# Infinite-Dilution Viscoelastic Properties of Linear and Star-Shaped Polybutadienes

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ABSTRACT: The Birnboim–Schrag multiple-lumped resonator has been used to measure storage ($G'$) and loss ($G''$) shear moduli, in the concentration range ($c$) from 0.0005 to 0.006 g/ml, of two linear and one four-armed star 1,4-polybutadiene, in three different good solvents. The frequency range was from 106 to 6050 Hz. Analysis of the concentration dependence of $G'/c$ and $(G'' - \omega\eta_s)/c$, where $\omega$ is radian frequency and $\eta_s$ is solvent viscosity, showed that the longest relaxation time is affected much more than others by incipient intermolecular interactions. The above quantities extrapolated to zero concentration, *i.e.*, $[G']$ and $[G'']$, were compared with the Zimm and Zimm–Kilb theories. The data for the linear polymers (molecular weights 2.2 and 9.1 × $10^5$) agreed closely with the Zimm theory, using exact eigenvalues, with the hydrodynamic interaction parameter $h^* = 0.15$ and the number of submolecules $N$ large; the reduced frequency range was 2.8 decades. The data for the star polymer (molecular weight 5.0 × $10^5$) agreed closely with the Zimm–Kilb theory, using exact eigenvalues, with $h^* = 0.10$ and $N$ large; the reduced frequency range was 2.2 decades. The frequency dependence of viscoelastic properties for the star polymer showed several distinctive features.

Recent measurements[1] of dynamic viscoelastic properties of polystyrene in very dilute solution, made with the Birnboim–Schrag multiple-lumped resonator[2] with computerized data acquisition and processing,[3] permitted extrapolation of data to infinite dilution for comparison with the predictions of molecular theories. It was found that the behavior of polystyrene in Θ solvents at low and intermediate frequencies agreed closely with the Zimm theory,[4] whereas in good solvents the behavior corresponded to the Tschoegl modification[5] of the Zimm theory with finite values for the parameters $h$ and $\epsilon$ describing hydrodynamic interaction and coil expansion, respectively.

The present paper reports similar measurements on 1,4-polybutadiene (with about 55% trans configuration), a polymer which would be expected to have much greater internal flexibility. Both linear and four-armed star molecules have been investigated. For comparison with molecular theory based on the bead–spring model, advantage has been taken of the exact eigenvalue calculations initiated by Lodge and Wu[6] and similar evaluations for star polymers[7] based on the theory of Zimm and Kilb.[8] The distinctive frequency dependence predicted by the theory for the star polymer has been confirmed.

## Experimental Section

**Materials.** The butadiene polymers were generously provided by Drs. W. V. Smith and F. C. Loveless, Uniroyal Research Center. They were synthesized with a *tert*-butyllithium catalyst and their microstructure was about 55% trans. The four-armed star configuration was achieved by tetrafunctional linkage of the arms with dimethyl terephthalate.[9] Some data for characterization furnished by Dr. Smith are given in Table I. The ratio of weight- to number-average molecular weights was judged from gel permeation chromatography measurements to be less than 1.1.

The solvents were $\alpha$-chloronaphthalene from Matheson Coleman and Bell, decalin (approximately half cis and half trans) from J. T. Baker, and Aroclor 1232 (a partially chlorinated diphenyl, Lot AK-7) from the Monsanto Co. Their viscosities at 25° were 0.0312, 0.0245, and 0.104 P, respectively. Solutions were made up by immersing the polymer in the solvent for one day at 5° and then stirring very gently at room temperature for several days. The most concentrated solution (0.01 g/ml or less) was measured first and then sequentially diluted to several lower concentrations. The linear sample of higher molecular weight was measured in $\alpha$-chloronaphthalene and decalin, the star sample in $\alpha$-chloronaphthalene and Aroclor 1232.

