $K_e/2$ or about equal to K_e depends on two questions, which are as yet difficult to decide upon. (i) Should one transfer the relation $K_{sl} = K_e/2$ found in the Appendix for the viscous drag mechanism to the case where η'_v/η'_s is definitely not equal to 2/3? (ii) Is the kinetics associated with K_r really rapid or can K_r and K_{sl} be allotted the same kinetics? The fact that $\eta'_v/\eta'_s = \text{const}$ holds over the entire frequency range (or, strictly speaking, no deviations from this relation have been indicated) suggests rather that the value found here as K_{sl} is, due to one or both reasons, a direct estimation of K_e.

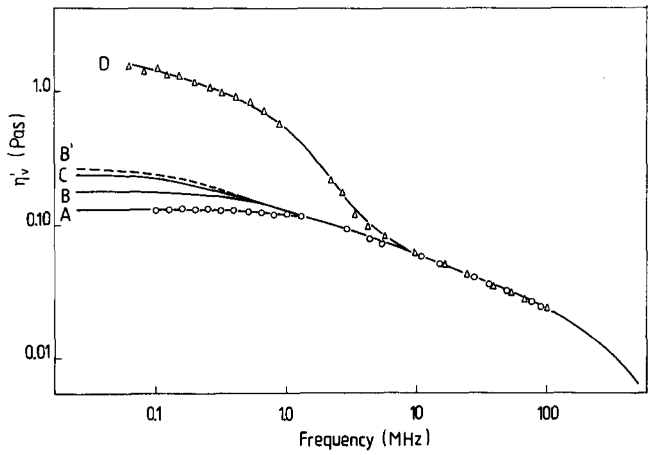

Figure 3 Evaluation of entanglement contribution to η'_v for PEG-6000. Points: A and D, measured values for $M = 1000$ and $M = 6000$. Calculated curves: A, B, B′, without restrictions by slip links for $M = 1000, 2250, 6000$ respectively; C, all rapid processes for $M = 6000$

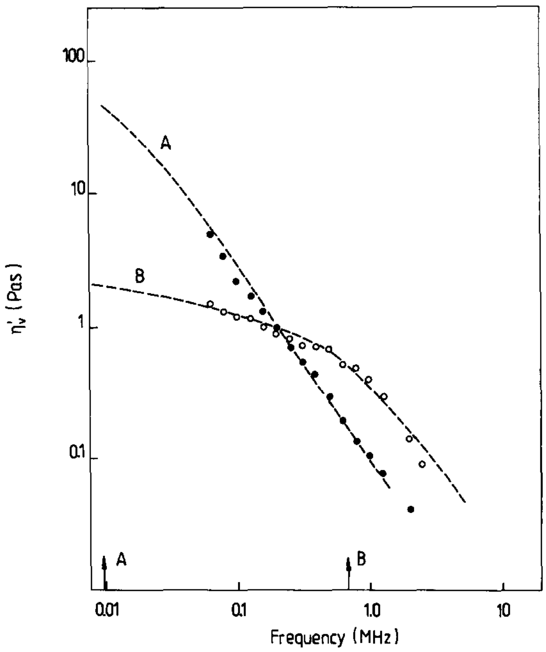

Figure 4 Entanglement contribution to η'_v for PEGs: $M = 6000$ (A) and 20 000 (B). Points are obtained by subtracting the contributions of rapid processes as shown in *Figure 3*. Curves are calculated by Doi–Edwards theory[9]. *MMD* is given by $M_w/M_n = 1.14$ and 1.12 for $M_w = 6000$ and 20 000 respectively. Arrows show relaxation frequencies (τ_e) for A and B

An independent calculation of τ_e is possible if the diffusion coefficient of a segment through the polymer is known. We used $D_c = 3 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$ found for polydimethylsiloxane[30], a polymer rather close to PEG in its molecular flexibility. The results are 1.0×10^{-6} s ($M = 6000$) and 3.5×10^{-5} s ($M = 20\,000$). The agreement seems quite satisfactory considering the approximate character of both d_e and D_c estimations (cf. ref. 22). Further analysis is required to decide whether this means that developed reptation actually dominates under these conditions.

We have to note that if one uses our $\eta_{\text{eff}}(f)$ curve to estimate $\eta'_s(f)$ (as $\eta_{\text{eff}}/3.3$) the estimations for τ_e and G_e differ somewhat from those found from ref. 24 by extrapolating the data obtained there for large M. Further studies are needed to elucidate this point.

CONCLUSIONS

It is shown that entanglements do contribute to volume as well as to shear viscosity of concentrated polymeric solutions and melts. The shape of the relaxation spectrum for volume viscoelasticity when $M > M_c$ (even at small $M_c - M$) conforms to that found by Doi and Edwards for shear properties. The ratio η'_v/η'_s does not coincide with the theoretical value found in the Appendix, but seems to remain constant over the entire frequency range, including that of entanglements, at least when M/M_c is not large.

