Viscoelastic Properties of Polymer Solutions in High-Viscosity Solvents and Limiting High-Frequency Behavior. III. Poly(2-substituted methyl acrylates)[1]

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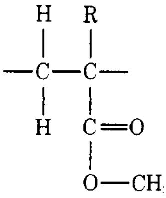
ABSTRACT: The storage (G') and loss (G'') shear moduli were measured for dilute solutions of four poly(2-substituted methyl acrylates) in two Aroclors with the modified Birnboim transducer. The substituents were methyl, ethyl, n-butyl, and phenyl. The molecular weights of the samples were between 6.5×10^4 and 2.85×10^6. The range of concentration was 0.73×10^{-2} to 4.28×10^{-2} g/ml and the temperatures were between 8.3 and 43.8°C. The frequency range was 0.25 to 630 Hz. Data at different temperatures for G' and $G'' - \omega\eta_s$, where ω is the radian frequency and η_s the solvent viscosity, were successfully combined by the method of reduced variables with a reference temperature of 25°C. The intrinsic dynamic viscosity at high frequency, $[\eta']_\infty$, is independent of the molecular weight for each polymer, but differs among the various polymers: poly(methyl methacrylate) 22.8 ml/g; poly(methyl-2-ethyl acrylate) 18.5 ml/g; poly(methyl-2-n-butyl acrylate) 13.3 ml/g; and poly(methyl-2-phenyl acrylate) 18.5 ml/g. A comparison of these results with former data on polystyrene and poly(α-methylstyrene) can be made; all these polymers have the vinyl group as the backbone supporting unit. The contributions to the high-frequency viscosity per monomer unit may then be interpreted in terms of the types of substitution of this vinyl group. They increase when the monomer substitution changes from single aromatic, through double aliphatic, to mixed aliphatic–aromatic. For the sufficiently monodisperse samples the frequency dependence of G' and G'' could be described by the Peterlin internal viscosity theory. On basis of the experimental results the latter theory is compared with more recent theories on the dynamic viscoelastic behavior of dilute polymer solutions.

Several studies of the limiting high-frequency viscoelastic behavior of polymers, dissolved in high-viscosity solvents, have been reported from this laboratory.[2–4] Some insight has been gained in the physical mechanism causing the real part of the dynamic viscosity η' to approach a finite limiting value η'_∞ at high frequencies which is higher than that of the solvent. Here we continue to use the symbol η'_∞ for the first high-frequency plateau value of η' (where the loss modulus $G'' = \omega\eta'$ becomes directly proportional to the radian frequency ω), even though at very much higher frequencies there may be a zone of further frequency dependence followed by a lower plateau,[3] so the subscript ∞ is somewhat arbitrary. In the preceding papers of this series,[3,4] hereafter referred to as I and II, it was shown that η'_∞ is independent of molecular weight and of the degree and extent of branching of the polymer molecule. It depends only on the concentration of the solution (but much less than the steady-flow viscosity η) and the type of polymer investigated. These results imply that at high frequencies only short-range internal dynamics of the polymer chains play a role. For example, the specific difference in the high-frequency viscoelastic behavior observed between polystyrene and poly(α-methylstyrene) in paper I should be attributed to a change in C–C backbone mobility due to the introduction of the α-methyl group.

To study the dependence on polymer species more extensively, in this paper an investigation is reported into the high-frequency viscoelastic behavior of a series of linear poly(2-substituted methyl acrylates) with various molecular weights. Their general structure may be designated by:



$$\begin{array}{ccc} & \mathrm{H} & \mathrm{R} \\ & | & | \\ - & \mathrm{C} - & \mathrm{C} - \\ & | & | \\ & \mathrm{H} & \mathrm{C{=}O} \\ & & | \\ & & \mathrm{O{-}CH_3} \end{array}$$

where the substituent R respectively represents a methyl, ethyl, n-butyl, or phenyl group. Their structure corresponds to that of polystyrene and poly(α-methylstyrene) in the sense that they all have the vinyl group as the backbone supporting unit. These polymers could be dissolved in the same highly viscous chlorinated diphenyl (Aroclor) as used in papers I and II. This will permit an interpretation of differences between the high-frequency viscoelastic behavior of the different polymer species in terms of their respective types of substitution of the vinyl group.

Experimental Section

The samples investigated were kindly provided by Professor M. Kurata of Kyoto University, Japan. The poly(methyl-2-ethyl acrylate) and poly(methyl-2-n-butyl acrylate) samples have been described before by Iwama and coworkers.[5] Poly(methyl-2-ethyl acrylate), poly(methyl-2-n-butyl acrylate), and poly(methyl-2-phenyl acrylate) were prepared by an anionic polymerization process. They were subsequently fractionated by means of an elution column. The weight average molecular weights $\bar{M}_w$ of the fractions used for this investigation are given in Tables I, II, and III. A determination of the polydispersity of some of the poly(methyl-2-ethyl acrylate) samples[5] provided a weight-to-number average ratio of the molecular weights of about 1.05. As will be shown later, the molecular weight distributions of the poly(methyl-2-n-butyl acrylate) and poly(methyl-2-phenyl acrylate) fractions are probably even narrower.