**Methods.** The storage and loss shear moduli, $G'$ and $G''$, of the solutions were measured with the multiple-lumped resonator.[2] With resonators IIIA and IVA, nine discrete frequencies from 106 to 6060 Hz were provided. Some solutions were measured with only one resonator at five frequencies, however. All measurements were made at 25.00 ± 0.01°.

## Results

**Concentration Dependence and Extrapolation.** An example of the extrapolation of $(G'/c)^{1/2}$ and $(G'' - \omega\eta_s)/c$, where $c$ is concentration in grams per milliliter, to zero $c$ is illustrated for the star sample in $\alpha$-chloronaphthalene in Figure 1 at nine frequencies. As explained previously,[1] a more nearly linear plot is obtained for $(G'/c)^{1/2}$ than $G'/c$. Similar extrapolations were made for each sample in each of the solvents employed for it. Numerical data will be given elsewhere.[10]

The initial concentration dependence can be characterized by the limiting values as $c \rightarrow 0$ of $(G'/c)^{-1}\mathrm{d}(G'/c)/\mathrm{d}c = \gamma'$ (twice the ratio of slope to intercept in the left panel of Figure 1) and the corresponding value of $\gamma''$, which is the ratio of slope to intercept in the right panel of Figure 1. Some values of these ratios, and their dimensionless ratio $\gamma'/\gamma'' = \gamma$, are listed in Table II for the linear sample of higher molecular weight and the star sample in $\alpha$-chloronaphthalene.

As shown previously,[1] these ratios can serve to distinguish between two alternative hypotheses concerning the initial concentration dependence of relaxation times $\tau_p$, according to which (i) all $\tau_p$ increase with $c$ by the same factor, or (ii) only the longest time $\tau_1$ increases at first, the others being to a first approximation independent of concentration. For a linear polymer, the bead–spring theories predict that $\gamma$ at low

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[1] R. M. Johnson, J. L. Schrag, and J. D. Ferry, *Polym. J.*, **1**, 742 (1970).
[2] J. L. Schrag and R. M. Johnson, *Rev. Sci. Instrum.*, **42**, 224 (1971).
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[4] B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
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[6] A. S. Lodge and Y.-J. Wu, *Rheol. Acta*, in press.
[7] K. Osaki and J. L. Schrag, to be submitted for publication.
[8] B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19 (1959).
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[10] Y. Mitsuda, forthcoming thesis, University of Wisconsin.

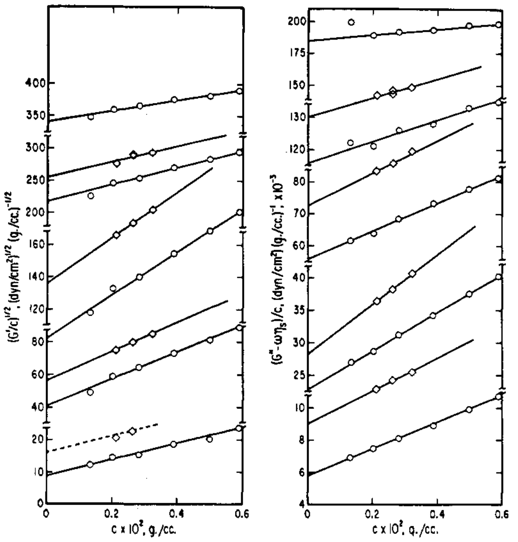

Figure 1. Plots of $(G'/c)^{1/2}$ and $(G'' - \omega\eta_s)/c$, each at nine frequencies (Hz), as follows, bottom to top: 106, 154, 425, 540, 1035, 1400, 2515, 3400, 6050, for star polymer in α-chloronaphthalene. Note that several different ordinate scales are used in each panel.

