Ultrasonic absorption and dynamic shear properties of the transition from dilute solution to the melt for polybutadiene

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The frequency dependence of ultrasonic absorption ($\alpha/f^2 \sim \eta_{eff}$) and dynamic shear data (G', G'', η_s') has been studied over a wide frequency range ($f = 10^4$–10^9 Hz) in solutions ($\phi = 0.03$–0.8) of polybutadiene in 2-methyl butyl benzene and toluene as solvents and in the melt ($\phi = 1$). The ultrasonic spectra and the frequency dependence of the shear properties are both described in terms of subchain motions, entanglement effects and local motions. For increasing concentrations the crossover from dilute solution behaviour to the entanglement regime was detected. We have attempted to describe, in terms of the subchain concept, the influence of concentration on motions at frequencies above the entanglement region. The subchain motion in dilute solutions and between the entanglements have been described by combining the Muthukumar–Freed theory with relaxation times calculated by the Moiseev version of the Zimm theory taking into consideration the solvent quality. Deviations from the expected screening of the hydrodynamic interaction for the highest concentrations and the melt have been attempted in order to describe additional local high frequency relaxations connected to the dynamic glass transition. By comparing longitudinal (η_{eff}) and shear (η_s') measurements it was possible to clarify the influence of subchain motions on shear and bulk properties.

(Keywords: polybutadiene; ultrasonic absorption; dynamic shear properties; dynamic bulk properties; concentration dependence; chain entanglements; subchain modes; local modes)

INTRODUCTION

The study of dynamic mechanical properties has proved to be a rich source of information about molecular motions and interactions in polymeric systems[1]. Much experimental and theoretical work has been done in this direction but several problems still have not been completely resolved. Firstly, there have been few systematic studies of the transition from a dilute solution via a concentrated solution to polymer melts, especially for high frequencies. Indeed, the high frequency range has been investigated relatively seldom even in dilute solution. This is partly because of the experimental difficulties, and partly due to the belief that theoretical treatments based on the Gaussian subchain model should not be applied to the shortest relaxation times. On the other hand, the question has been raised whether this model can formally describe the total spectrum. This matter deserves experimental elucidation.

Another group of problems arises from the studies of volume relaxation properties, which have been investigated even less than shear ones, although it has been already proved that they provide an effective method for the study of dynamic properties of polymer solutions, melts and bulk polymers[2,3]. To arrive at a sufficiently deep understanding one should compare the volume and

shear relaxation spectra. This requires parallel measurements of both types of properties on the same sample and in the same frequency and temperature ranges.

Another reason for parallel measurements is the fact that volume properties are measured by the propagation of longitudinal waves, in which volume and shear deformations are superimposed. Thus information purely on volume relaxation is inaccessible unless shear properties are also measured.

The relationships between the components of the complex longitudinal modulus M^*, the dynamic bulk modulus K^*, the dynamic shear modulus G^* and the corresponding dynamic bulk or volume η_v^* and shear η_s^* viscosities are given by:

$$M^* = K^* + 4/3G^*$$
$$K^* = K' + iK'' = K' + i\omega\eta_v' \tag{1}$$
$$G^* = G' + iG'' = G' + i\omega\eta_s'$$

The longitudinal wave used in the ultrasonic absorption and velocity experiment is a combination of both shear and compression. The two properties usually studied in the longitudinal experiment are the ultrasonic absorption α and the sound velocity, v. The first is generally expressed as α/f^2 because, for non-relaxing liquids, α is proportional to ω^2 ($\omega = 2\pi f$). The relation to the dynamic moduli or the dynamic viscosities is given in

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the following equations:

$$v^2 = (K' + 4/3G')/\rho \qquad (2a)$$

$$\alpha/f^2 = (2\pi^2/\rho v^3)(\eta'_v + 4/3\eta'_s) \qquad (2b)$$

$$= (\pi/\rho v^3 f)(K'' + 4/3G'')$$

where ρ is the density.

In order to be able to compare the absorption to the shear viscosity data we shall also use the effective viscosity η_{eff}, which is related to the absorption coefficient by the following equation:

$$\eta_{eff} = \eta'_s(\omega) + 3/4\eta'_v(\omega) = (3\rho v^3/8\pi^2)\alpha/f^2 \qquad (3)$$

Modern acoustical measurements for longitudinal waves deal with the investigation of dynamic processes using high frequency sound waves over a wide frequency range from a few kHz up to GHz. Accordingly, with these methods it is possible to detect a variety of motional processes involved in polymer dynamics, ranging from very localized modes to movements of the subchain (Rouse-type normal modes) and motions attributed to the effects of entanglements. In recent years a number of ultrasonic investigations have been published (e.g. refs 2–7 and references therein), but there are fewer studies of polymer melts[8-13]. Parallel measurements of the longitudinal and shear properties (i.e. ultrasonic absorption and dynamic shear viscosity) of the same system have been rare up to now[4,10,13]. The logitudinal[9,12] and shear[1] studies of the transition from solution to the melt are even more scarce and never have been performed parallel.