The poly(methyl methacrylate) was a radically polymerized commercial sample. To eliminate any unreacted monomer or low molecular weight contaminations the sample was precipitated four times using toluene as a solvent and methanol as a nonsolvent. Finally, the polymer was freeze dried from a benzene solution. As the limiting high-frequency viscosity has been shown to be independent of the molecular weight of the polymer, no efforts were made to fractionate this sample. Its intrinsic viscosity in benzene at 25.0°C amounts to 275 ml/g, corresponding[6] to a viscosity average molecular weight $\bar{M}_\eta$ of 1.5×10^6.

Prior to use the samples were dried in vacuo at 60°C. The samples were dissolved in Aroclor 1254, Lot D-612, by heating at 60°C with occasional stirring. Two solutions were made in Aroclor 1248, Lot D-501. Depending on the molecular weight and concentration, complete dissolution was obtained within a period of 2 days to 3 weeks. The concentrations of the solutions are given in Tables I–IV.

Storage (G') and loss (G'') moduli were measured with the modified Birnboim transducer, equipped with a computerized on-line data acquisition and processing system as described elsewhere.[7] The frequency range was 0.25 to 630 Hz. Measurements were usually performed at 5°C intervals, the maximum range being from 8.3 to 43.8°C. The viscosity of the Aroclor 1254 ranged from 12,000

Table I
Parameters at Low and High Frequencies, Reduced to 25°C, for Poly(methyl-2-ethyl acrylate) in Aroclor 1254

	Sample $\overline{M}_w \times 10^{-4}$					
	45.9	45.9	68.7	68.7	68.7	100.0[a]
$c \times 10^2$, g/ml	1.15	2.11	1.60	2.88	4.28	1.41
η, P	187	367	349	775	1788	12.12
log J_e^0	−3.54	−3.54	−3.36	−3.46	−3.54	−3.21
$[\eta/(\eta - \eta_s)]^2 J_{eR}^0$	0.44	0.49	0.39	0.43	0.48	0.35
η'_∞, P	82.0	94.1	89.9	115.4	148.8	3.33
P/N	23	23	23	23	23	23
h^*	0.20	0.15	0.17	0.14	0.11	0.17
φ/f	2.5	1.9	1.8	1.7	1.6	1.8
log τ_1	−1.00	−0.81	−0.50	−0.36	−0.14	−1.83
log $\overline{M}_{ve}/\overline{M}_w$	0.07	0.10	0.14	0.14	0.14	0.08
log G'_∞	4.46	4.77	4.60	4.89	5.07	4.63
log (G'_∞/v_2)	6.47	6.54	6.47	6.50	6.51	6.53

[a] Results in Aroclor 1248 (η_s = 2.57 P at 25°C).

P at 8.3°C to 2.68 P at 43.8°C.; at 25.0°C it was 67.7 P. The temperature range used for the solutions in Aroclor 1248 was −0.1 to 25.0°C., the corresponding Aroclor viscosity range being from 555 to 2.57 P.

Results

Storage and Loss Moduli. Figures 1–4 show some examples of the viscoelastic behavior, one for each polymer. All data obtained on the storage and loss moduli for the solutions are plotted in reduced form[8] as $G'_p = (\rho_0 T_0/\rho T)G'$ and $(G'' - \omega\eta_s)_p = (\rho_0 T_0/\rho T)(G'' - \omega\eta_s)$ against the reduced radian frequency ωa_T with logarithmic scales. Here ρ and T are the density of the solution and the absolute temperature, respectively, at which the measurements were made. The subscript zero refers to the reference temperature of 25°C; η_s is the viscosity of the solvent; the shift factor a_T is obtained either from the temperature dependence of the polymer contribution to viscosity or empirically, as described in papers I and II.

Figure 1 shows the results for a solution of poly(methyl-2-ethyl acrylate) of molecular weight 1.0×10^6, concentration 1.41×10^{-2} g/ml, in Aroclor 1248. It shows the familiar behavior of polymers of high molecular weight. The terminal, low-frequency zone, and the intermediate-frequency region are well developed. At high frequencies, since the slope of log $(G'' - \omega\eta_s)_p$ against log ωa_T is unity, the limiting high-frequency value η'_∞ of the real part of the dynamic viscosity is determined, and it is higher than the solvent viscosity.