TABLE I
CHARACTERIZATION OF 1,4-POLYBUTADIENES

| Code no. | Type[a] | $M_n \times 10^{-3}$ | [η], ml/g, 30° |
|---|---|---|---|
| 67-3 | L | 220 | |
| FCL-F120D | L | 910 | 610[b] |
| P-PB-18(637-876) | 4S | 500 | 324[c] |

[a] L = linear, 4S = star with four arms of equal length. [b] In toluene. [c] In tetrahydrofuran.

TABLE II
PARAMETERS DESCRIBING INITIAL CONCENTRATION DEPENDENCE IN α-CHLORONAPHTHALENE

| | Linear, $M$ = 910,000 | | | Star, $M$ = 500,000 | | |
|---|---|---|---|---|---|---|
| Frequency | $\gamma'$ | $\gamma''$ | $\gamma$ | $\gamma'$ | $\gamma''$ | $\gamma$ |
| 106 | 559 | 188 | 3.0 | 607 | 144 | 4.2 |
| 425 | 205 | 61 | 3.3 | 415 | 131 | 3.2 |
| 1035 | 117 | 37 | 3.2 | 263 | 81 | 3.3 |
| 2515 | 78 | 20 | 3.8 | 115 | 29 | 4.0 |
| 3400 | 77 | 17 | 4.4 | | | |
| 6050 | | | | 50 | 13 | 3.8 |

frequencies should be 2.0 for assumption i and 3.0–4.1 for assumption ii, depending on the degree of hydrodynamic interaction. It is clear that for linear polybutadiene as for polystyrene[1] assumption ii is supported. For a four-arm star polymer, the appropriate values[10] are 2.0 for assumption i and 2.6–3.4 for assumption ii; again, the data support assumption ii. Furthermore, according to assumption ii, the ratios $\gamma'$ and $\gamma''$ decrease enormously with increasing frequency,[1] whereas assumption i provides more limited decreases by factors of $^1/_4$ to $^2/_3$. The data in Table II confirm assumption ii.

**Extrapolated Viscoelastic Functions.** The intercepts of plots such as Figure 1, representing the intrinsic values $[G']$ and $[G'']$, were reduced to the corresponding dimensionless quantities $[G']_R$ and $[G'']_R$ by multiplying by $M/RT$, where $M$ is the molecular weight, and plotted against the reduced radian frequency $\omega\tau_{01}$, where $\tau_{01}$ is the terminal relaxation time extrapolated to infinite dilution. The latter is obtained from the equation $\tau_{01} = \eta_s[\eta]M/RTS$, where $\eta_s$ is solvent viscosity, $[\eta]$ the intrinsic viscosity in the solvent employed, and $S$ the sum $\Sigma(\tau_{0p}/\tau_{01})$ provided by theory as described in the Discussion section; $\tau_{0p}$ are the relaxation times corresponding to the various modes of the bead–spring model. This equation is derived from the bead–spring molecular theory of Rouse and Zimm[4] and holds also for various modifications,[5–8] with suitable values of $S$. The intrinsic viscosity was obtained from $[G'']$ at the lowest frequencies by the relation

$$[\eta] = \lim_{\omega\to 0} [G'']/\omega\eta_s$$

except for the linear sample in decalin; here the measurements did not extend to low enough frequency, but $[\eta]$ was assumed to be the same as in α-chloronaphthalene. For two solutions in α-chloronaphthalene, the intrinsic viscosity was also determined by conventional capillary viscometry and agreed very well with those derived from the multiple-lumped resonator measurements. The intrinsic viscosities and terminal relaxation times are given in Table III.