In this paper we will present an acoustic study of amorphous polybutadiene which has a molecular mass above the critical one. Both ultrasonic absorption and dynamic shear modulus measurements, which have been made at frequencies ranging from approximately 2×10^4 to 10^9 Hz, have been included.

It is our aim to study the modification of different molecular motions such as subchain motions (usually described in terms of normal modes), modes which are connected to the onset of entanglement effects and localized segmental modes, for the transition from dilute solution to the polymer melt by longitudinal, shear and bulk properties.

EXPERIMENTAL

The ultrasonic absorption measurements were performed by using the reverberation method[14,15] (0.1–2 MHz) and the resonator method[16] (0.3–6 MHz) in the low frequency range, and different pulse methods[6,17,18] over the range 3×10^6–10^8 Hz with an accuracy of between $5 \ldots 10\%$, $3 \ldots 5\%$ and $3 \ldots 10\%$, respectively. The limiting high frequency value $(\alpha/f^2)_\infty$ was obtained from Brillouin light scattering measurements[19] at about 6 GHz. The velocity was measured by an interferometer method at 1 MHz with an accuracy of 1%.

The dynamic shear properties $(G', G''$ or $\eta'_s)$ were determined by means of a torsional resonator[20] (0.2–1.5 MHz) at temperatures between 183 and 353 K and by an inclined incidence shear wave reflection technique[21] in the frequency range from 3–150 MHz at 293 K. Errors in the values of G' and G'' are estimated to be less than 10%.

The polybutadiene (PB) sample used in this study had a weight and number average molar mass of 1.3×10^4 and

Table 1 Parameters of the Vogel–Fulcher–Tamman–Hesse equation for the steady flow viscosities[a] in 2-methyl butyl benzene at different volume fractions of the polymer ϕ

ϕ	A (mPa)	B (K)	T_0 (K)
0.2	0.21	850	105
0.4	0.53	990	125
0.6	1.4	1020	145
0.8	2.3	1185	160
1.0	3.5	1345	176

[a] $\eta_0 - (1 - \phi)\eta_{0,s} = A \exp[B/T - T_0)]$

8.6×10^3, respectively $(M_w/M_n = 1.5)$. The molar mass was determined by g.p.c. Its chemical micro-structure, determined by n.m.r.[22], consists of 71% 1.2 (vinyl), with 62% iso and 38% *syndio* dyads, 20% 1.4-*trans* and 9% 1.4-*cis*. The glass temperature was determined in a DSC-2C (Perkin-Elmer) at a scan rate of 8 K/min to be 222 K. No crystallization effects could be detected. The temperature dependence of the steady flow shear viscosity was measured by using a capillary viscosimeter for the solutions and a Couette-type viscosimeter (Rheotest 2, MLW Medingen) for the melt. The viscosities for temperatures below 273 K were measured by a falling ball method. The experimental steady flow viscosity values $\eta'_s(0) = \eta_0$ were fitted by a Vogel–Fulcher–Tamman–Hesse (VFTH) equation:

$$\eta_0 - (1 - \phi)\eta_{0,s} = A \exp[B/(T - T_0)] \qquad (4)$$

where $\eta_{0,s}$ is the solvent viscosity. The parameters are summarized in *Table 1* for the different volume fraction of the polymer $\phi = c/\rho_0$. Using the steady flow viscosities, the time–temperature superposition method[22] was applied for an extension of the frequency range of the viscoelastic data (G', G'', η'_s). The measurements were reduced to 293 K. It should be noted here that the high frequency values are directly measured at 293 K in order to eliminate any errors from different shift factors.

RESULTS AND DISCUSSION

Dilute and semidilute solutions

In the systems studied it was possible to detect the limiting values $\eta'_{s,\infty}$ and $\eta_{eff,\infty}$ directly from high frequency measurements. Therefore, the dynamic shear properties and the effective viscosities for different concentrations could be expressed in terms of $\eta'_s(\omega) - \eta'_{s,\infty}$, G', $G'' - \omega\eta'_{s,\infty}$ and $\eta_{eff} - \eta_{eff,\infty}$, respectively.

The results for the reduced frequency dependence of shear and effective viscosity for 2-methyl butyl benzene (MBB) solution $(\phi = 0.03$ and $0.2)$ and toluene solution $(\phi = 0.1$ and $0.2)$ are plotted in *Figure 1*. The corresponding reduced values of G' and $G'' - \omega\eta'_{s,\infty}$ are given in *Figure 2*. All the data were reduced to the concentration of 3% of the MBB solution. The reduction to $\phi = 0.03$ was done by multiplying the data by $0.03/\phi$. The sets of data for the two solvents were superimposed by the usual reduction procedure with the shift factor $a_f = (\eta_0^{tol}/\eta_0^{MBB}) = (\eta_{0,s}^{tol}/\eta_{0,s}^{MBB}) = 0.42$. The dynamic shear viscosity data for the two solvents at $\phi = 0.2$ support the reduction method used.