Figure 2 shows the data for a solution of poly(methyl-2-n-butyl acrylate) of molecular weight 2.35×10^5, concentration 1.86×10^{-2} g/ml, in Aroclor 1254. Data for a solution of poly(methyl-2-phenyl acrylate) of molecular weight 2.63×10^5, concentration 3.23×10^{-2} g/ml, in Aroclor 1254 are given in Figure 3. These two figures show the behavior of lower molecular weight polymers; the intermediate frequency region is narrower than in Figure 1, leaving only a small inflection in $(G'' - \omega\eta_s)_p$ between the terminal and high-frequency regions.

Figure 4 shows the results for a solution of the poly(methyl methacrylate) sample in Aroclor 1254, with a concentration of 3.95×10^{-2} g/ml. It shows the typical behavior of a polydisperse polymer, characterized by the absence of a clear transition between the terminal zone and the intermediate frequency region. The additional effect of the high molecular weight of this sample makes it impossible to observe any terminal zone even at the lowest frequencies attainable. The high-frequency behavior, however, is uninfluenced by the polydispersity. The unit slope of log $(G'' - \omega\eta_s)_p$ against log ωa_T again provides for the calculation of η'_∞.

From the data in the terminal zone, the steady flow viscosity η and the steady-state compliance J_e^0 of the solutions may be calculated. These results, together with the values of η'_∞ for the solutions investigated, are assembled in Tables I to IV. Because of the absence of a terminal zone for the highest molecular weight sample of poly(methyl-2-n-butyl acrylate) and for poly(methyl methacrylate), the last two columns of Tables II and IV contain only the high-frequency viscosity data.

High-Frequency Viscosity. The results on η'_∞ for all the solutions are summarized in Figure 5. As in papers I and II, the data are plotted as log (η'_∞/η_s) against c, where c is the concentration in grams per milliliter. The results formerly obtained for polystyrene and poly(α-methylstyrene) are also indicated in this figure by means of dashed lines.

The conclusions put forward in papers I and II are all confirmed by these results. In particular, η'_∞ is again independent of the molecular weight of the polymers, within the ranges covered. Second, because the time–temperature superposition can be applied at all temperatures, the relative viscosity at high frequency, η'_∞/η_s, does not depend on the solvent viscosity for the Aroclor solvent. The two measurements made on solutions in Aroclor 1248, designated

Table II
Parameters at Low and High Frequencies, Reduced to 25°C, for Poly(methyl-2-n-butyl acrylate) in Aroclor 1254

	Sample $\overline{M}_w \times 10^{-4}$						
	7.52	23.5	23.5	23.5	23.5	285[a]	285
$c \times 10^2$, g/ml	4.09	1.86	2.30	2.74	3.96	0.73	1.38
η, P	209	163	188	216	359		
log J_e^0	−5.14	−4.42	−4.42	−4.39	−4.36		
$[\eta/(\eta - \eta_s)]^2 J_{eR}^0$	0.22	0.26	0.23	0.25	0.28		
η'_∞, P	114.3	88.8	91.0	96.4	115.4	2.86	80.9
P/N	22	22	22	22	22		
h^*	0.22	0.22	0.20	0.22	0.20		
φ/f	4.0	3.0	2.7	2.7	2.3		
log τ_1	−2.45	−1.79	−1.72	−1.70	−1.50		
log $\overline{M}_{ve}/\overline{M}_w$	−0.14	−0.11	−0.08	−0.06	−0.03		
log G'_∞	4.97	4.71	4.80	4.87	5.03		
log (G'_∞/v_2)	6.42	6.50	6.49	6.49	6.48		

[a] Results in Aroclor 1248 (η_s = 2.57 P at 25°C).

Table III
Parameters at Low and High Frequencies, Reduced to 25°C, for Poly(methyl-2-phenyl acrylate) in Aroclor 1254

	Sample $\bar{M}_w \times 10^{-4}$				
	6.5	6.5	6.5	26.3	26.3
$c \times 10^2$, g/ml	0.96	1.81	4.21	1.94	3.23
η, P	89.4	118	267	168	304
log J_e^0	−5.55	−5.32	−5.11	−4.34	−4.04
$[\eta/(\eta - \eta_s)]^2 J_{eR}^0$	0.18	0.18	0.22	0.24	0.46
η'_∞, P	80.5	94.4	150.7	92.3	121.3
P/N	33	33	33	33	33
h^*	0.25	0.25	0.25	0.25	0.20
φ/f	7.0	6.0	4.5	3.0	2.8
log τ_1	−2.81	−2.72	−2.34	−1.62	−1.43
log $\bar{M}_{ve}/\bar{M}_w$	−0.29	−0.28	−0.28	−0.01	0.01
log G'_∞	3.96	4.29	4.62	4.40	4.59
log (G'_∞/v_2)	6.08	6.13	6.10	6.21	6.19

Table IV
High-Frequency Viscosity, Reduced to 25°C, for Poly(methyl methacrylate) in Aroclor 1254