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APPENDIX

On the relaxational bulk modulus in the framework of Doi–Edwards theory

As in the theories of rubber elasticity, Doi and Edwards introduce a pressure that accounts for the fact that slip links have certain equilibrium positions. We assume that this pressure does not vary when the chains undergo relaxational changes of configuration. In such a case the theory is readily generalized to include volume strains: only the kinetic contribution to the stress tensor needs to be considered.

After Rouse-like relaxation inside the primitive chain segments is completed, the stress tensor is:

$$\begin{aligned}\sigma_{lm} &= (3c/M)RTN[\langle(\boldsymbol{E}\cdot\boldsymbol{u})_l(\boldsymbol{E}\cdot\boldsymbol{u})_m\rangle - \delta_{lm}]\\ &= 2(c/M)RTN\varepsilon_{lm}\\ &= K_e\varepsilon_{jj}\delta_{lm} + 2G_e\varepsilon_{lm} \qquad \text{(A.1)}\end{aligned}$$

leading to:

$$K_e = \tfrac{2}{3}G_e = \tfrac{4}{3}(c/M)RT$$

Here R is the gas constant, T is the temperature, c/M is the number of moles per unit volume, $\boldsymbol{u}$ is the unit vector of direction between adjacent slip links, and the strain tensor $\boldsymbol{E}$ defines the transformation of radius vectors as:

$$\boldsymbol{r}' = \boldsymbol{E}\cdot\boldsymbol{r} \qquad \varepsilon_{lm} = \tfrac{1}{2}(E_{lm} + E_{ml}) - \delta_{lm}$$

Next, the 'rapid' stage is the equilibration of actual lengths of polymer molecules between slip links. After this is completed

$$\begin{aligned}\sigma_{lm} &= \frac{3c}{M}RTN\left(\left\langle\frac{(\boldsymbol{E}\cdot\boldsymbol{u})_l(\boldsymbol{E}\cdot\boldsymbol{u})_m}{|\boldsymbol{E}\cdot\boldsymbol{u}|}\right\rangle - \delta_{lm}\right)\\ &= (c/M)RTN(-\tfrac{1}{5}\varepsilon_{jj}\delta_{lm} + 2\times\tfrac{4}{5}\varepsilon_{lm})\\ &= K_{sl}\varepsilon_{jj}\delta_{lm} + 2G_{sl}\varepsilon_{lm} \qquad \text{(A.2)}\end{aligned}$$

which leads to:

$G_{sl} = \frac{4}{5}(c/M)RTN$ (as in ref. 22) and $K_{sl} = \frac{1}{2}K_e$

Note that unlike ref. 1 the change in the average number of primitive chain segments $N \rightarrow N\langle|\boldsymbol{E}\cdot\boldsymbol{u}|\rangle^{-1}$ during the 'rapid' process is not considered. Since $|\boldsymbol{E}\cdot\boldsymbol{u}| = 1 + \varepsilon_{jj}/3 + O(\varepsilon_{lm}^2)$, this change can be ignored in shear (the fact used by Graessley[22] in correcting the original result of ref. 1) but would seem to be important in a volume strain. This would lead to a contradiction: whereas escaping of chain ends through links on extension is really possible, finding new ones on contraction is clearly meaningless. We argue that if the strain is small and chains are not overlong, the existence of loose ends will enable the chains to slip through links without actually losing any appreciable number of them. Thus we can ignore the change of N.

The values $K_e/G_e = 2/3$, $K_{sl}/G_{sl} = 5/12$ and $K_r/G_r = 5/3$ following from the above calculation must not be considered as rigorous since they are really based on the approximate model of Gaussian elastic subchains. The extension of elementary subchains can be considered as an approximate description, for instance, of the orientation of freely linked rigid segments. But if rigid segments were not linked they would reorient only in a shear flow, not in a volume one. Thus at least the meaning of the elementary subchain must be different for the two kinds of deformation. Still, for the model described here it seems that multiplying all K/G ratios by a common coefficient $\nu/(2/3)$ would take care of this uncertainty. We cannot suggest any numerical value for ν but believe that it should not differ too much from the value 2/3 given by the model of Gaussian subchains. As argued elsewhere[14,15] the experimental findings seem to suggest that the kinetic elasticity contribution to pressure is not sufficient and some thermodynamic contribution must be considered. A possible explanation of the reason for the latter to possess a relaxation spectrum of the same shape as for the shear strain has been suggested[14,15]; if it is true, it should be applicable as well to the entanglement part of the spectrum.