The plot of $\eta_0(\phi)$ is linear within the error limits of measuring the dynamic properties up to $\phi \approx 0.05$, which is also the reciprocal value of the intrinsic viscosity $[\eta_0]$.
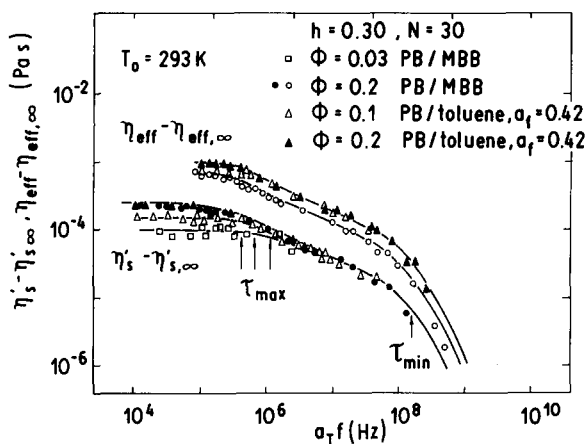
Figure 1 Frequency dependence of dynamic shear and effective viscosity for polybutadiene solutions in 2-methyl butyl benzene and toluene reduced to a concentration of $\phi = 0.03$ (2-methyl butyl benzene solution); solid lines are calculated with the parameters given in *Table 2*
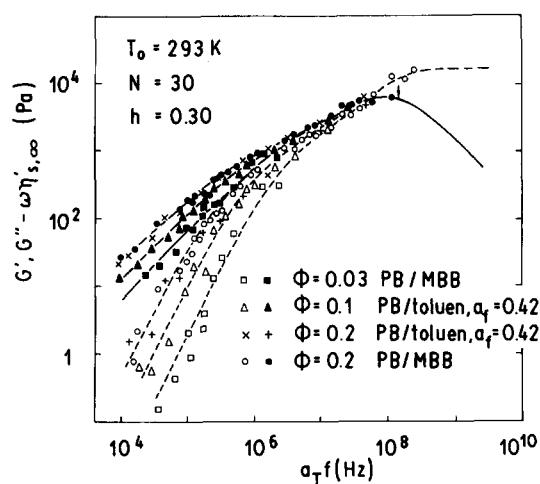

Figure 2 Frequency dependence of G' ($\bigcirc$, $\times$, $\triangle$, $\square$) and $G'' - \omega\eta'_{s,\infty}$ ($\bullet$, $+$, $\blacktriangle$, $\blacksquare$) for polybutadiene solutions in 2-methyl butyl benzene and toluene reduced to a concentration of $\phi = 0.03$ (2-methyl butyl benzene solution); curves as in *Figure 1*; arrow denotes τ_{min}

Thus, $\phi = 0.03$ can be considered as an infinite dilution, with respect to the properties of interest here. As for the high frequency range, all the data for $\phi \leqslant 0.2$ coincide quite well at $f \geqslant 2$ MHz. We thus have a sufficiently accurate representation of an infinite diluted polymer. The representation is sufficiently accurate and broad enough in the frequency range to justify a detailed comparison with theory. The Rouse–Zimm theory[23,24] with the Moiseev's method[25–27] of approximating the eigenvalues has been used to fit the theoretical calculations of η'_s and G' to these data by adjusting the values of the hydrodynamic interaction parameter h, the number of subchains in the molecule N and the shortest relaxation time τ_{min}.

$$G^* = \sum_{p=1}^{N} \frac{i\omega\tau_p G_p}{1 + i\omega\tau_p} + i\omega\eta'_{s,\infty} \tag{5}$$

$$G_p = \phi \frac{\rho N_A \kappa l^2}{M} \frac{1}{3}; \qquad \tau_p = \zeta/2\kappa\lambda_p; \qquad \kappa = 3kT/l^2 \tag{6}$$

$$\lambda_p = 2^{3/2 + \delta} h\lambda'_p/(N+1)^{1+\delta} + [1 + 2\sqrt{2}hZ(\delta)]\Theta_p^2$$

$$\text{for } p = 1, \ldots, 4 \tag{7}$$

$$\lambda_p = 2(1 - \cos\Theta_p)\left(1 + 2\sqrt{2}h \sum_{n=1}^{N-1} n^{-\delta}\cos n\Theta_p\right)$$

$$+ 2\sqrt{2}h(N-1)^{-\delta}\cos N\Theta_p$$

$$- 2\sqrt{2}N^{-\delta}\cos(N-1)\Theta_p \qquad \text{for } p > 4 \tag{8}$$

where $\Theta_p = p\pi/(N+1)$, λ'_p are Zimm eigenvalues with respect to solvent quality, κ is the force constant, ζ is the friction coefficient, k is the Boltzmann constant and $Z(\delta)$ is the Rieman zeta function. δ is the parameter of thermodynamic quality and was taken as $\delta = 0.6$, which is usual for good solvents.

The theoretical curve for the shear data $\phi = 0.03$ in *Figures 1* and *2* were obtained as the best fit with $h = 0.30$, $N = 30$ and $f_N = (2\pi\tau_{min})$, as marked by the arrow. The margin of uncertainty is estimated as 10–20%.