	Sample $\bar{M}_n \times 10^{-4}$				
	150	150	150	150	150
$c \times 10^2$, g/ml	1.39	1.45	2.27	2.73	3.95
η'_∞, P	92.9	92.9	113.2	126.4	163.0

Table V
Summary of the Limiting High-Frequency Results for All Polymers Investigated

Polymer	$[\eta']_\infty$, ml/g	$[\eta']_\infty \times M_0/N_A \times 10^{20}$, ml	log G'_∞/v_2
Polystyrene	14.3	0.247	6.62
Poly(methyl-2-*n*-butyl acrylate)	13.3	0.314	6.48
Poly(methyl-2-ethyl acrylate)	18.5	0.350	6.50
Poly(methyl methacrylate)	22.8	0.379	
Poly(α-methylstyrene)	22.2	0.435	6.38
Poly(methyl-2-phenyl acrylate)	18.5	0.498	6.15

by small symbols, fall on the same lines as those made on solutions in Aroclor 1254.

The intrinsic viscosities at high frequency for these polymers, $[\eta']_\infty$, can be obtained from the slope of the straight lines in Figure 5 as $[\eta']_\infty = \ln(\eta'_\infty/\eta_s)/c$. The values are given in Table V.

Discussion

Low-Frequency Behavior. From the steady-flow viscosity η and the steady-state compliance J_e^0, as given in Tables I to III, we may derive another quantity characterizing the linear viscoelastic behavior of polymers at low frequencies:

$$\left(\frac{\eta}{\eta - \eta_s}\right)^2 J_{eR}^0 = \frac{cRT}{M}\left(\frac{\eta}{\eta - \eta_s}\right)^2 J_e^0 \qquad (1)$$

where R is the gas constant and J_{eR}^0 is the reduced steady-state compliance. In the limit of zero concentration:

$$j_{eR}^0 = \lim_{c \to 0}\left(\frac{\eta}{\eta - \eta_s}\right)^2 J_{eR}^0 = S_2/S_1^2 \qquad (2)$$

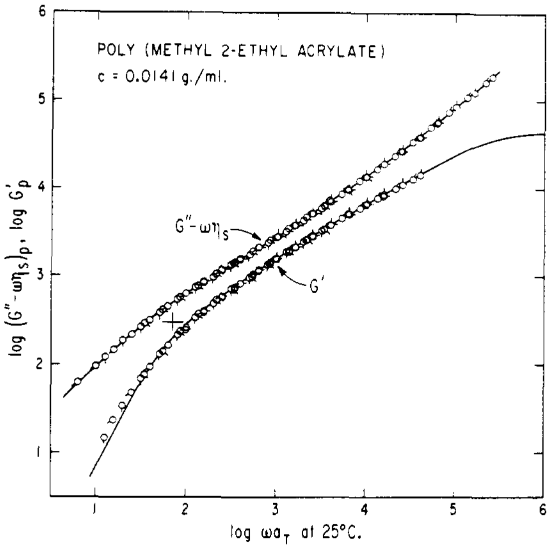


Figure 1. Storage (G'_p) and loss ($(G'' - \omega\eta_s)_p$) moduli, reduced to 25°C, plotted logarithmically against frequency for poly(methyl-2-ethyl acrylate) in Aroclor 1248, $\bar{M}_w = 1.0 \times 10^6$. Directions of pips show temperatures of measurement: pip up, −0.1°C; 45° clockwise rotations, 5.1, 9.8, 14.7, 20.1, and 25.0°C, respectively. Curves drawn according to Peterlin theory with $N = 381$, $h^* = 0.17$, and $\varphi/f = 1.8$.

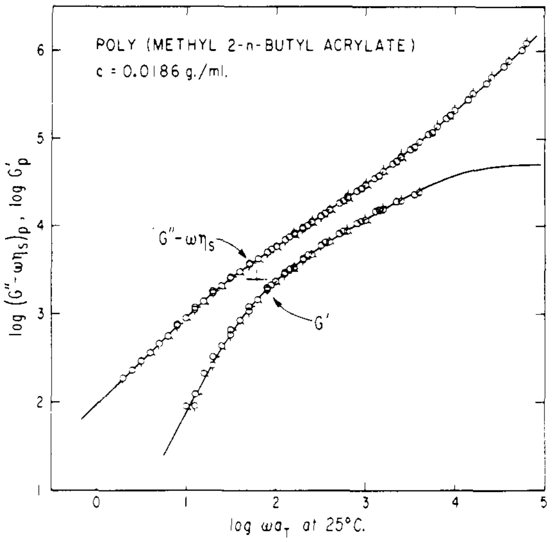


Figure 2. Plots of G'_p and $(G'' - \omega\eta_s)_p$, reduced to 25°C, for poly(methyl-2-*n*-butyl acrylate) in Aroclor 1254, $\bar{M}_w = 2.35 \times 10^5$. Pip up, 9.7°C; 45° clockwise rotations, 15.2, 20.2, 24.9, and 30.0°C, respectively. Curves drawn according to Peterlin theory with $N = 75$, $h^* = 0.22$, and $\varphi/f = 3.0$.