The rms length l of the subchain and its hydrodynamic radius a (i.e. that of the equivalent bead) estimated from h and assuming the local viscosity η_{loc} to be equal to $\eta_{0,s}$, are

$$l = (\sqrt{3}\tau_{min}\lambda_N kT/\pi^{3/2}\eta_{loc}h)^{1/3} = (18 \pm 1)10^{-10} \text{ m} \tag{9}$$

$$a = hl(\pi/3)^{1/2} = (5.5 \pm 1)10^{-10} \text{ m} \tag{10}$$

where λ_N is the maximum eigenvalue, k is the Boltzmann constant and T is the temperature. From these estimations the size of the molecular coil will be $L = l\sqrt{N} = 90 \times 10^{-10}$ m. The value found from Kuhn's statistical segment length $l_K = 11.7 \times 10^{-10}$ m and its molecular mass 260 (ref. 28) is $L = 80 \times 10^{-10}$ m. The agreement is satisfactory.

The relation between l and l_K also seems plausible. One further illustration of the adequacy of the model is provided by the calculation of the limiting high frequency shear modulus G'_∞:

$$G'_\infty/\phi = (\rho RT/M_n)N = 8.3 \times 10^6 \text{ Pa} \tag{11}$$

Table 2 lists the values found experimentally together with the adjustable parameters mentioned above and the maximum relaxation time $\tau_{max} = \tau_1$. The experimental and calculated values of $(\eta'_s - \eta'_{s,\infty})/\phi$ for the frequency f_N are also listed in *Table 2*.

The difference between theory and experiment is not significant. The important conclusion is the ability of the bead spring model to account for experimental data even in the high frequency region where it certainly cannot be expected literally. Up to now the only deviation from the behaviour predicted by this model is the high value of $\eta'_{s,\infty}$ (ref. 1). No unanimously accepted explanation of this high value has been suggested,

It should be mentioned here that the high frequency limiting intrinsic viscosity $[\eta'_{s,\infty}] = \lim_{c\to 0} (\eta'_{s,\infty} - \eta_{0,s})/(c\eta_{0,s})$ is about 0.8×10^{-3} m^{-3} kg^{-1} for the PB/MBB system. Although the high frequency behaviour of $G''/\omega = \eta'_s$ is somewhat doubtful[1], this low value is rather surprising, compared with other authors[1,29]. No final explanation of this fact can yet be given, but we feel that there is a connection with the high flexibility of the PB chains and the low viscosity of our solvents. The high frequency limiting value for the effective viscosity $[\eta_{eff,\infty}]$ is also about 0.7×10^{-3} m^{-3} kg^{-1}. Following Cooke and Matheson[30], this low value can be attributed to local motions with low relaxation amplitudes for our systems.

As the concentration increases (see *Figure 1*) the slow relaxation of the subchain motions progressively shifts to longer times, while the nature of the higher modes remains

Table 2 Characteristic parameters for the subchain motions in the system PB/2-methyl butyl benzene estimated by a combination of the Muthukumar–Freed theory with relaxation times from the Moiseev theory

ϕ	h	τ_{min} (10^{-9})	τ_{max} $(10^{-7}\,s)$	N or $(N_c)_{soln}$	$\dfrac{\eta_{eff}-\eta_{eff,\infty}}{\eta'_s-\eta'_{s,\infty}}$	ζ $(10^{-11}\,mPa)$	η_{loc} (mPa)	\multicolumn{2}{c}{$\dfrac{(\eta'_s(f_N)-\eta'_{s,\infty})/\phi}{(mPa)}$}	G'_∞/ϕ $(10^6\,Pa)$
								Experimental	Theoretical	
0.03	0.30	–	1.38	30	–	1.5[b]	1.42[b]	–	3.8	–
0.1[a]	0.30	1.1	1.60	30	4.8	1.5[b]	1.42[b]	2.6	3.8	6.0
0.2	0.30	1.1	3.70	30	2.7	1.5[b]	1.42[b]	2.6	3.8	6.0
0.4	0.25	1.6	–	23	2.7	2.2	2.1	5.0	4.4	9.5
0.6	0.2	2.0	–	15	2.5	2.5	2.4	11	5.8	13
0.8	0.16	2.7	–	11	2.4	3.3	3.2	28	6.7	30
1.0	0.3	3.8	–	9	2.2	5.3	5.1	93	12	82

[a] Solvent: toluene

[b] $\eta_{loc} = \eta_{0,s}$

essentially unchanged with higher concentration. As stated above the solution with $\phi > 0.05$ cannot be regarded as infinitely dilute. This is seen from the data for $\phi = 0.10$ and $\phi = 0.20$, at low frequencies. The corresponding points in *Figures 1* and *2* illustrate the trend to prolong the relaxation spectrum to longer times. This can be related to the theory of Muthukumar and Freed[28], for semi-dilute solutions, which predicts the concentration dependence of relaxation times:

$$\tau_p = \tau_p^0(1 + c\mathscr{A}p^{-\kappa}) \qquad (12)$$

where c is the concentration, p the mode index, τ_p^0 is the infinite dilution relaxation time (in our case obtained from the Moiseev theory) and κ is a parameter for the solvent quality (in accordance with the above value of δ we used $\kappa = 0.8$). The value of $\mathscr{A}$ has been calculated from the shifts of the lowest relaxation times $\tau_1 = \tau_{max}$ at $\phi = 0.1$ and $\phi = 0.2$ and was found to agree with the value given in ref. 31 for Θ-solvents:

$$\mathscr{A} = \pi N_A l^2/2M_s(1/3)^{1/2}(Nl/2\pi)^{1/2} \qquad (13)$$

where N_A is the Avogadro's number and M_s is the molecular mass of the statistical segment. Note that the smallest relaxation times are not affected by equation (8) (cf. ref. 32) which removes possible doubt as to the reliability of Muthukumar's treatment for large p.

From *Figure 1* it is obvious that the frequency dependence of the effective viscosity shows the same type of frequency dependence as measured for $\eta'_s(\omega)$: the ratio $(\eta'_v - \eta'_{v,\infty})/(\eta'_s - \eta'_{s,\infty})$ is independent of frequency (and temperature) but does depend on the solvent. The ratio for the MBB solution is 2.4, whereas it is about 5 for the toluene solutions[4]. This kind of difference was found for all concentrations $0.1 \leqslant \phi \leqslant 0.8$ (ref. 33) which can be seen from *Table 2*. Only the value $(\eta'_v - \eta'_{v,\infty})/(\eta'_s - \eta'_{s,\infty})$ varies with concentration. The explanation of the values of η'_v/η'_s found here requires special attention. Due to the fact that the spectra of volume and shear relaxation in the frequency region of the subchain motions were very similar in shape for the systems considered, very similar molecular mechanisms can also be suggested for both. This could have been expected on general grounds which were also recognized in the case of structural relaxations in low molecular liquids[34]. The similar frequency dependence of volume and shear viscosities can be explained on the basis of the model of Gaussian subchains[35]. The purely viscous drag gives $\eta'_v/\eta'_s = 2/3$ which coincides with the result obtained by Okano[36,37] but deviates from a ratio of $-1/3$, also given in literature for polymer

solutions[38,39]. However, the experimental values seem to be in excess of this ratio. Therefore, a thermal relaxation is suggested[35] involving a part of rotation–isometric heat capacity and characterized by the Zimm-like spectrum. The possible influence of the changes in the environment of a subchain accompanying its deformation can be discussed as an alternative[4,35]

Concentrated solutions and melt

Proceeding to higher polymer content one can expect a gradual development of several new features. In the lowest frequency range the so-called entanglement effects should be setting on. As to the range of motions unhindered by entanglements, it is customary to believe that interchain mutual influence leads to an increase in the local viscosity over that of the solvent and to a further screening of the intrachain hydrodynamic interaction, ending with $h = 0$ in the melt. However, the basic picture of the chain as a series of beads connected with Gaussian springs can be retained. Here we shall analyse the possibility of explaining the present results under this assumption without changing the geometrical parameters of a subchain (l and a) or the number of subchains in the molecule N. Alternative possibilities will be discussed below.

Entanglement effects. The experimental values for the dynamic shear viscosities $\eta'_s - \eta_{0,s}$ reduced to 293 K are given in *Figure 3* to show the adequacy of the temperature–frequency superposition[1] and the high frequency limiting values. The results for the concentration dependence of excess effective $\eta_{eff} - \eta_{eff,\infty}$ and shear viscosities $\eta'_s - \eta'_{s,\infty}$ of PB in MBB solutions at 293 K are given in *Figures 4* and *5*. The corresponding concentration dependence of G' and $G'' - \omega\eta'_{s,\infty}$ are shown in *Figures 6* and *7*. One can see a qualitative change in the frequency dependence of viscoelastic properties between $\phi = 0.2$ and $\phi \geqslant 0.4$ (see deviations from the solid lines in *Figures 4–7*). It is natural to assume a crossover to the 'entanglement behaviour' which is known to be most obvious in the change of the slope of $\eta_0(M)$ curves for the melt at a critical molecular mass.

In concentrated solutions the critical molecular mass for the solution $(M_c)_{sol}$ can be assumed to be inversely proportional to the volume fraction ϕ of the polymer[40]:

$$(M_c)_{sol} = M_c/\phi \qquad (14)$$

where M_c is the characteristic molecular mass of undiluted linear polymers. From equation (10) and from
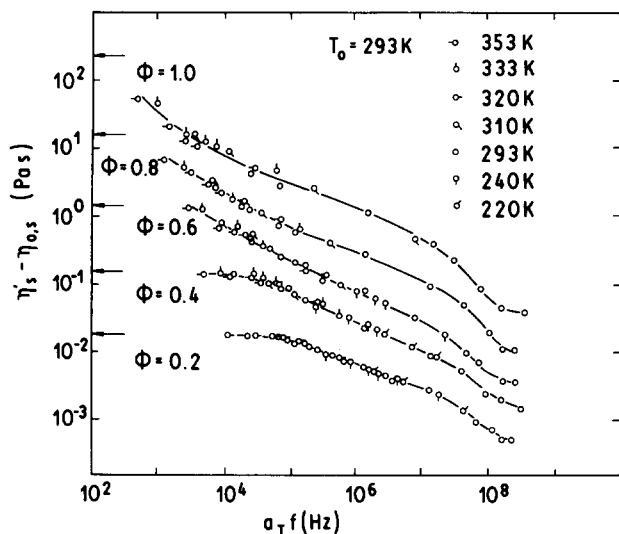
Figure 3 Frequency dependence of the dynamic shear viscosity for different volume fractions of polybutadiene in 2-methyl butyl benzene. The steady flow viscosities are indicated by arrows. ϕ is the polymer volume fraction
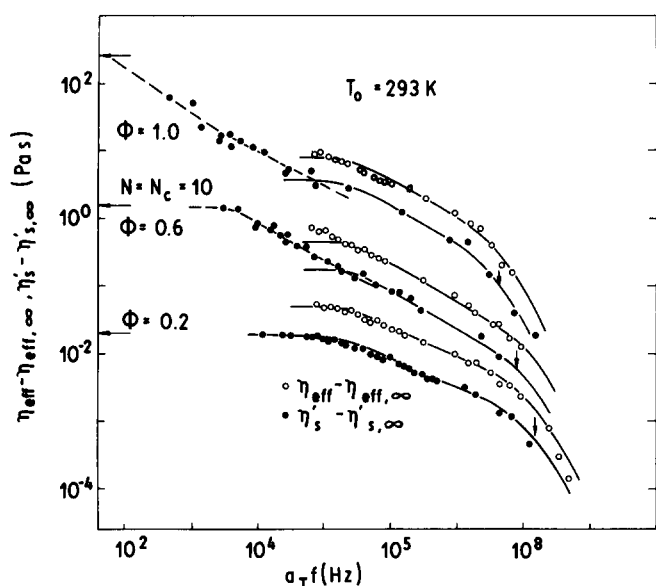

Figure 4 Frequency dependence of excess effective $\eta_{eff} - \eta_{eff,\infty}$ and dynamic shear viscosity $\eta'_s - \eta'_{s,\infty}$ of polybutadiene in 2-methyl butyl benzene at 293 K for polymer volume fractions $\phi = 1.0$, $\phi = 0.6$ and $\phi = 0.2$. Solid lines: Muthukumar–Freed–Moiseev theory; dotted lines: Edwards–Grant model; the steady flow viscosities and f_N are indicated by arrows

$M_c = 4100$ for 1.2 polybutadiene[28] we calculated for $M_w = 13\,000$ a critical volume fraction of the polymer ϕ_c of about 0.3. This agrees with the value $0.2 < \phi_c < 0.4$ estimated above.

The polymer studied here is not sufficiently monodisperse to justify attempts to distinguish between several existing approaches to the effect of entanglements (see for example refs 40–44). Actually there is not much qualitative difference between the results of those approaches. Therefore, we choose, rather arbitrarily, the approach of Edwards and Grant[44] using for the estimation of the 'tube parameter', the method suggested in reference 45. (The choice can be backed by the opinion of Doi and Edwards that Edwards and Grant's model may be suitable for shorter chains or for lower concentrations[43].)

A fairly good representation of the low-frequency portion of the curves is obtained in this way as shown by the dashed lines in *Figures 4* and *5*. Deviations at higher frequencies can be understood as manifestation of the crossover to the motions of unrestrained portions of the chains.

Subchain motions. From the double logarithmic plots in *Figures 4* and *5* it can be seen that the curves of the frequency dependence of the effective and shear viscosity are parallel for all concentrations and the melt. This means that the ratio $(\eta'_v - \eta'_{v,\infty})/(\eta'_s - \eta'_{s,\infty})$ is independent of frequency and temperature. This ratio (see *Table 2*) varies between 2.2 and 2.8 for all concentrations, including the dilute solution.
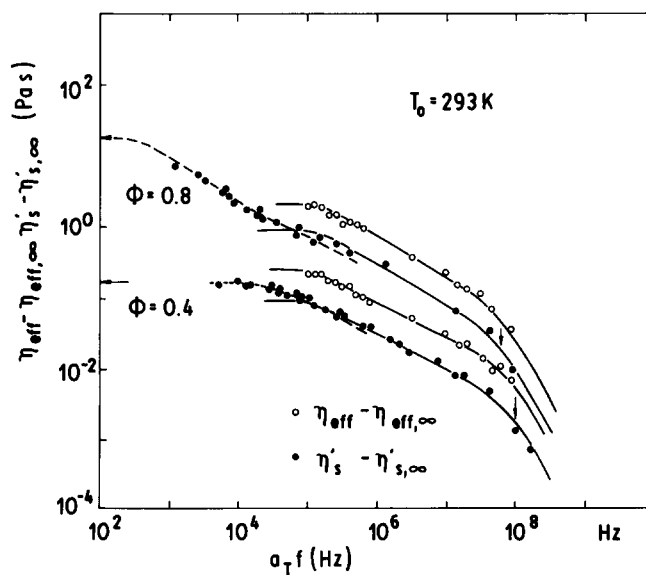