where j_{eR}^0 is the intrinsic reduced steady-state compliance; S_2/S_1^2 is a dimensionless ratio, where $S_1 = \Sigma_p(\tau_p/\tau_1)$ and $S_2 = \Sigma_p(\tau_p/\tau_1)^2$, τ_p being the relaxation times corresponding to the normal modes of motion of the macromolecule. Theoretical predictions of the numerical value of S_2/S_1^2 are strongly dependent on the molecular model employed in describing the viscoelastic behavior of the macromolecule.[8] Values of particular interest are the Rouse[9] free-draining value of 0.4 and the Zimm[10] result of 0.206, as obtained for a macromolecule with dominant hydrodynamic interaction. Both values hold for a macromolecule represented by a bead-spring chain with an infinite number of beads. Lowering the number of beads increases the theoretical value of S_2/S_1^2; a value of 1.0 is attained for the case of an elastic dumbbell (two beads connected by one spring).[11]

Experimentally, the corresponding quantity $[\eta/(\eta -$

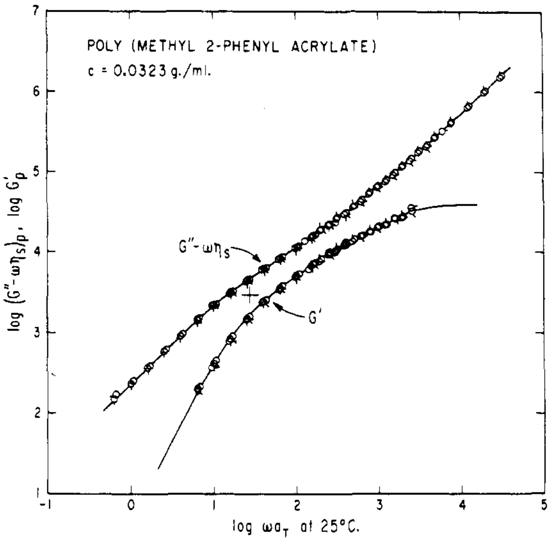


Figure 3. Plots of G'_p and $(G'' - \omega\eta_s)_p$, reduced to 25°C, for poly(methyl-2-phenyl acrylate) in Aroclor 1254, $\bar{M}_w = 2.63 \times 10^5$. Pip up, 9.5°C; 45° clockwise rotations, 14.6, 20.1, 25.1, 31.1, and 35.6°C, respectively. Curves drawn according to Peterlin theory with $N = 50$, $h^* = 0.20$, and $\varphi/f = 2.8$.

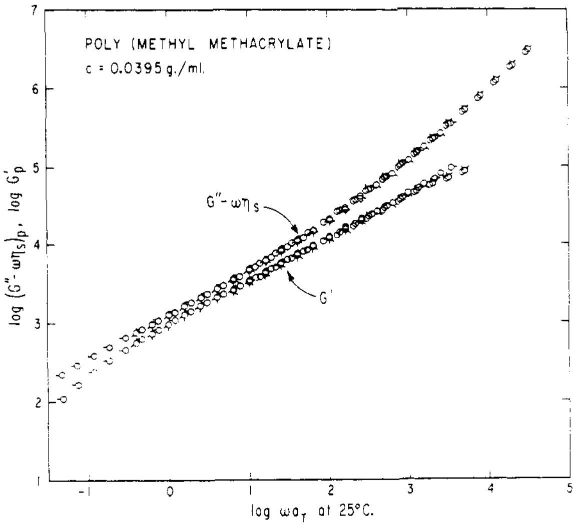


Figure 4. Plots of G'_p and $(G'' - \omega\eta_s)_p$, reduced to 25°C, for poly(methyl methacrylate) in Aroclor 1254, $\bar{M}_\eta = 1.5 \times 10^6$. Pip up, 9.5°C; 45° clockwise rotations, 14.6, 20.1, 25.0, 31.1, 35.8, and 43.8°C, respectively.

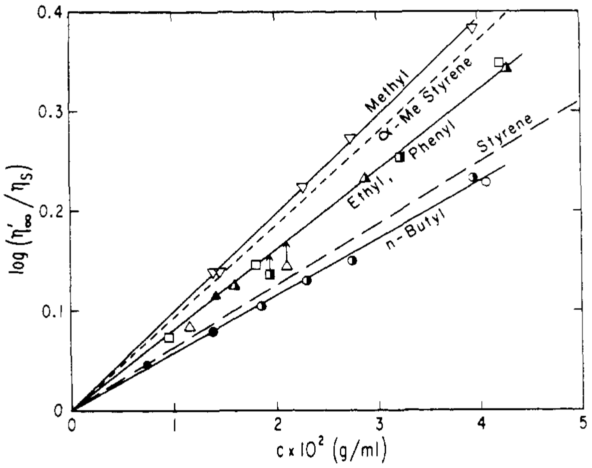


Figure 5. Plot of log (η'_∞/η_s) against concentration for all samples investigated. The origins of the points are indicated by the names at the curves. Various fillings of the symbols indicate different molecular weights: open symbols, lowest molecular weight samples; half-filled, intermediate molecular weight; filled, highest molecular weight. Small symbols represent measurements done in Aroclor 1248.