Figure 5 Frequency dependence of excess effective $\eta_{eff} - \eta_{eff,\infty}$ and dynamic shear viscosity $\eta'_s - \eta'_{s,\infty}$ of polybutadiene in 2-methyl butyl benzene at 293 K for polymer volume fractions $\phi = 0.8$ and $\phi = 0.4$. Symbols as for *Figure 4*
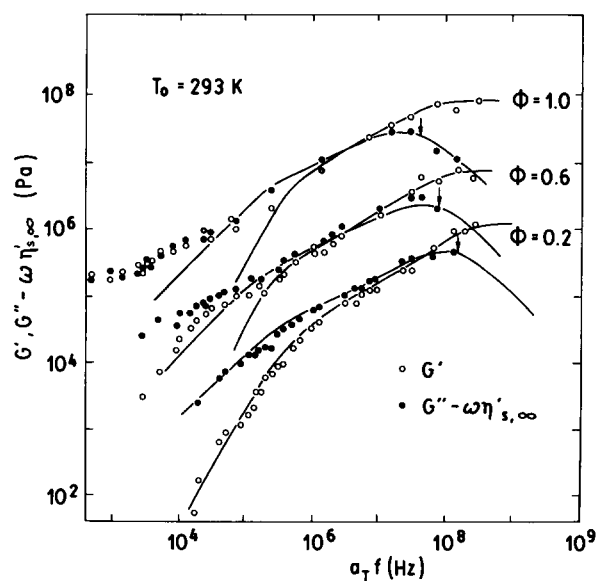

Figure 6 Frequency dependences of G' and $G'' - \omega\eta'_{s,\infty}$ of polybutadiene in 2-methyl butyl benzene reduced to 293 K (ϕ, polymer volume fraction: 1.0, 0.6, 0.2). The solid lines are calculated from the Muthukumar–Freed theory using Moiseev's eigenvalues

Figure 7 Frequency dependences of G' and $G''-\omega\eta'_{s,\infty}$ of polybutadiene in 2-methyl butyl benzene reduced to 293 K (ϕ, polymer volume fraction: 0.8, 0.4). The solid lines are calculated from the Muthukumar–Freed theory using Moiseev's eigenvalues
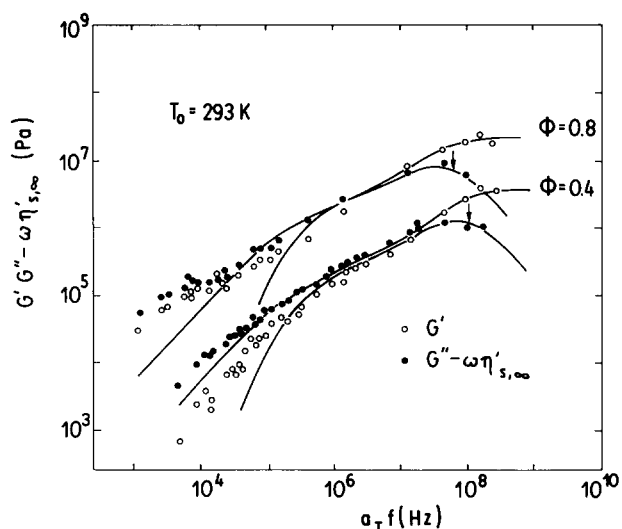
From the constant ratio $(\eta_{eff}-\eta_{eff,\infty})/(\eta'_s-\eta'_{s,\infty})$ one can conclude that $\eta'_v(\omega)$ can also be expressed by a broad relaxation spectrum in the region of subchain motions and that the shape of the relaxation spectra for $\eta'_v(\omega)$ is similar to that for $\eta'_s(\omega)$, as in the case of dilute solutions (see above).

We shall try to describe subchain motions retaining all the essential features of the theories evolved for dilute and semidilute solutions. The number of subchains in the unrestrained portion of the chains will be taken as

$$N_c = N\phi M_c/M = \phi M_c/M_s \qquad (15)$$

where M_s is the molar mass of the statistical segment.

The values of h in *Table 2* are estimated from the shape of the curves. A number of theoretical curves with a different h is drawn for each N using Moiseev's method for calculating relaxation times and introducing a Muthukumar–Freed first order correction (equations (12) and (13); note that the latter does not involve any new adjustable parameters), and the best fit curve is chosen by superimposing them on the experimental points. The value τ_{min} is found from the horizontal positioning of the curve. The independent vertical positioning of the curves $\eta'_s - \eta_{s,\infty}$ and G' gives the degree of agreement between calculations and experimental results, as shown in *Figures 4* and *5*. The values of parameters are listed in *Table 2*.

First of all one should notice the nonmonotonous variation of h with concentration. In all solutions, including $\phi = 0.8$, the variation is in the expected direction, meaning an additional screening of intramolecular hydrodynamic interaction, not covered by Muthukumar–Freed's correction. But the reversal to a high value of h in the melt implies that there is another effect changing the shape of the relaxation spectrum in the same direction as hydrodynamic interaction but having quite a different physical nature. One of the possibilities is given by the suggestion of a frequency- (or, rather, scale-of-motion) dependent tube diameter in the frames of Edwards–Grant model[45]. The overall variation of h shown in *Table 2* may reflect the competition of those two effects. In the absence of a comprehensive theory we shall retain h as the

parameter describing the shape of the spectrum but having, at least in the melt, a purely formal meaning.