$\eta_s)]^2 J_{eR}^0$ appears to be dependent on the molecular weight distribution of the polymer[12] and the concentration of the solution. The results in Tables I to III do not show a significant molecular weight dependence, so the molecular weight dependence of j_{eR}^0 does not seem to play a detectable role for the present samples. While most of the values of $[\eta/(\eta - \eta_s)]^2 J_{eR}^0$ for the poly(methyl-2-*n*-butyl acrylate) and poly(methyl-2-phenyl acrylate) samples are close to the Zimm result, all values for the poly(methyl-2-ethyl acrylate) samples appear to be even higher than the Rouse result. This indicates that the former samples probably have a narrower molecular weight distribution than the latter.

In all cases the value of $[\eta/(\eta - \eta_s)]^2 J_{eR}^0$ tends to increase with an increase of concentration. This effect, representing a progressive change from Zimm-like to Rouse-like behavior,[13] has recently been treated theoretically by Wang and Zimm.[14]

High-Frequency Behavior. In general the present results are in agreement with the observations made previously[3,4] on polystyrene and poly(α-methylstyrene). The high-frequency behavior of a polymer is related to the short-range internal dynamics of the chain. The availability of data on six different polymer species now enables us to look for a relation to chemical structure. Apparently, the way the data are plotted in Figure 5 does not give an indication of any such relation.

Fixman and Kovac[15] recently made an intensive theoretical study of the viscoelastic behavior of models in which constraints of constant bond lengths and constant bond angles are introduced. For a freely jointed chain of beads connected by rods, without hydrodynamic interaction between the beads, they derive that the high-frequency viscosity is overwhelmingly an effect realized on a very local scale. This explains why the intrinsic high-frequency viscosity $[\eta']_\infty$ is independent of molecular weight and solvent viscosity. The actual value of $[\eta']_\infty$ depends on the structural details of the chain. This can be treated by imposing different constraints on bond angles in the model chains.

In this sense a plotting of high-frequency viscosity data as a function of concentration appears to be rather arbitrary. In order to compare results for different polymers, they should be related to the number of monomeric chain units present per unit volume. Therefore, the results in Figure 5 have been replotted in Figure 6 to give log (η'_∞/η_s) as a function of the number of monomer units per milliliter: $N_A c/M_0$, where N_A is Avogadro's number and M_0 the molecular weight of the monomer unit. Three groups of polymers are now clearly discernable in Figure 6: (i) a group with polystyrene as the only representative, containing single aromatic substituted monomer units, giving the lowest contributions to the high-frequency viscosity; (ii) the groups of poly(methyl methacrylate), poly(methyl-2-ethyl acrylate), and poly(methyl-2-*n*-butyl acrylate), with double aliphatic (or aliphatic ester) substituted monomer units giving rise to intermediate contributions to the high-frequency viscosity; (iii) the group of poly(α-methylstyrene) and poly(methyl-2-phenyl acrylate), with mixed aliphatic–aromatic substituted monomer units, giving the largest contributions to the high-frequency viscosity. Attributing these results to structural effects in the chains is quite obvious. Values of $[\eta']_\infty M_0/N_A$, derived from the slopes of the lines, are included in Table V.

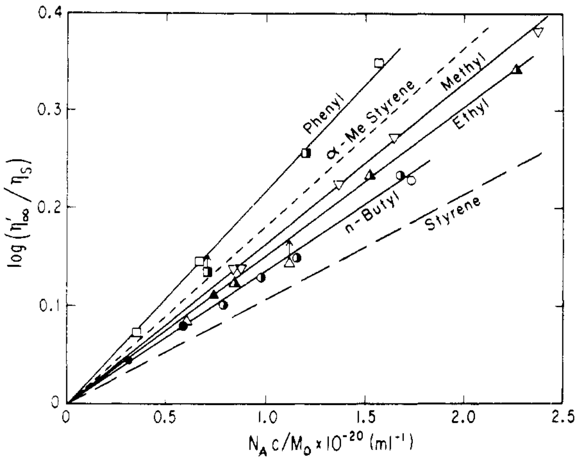


Figure 6. Data of Figure 5, replotted as log (η'_∞/η_s) against the number of monomer units per milliliter: cN_A/M_0. Symbols as in Figure 5.

In the case of the aliphatic disubstituted chains it turns out that an increase of the size of the side groups decreases the contribution to the high-frequency viscosity to a small extent. Apparently, no direct steric effects are involved in the high-frequency viscosity, because one would have expected the opposite effect in that case. This agrees with the experimental observations that the unperturbed chain dimensions of poly(methyl-2-ethyl acrylate), poly(methyl-2-*n*-butyl acrylate),[5] and poly(methyl-2-phenyl acrylate)[16] are of approximately the same magnitude and comparable with literature values for other polymers. Various other reasons, however, might be responsible for this effect such as differences in tacticity between the polymers, differences in solvent power, or a certain degree of coupling between neighboring monomer units. The latter makes an interpretation of high-frequency viscosity data in terms of individual bonds perhaps a too simplistic approach.

Frequency Dependence of G' and G''. As in papers I and II, an attempt was made to fit the experimental data to the Thurston–Peterlin[17] formulation of the Peterlin[18] theory, which incorporates internal viscosity into the Rouse–Zimm theory. This led to satisfactory results only in the cases of sufficiently monodisperse samples. Figures 2 and 3 give examples of the excellent fits obtained for the poly(methyl-2-*n*-butyl acrylate) and the poly(methyl-2-phenyl acrylate) samples. In the case of the less monodisperse poly(methyl-2-ethyl acrylate) samples, Figure 1, rather poor fits of G' are observed at low frequencies. This is directly related to the high values of $[\eta/(\eta - \eta_s)]^2 J_{eR}{}^0$ obtained for these samples.

The parameters needed to describe the shape and the spacing of the curves are the finite number of submolecules N, the hydrodynamic interaction parameter h^*, and the ratio φ/f, where φ is the internal viscosity parameter and f the friction factor of a bead. N should be proportional to the molecular weight of the polymer, so that P/N (P being the degree of polymerization) is a constant. Formerly,[4] a value of P/N for polystyrene was chosen on the basis of oscillatory flow birefringence data. However, for the present polymers no birefringence data are available so the assignment of the parameters is somewhat less certain. The parameters used are given in Tables I to III.

The calculated magnitudes of G' and G'' have been adjusted slightly as indicated by the crosses in Figures 1–3. Their ordinates correspond to $G_+ = cRT/M$ in the theory. The experimental value of G_+ corresponds to a molecular weight $\bar{M}_{ve}$ which is somewhat different from the actual molecular weight. The values of $\bar{M}_{ve}/\bar{M}_w$ are given in Ta- them. The position of the curves along the frequency scale bles I to III; no attempt is made at present to interpret is determined by the magnitudes of the relaxation times in the solvent used. In particular the longest relaxation time τ_1 may be obtained from matching the theoretical and experimental curves along the frequency axis. Values of τ_1 are given in Tables I to III also.

The Peterlin theory provides us with a means of extrapolation to obtain limiting high-frequency values of G'. The values of G'_∞ obtained in this way are given in Tables I to III. In paper II it was shown that the ratio of G'_∞/v_2, where v_2 is the volume fraction of the polymer, was nearly constant for polystyrene. The value of G'_∞, however, is the only quantity in the Peterlin theory which depends on P/N. For a slightly different choice of P/N one can obtain theoretical curves which fit the data as well by small changes in the values of h^* and φ/f. However, this will introduce a molecular weight dependence of G'_∞/v_2, which would be in contradiction to the independence of the high-frequency viscoelastic behavior of polymers of their overall dimensions. Therefore a constant G'_∞/v_2 can be an indication of a proper choice of P/N. The average values of G'_∞/v_2 for all polymers investigated up to the present are gathered in Table V. They decrease in the same order as $[\eta']_\infty M_0/N_A$ increases. Although this looks like a definite trend, it should be kept in mind that it is strongly related to the choices of P/N in the first place.

Significance of the Peterlin Theory. At this point the question may be raised as to what is the significance of the parameters derived from the Peterlin theory. Undoubtedly, this theory predicts the right shape of the G' and G'' curves within the frequency range considered. Recent measurements of Miller and Schrag[19] and of Plazek et al.,[20] however, have shown that at still higher frequencies phenomena are observed which cannot be interpreted in terms of the Peterlin theory. In particular, G'_∞ would only correspond to a temporary plateau in G', which starts to rise again at higher frequencies.

As to the internal viscosity parameter φ/f, the same effect is observed as has been reported already in paper II for linear polystyrenes: it increases with a decrease of molecular weight. At first φ/f was always considered to be a characteristic parameter of the macromolecule, independent of molecular weight, while on the other hand φ should be independent of solvent viscosity. The independence of φ of solvent viscosity had to be dropped[2] to account for the perfect superposition of the measurements done at different temperatures. Moreover, a closer look at the Peterlin theory reveals[21] that a molecular weight independence of φ/f is incompatible with a molecular weight independent high-frequency viscosity. Experimentally, the increase of φ/f required to fit the data at low molecular weights agrees with this observation.