According to equation (6) we calculated the friction coefficient ζ from τ_{min} and λ_{N_c} and the local viscosity $\eta_{loc} = \zeta/6\pi a$. For l and a we used the values from equations (9) and (10). *Table 2* shows an increase in ζ and η_{loc} with an increasing polymer content, as expected from the substitution of solvent molecules by polymer segments in the vicinity of the macromolecules.

The next striking conclusion obtained from the attempt to use the ideas which proved to be quite acceptable for dilute and semidilute solutions for higher concentrations, is a very large disagreement in the absolute values of both G' and η'_s. The theory predicts $G'_\infty/\phi = 8.3 \times 10^6$ Pa for all ϕ, and $(\eta'_s(f_N)-\eta'_{s,\infty})/\phi$ (where $f_N = 1/2\pi\tau_{min}$) to be approximately proportional to τ_{min}. The values given in *Table 2* show that for the melt G'_∞ is about 10 times and $\eta'_s(f_N)-\eta'_{s,\infty}$ about 8 times greater than the theoretical values. The difference between the dilute solutions and the melt is even greater since the former have experimental values about 1.4 times below theoretical ones. If one considers N, l and a to be purely intramolecular characteristics, the only way to deal with this disagreement is to assume that not only the friction coefficients but also the elastic moduli associated with relaxation times in the spectrum correspondingly increase as a result of interchain interactions.

Another explanation can be suggested if one assumes that in concentrated systems some local motions at high frequencies (see for example, references 1, 48, 49) contribute to viscoelastic properties. One can argue that the idea of the discrete subchains of the size l is an indirect way of describing the systems where the spectrum is limited by the influence of internal viscosity[51].

By comparing ultrasonic, n.m.r., dynamic light scattering and dielectric measurements in PB melts[49,50] one can conclude that the highest mode of the ultrasonic and shear spectra in PB are directly connected to the main transition (dynamic glass transition). Furthermore it has been shown[52] that a superposition of a single relaxation, connected to the main transition ($\tau_0 \approx \tau_{min}$) and the original Rouse behaviour ($h=0$) can also describe the deviations from the free-draining behaviour in the high frequency part for high polymer concentrations. The formal superposition of additional relaxation processes to subchain motions can be considered as an increasing number of relaxators due to intermolecular interactions (which may be described by intermolecular springs). However, no molecular concept for the main transition exists up to now.

CONCLUSIONS

By choosing a polymer of moderately low molecular mass and employing sufficiently wide frequency and temperature ranges, we have been able to obtain reliable curves for dynamic shear viscosity and modulus viscosity as a function of reduced frequency covering for dilute and semidilute solutions over the entire dispersion range and for concentrated solutions and melt over most of the dispersion range. More explicitly, there is sufficient evidence that the relaxation spectrum of a continuous or quasi-continuous nature is limited on both sides with no direct indications of other relaxation frequencies in the immediate vicinity of the covered range. It follows that a continuous spectrum of scales of motion, most probably

those of the chain backbone, is represented by the experimental data. There seems to be no doubt that the longest scale is that of the chain length. Effects of 'entanglements' must be considered for concentrated systems. The nature of the shortest scale is not so clear. For dilute and semidilute solutions the quickest possible motion was estimated to involve the length of the chain in the order of the statistical segment (the rms length of the shortest subchain $l = 1.8$ nm) which is in sufficient quantitative agreement with the model of discrete Gaussian subchains. The actual reason for this limiting scale may be the internal viscosity, though we have not tried to go into quantitative details of such a picture.

The most important question is whether this limit of the motion scales remains unchanged with increasing polymer content or whether new motions come into play in concentrated systems. Here we have given priority to exploring the conclusions suggested by the first assumption. The result is the formal possibility of quantitative description of our data, with due allowance for entanglement effects, by the theory in which the local viscosity η_{loc}, and the intrachain hydrodynamic interaction parameter h depend on the concentration of the polymer. The increase of η_{loc} with ϕ is as expected. However, the value of G'_∞/ϕ also shows a strong concentration dependence which deviates from the model of Gaussian subchains and seems to be connected to the interchain cooperation.

The variation of h with polymer concentration is not monotonous. First it decreases with increasing ϕ, which means that the Muthukumar–Freed correction for interchain screening of interaction is not sufficient for high values of ϕ. But when $\phi \rightarrow 1$, h again increases. This indicates that the competing influence of some quite different effects causes a change in the shape of the relaxation spectrum from the expected Rouse-like behaviour.

The comparison of the data obtained from longitudinal and shear measurements shows that relaxation spectra for volume and shear deformations have the same shape and similar temperature dependences of relaxation times. (The latter follows from equality of shift factors used in reduction of both sets of data). This leaves no doubt that the molecular motions responsible for shear and volume relaxation processes are the same. But the ratio of shear and volume viscosities substantially exceeds the theoretically predicted value 2/3 and depends on the solvent nature and concentration.

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