Recent works on the viscoelastic properties of bead-rod models[22,23] and models containing constraints on bond lengths and bond angles[15,24] have shown that the absence of an infinite-frequency contribution to the dynamic viscosity in the Rouse–Zimm theory is a characteristic feature of approximating a macromolecule by a bead-spring model. The Fixman–Kovac theory[15] for freely jointed linear bead-rod models predicts a frequency dependence of the moduli G' and G'' which agrees rather well with the experimental observations over the whole frequency range, provided their parameter N is not interpreted as the number of chain bonds, but rather as a number of subunits each comprising several chain bonds. Otherwise, it underestimates the magnitude of the intrinsic high-frequency viscosity, though correctly predicting its molecular weight independence.[25] It avoids the use of internal viscosity which in the

Peterlin theory leads to an extra adjustable parameter, the actual physical meaning of which is poorly understood.

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Relationship between Hydrodynamic Volume and the Scission of Polymer Chains by High-Speed Stirring in Several Solvents

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ABSTRACT: Five different vinyl polymers, poly(methyl methacrylate), poly(α-methylstyrene), polystyrene, and polyisobutylene, were stirred at 30,000 rpm by a T. K. Homomixer at a polymer concentration of 0.04% w/v in various solvents for 2 hr in order to investigate the relationship between final chain length and the hydrodynamic volume of the polymer chains in the solvents. After prolonged stirring at low concentration the ruptured polymer chains reached a nearly constant hydrodynamic volume independent of the type of solvent, and polymers with higher T_g's, i.e., the more rigid polymers, attained lower hydrodynamic volumes. The results indicate that there is a relation between mechanical scission of polymer chains in solution and their hydrodynamic volume.

The authors have been studying various factors which affect the scission by high-speed stirring[1–5] of solutions of long-chain polymers such as poly(methyl methacrylate) and polystyrene. It has been found that the rate of scission of polymer chains is higher and the final chain length is shorter in good than in poor solvents at a low concentration.[4] Because polymer chains are more extended and thus have larger intrinsic viscosities in good than in poor solvents, the products of final chain lengths and their intrinsic viscosities in the results[4] seemed to approach a constant value regardless of the kinds of solvents used at low concentrations. According to Flory,[6] the following equation holds for polymers in solution

$$[\eta]M = \Phi(6\bar{S}^2)^{3/2}$$

where $[\eta]$ is the intrinsic viscosity, M is the molecular weight, Φ is the Flory constant, and $(\bar{S}^2)$ is the mean-square distance of an element from the center of gravity. Therefore, the products described above can be estimated in terms of hydrodynamic volumes.

In this study, the relationship between hydrodynamic volumes and the final chain lengths of various polymers was investigated after stirring at low concentration in several solvents.

Experimental Section

Materials. The linear long-chain polymers used for degradation were prepared as follows. Poly(methyl methacrylate) (PMMA) was prepared in the same way as described in a previous paper.[4] Viscosity average degree of polymerization, ($\bar{P}_v$), was 6250 and molecular weight, ($\bar{M}_v$), was 625,000. Polystyrenes (PSt-1 and PSt-2) with different molecular weights and molecular weight distributions were used. PSt-1 was described in the previous paper[4] and PSt-2 was obtained from Pressure Chemical Co. $\bar{P}_v$ of PSt-1 was 5610 and $\bar{M}_v$ was 583,000. The nominal molecular weight and $\bar{M}_w/\bar{M}_n$ of PSt-2 were 2,000,000 and less than 1.30, respectively. $\bar{P}_v$ and $\bar{M}_v$ of PSt-2 measured by the authors were 15,300 and 1,590,000, respectively. Poly(methyl acrylate) (PMA) was spontaneously polymerized by sunlight in a sealed glass container in the absence of initiator. $\bar{P}_v$ was 17,800 and $\bar{M}_v$ was 1,530,000. Poly(α-methylstyrene) (PαMSt) was obtained by polymerizing the purified monomer using living tetramer of α-methylstyrene obtained by reacting the monomer with sodium metal in THF. $\bar{P}_v$ was 8980 and $\bar{M}_v$ was 1,060,000. Polyisobutylene (PIB) (Vistanex MML-100 supplied by Esso Standard Petroleum Co.) had a $\bar{P}_v$ of 16,500 and a $\bar{M}_v$ of 927,000. Solvents were used after purifying by the usual methods. The $\bar{P}_v$ and $\bar{M}_v$ values listed for the above polymers were determined from equations contained in the next section.

Procedure. Solutions of each polymer (200 ml) in each solvent at a given concentration were prepared and stirred at 30,000 ± 500 rpm at 30 ± 5° for a given time by a high-speed mixer. The experiments with PSt–cyclohexane were carried out at 40 ± 5°. The