All the data for the linear polymers are plotted in Figure 2; with the dimensionless variables chosen, the frequency dependences are identical for the different molecular weights and solvents. Similarly, Figure 3 shows that the four-armed star polymer has the same frequency dependence in the two solvents. This can be expected only if the solvents all have about the same thermodynamic interaction, though judging from the intrinsic viscosities the Aroclor is a somewhat poorer solvent

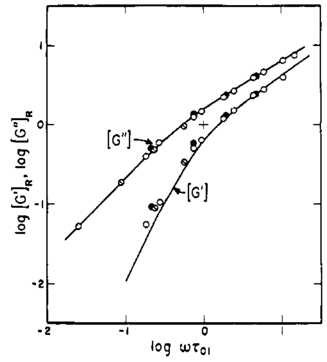

Figure 2. The reduced intrinsic shear moduli $[G']_R$ and $[G'']_R$ plotted logarithmically against $\omega\tau_{01}$ for linear samples: (○) $M$ = 910,000 in α-chloronaphthalene, (⊘) $M$ = 220,000 in α-chloronaphthalene, (●) $M$ = 910,000 in decalin. Curves drawn for Lodge–Wu exact eigenvalue calculation based on Zimm theory with $h^* = 0.15, N = 222$.

TABLE III
INTRINSIC VISCOSITIES AND TERMINAL RELAXATION TIMES

| Type, $M \times 10^{-3}$ | Solvent | [η],[a] ml/g | [η],[b] ml/g | Log $\tau_{01}$, sec |
|---|---|---|---|---|
| L, 220 | α-Chloronaphthalene | 200 | | −4.58 |
| L, 910 | α-Chloronaphthalene | 510 | 505 | −3.56 |
| L, 910 | Decalin | 510[c] | | −3.67 |
| 4S, 500 | α-Chloronaphthalene | 287 | 287 | −4.41 |
| 4S, 500 | Aroclor 1232 | 218 | | −4.01 |

[a] From multiple-lumped resonator measurements at low frequency. [b] From capillary measurements. [c] Assumed the same as in α-chloronaphthalene.

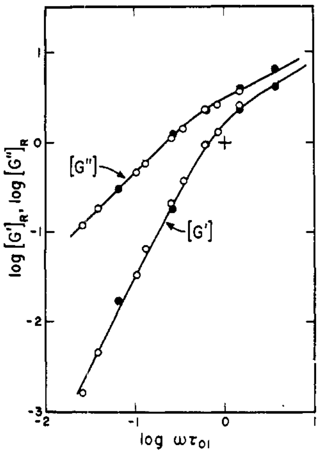

Figure 3. Logarithmic plots of $[G']_R$ and $[G'']_R$ against $\omega\tau_{01}$ for four-armed star sample: (○) in $\alpha$-chloronaphthalene, (●) in Aroclor 1232. Curves drawn for Osaki exact eigenvalue calculation based on Zimm–Kilb theory with $h^* = 0.10$, $N_b = 40$.

than the others. In both cases, the proportionality of $\tau_{01}$ and all other relaxation times to $\eta_s[\eta]M$ is confirmed.

## Discussion

The frequency dependence for the linear polymers can be described either by the Tschoegl modification[5] of the Zimm theory with suitable values of the parameters $h$ and $\epsilon$ or by the evaluation of Lodge and Wu[6] using exact eigenvalues and adjusting the reduced hydrodynamic interaction parameter $h^*$. The curves drawn in Figure 2 represent the Lodge–Wu calculation for $h^* = 0.15$, $N = 222$; the number of submolecules, $N$, may be considered as indeterminate but large for the limited frequency range concerned, since the results become sensitive to a value of $N$ of this magnitude only at higher frequencies. The value of the sum $S$ for this case is 2.11, used for calculation of $\tau_{01}$ in Table III. The agreement is excellent except that the experimental values of $[G']_R$ at the lowest frequencies are a little high; this discrepancy may be attributed to a slight molecular weight distribution.

The frequency dependence for the four-armed star polymer is described by the Osaki evaluation[7] of the theory of Zimm and Kilb.[8] The curves in Figure 3 are drawn for functionality (number of branches) $f = 4$, $h^* = 0.10$, and number of submolecules per branch $N_b = 40$. Here also, $N_b$ is indeterminate but large for the purposes of the frequency range concerned. The value of $S$ is 4.63. The agreement with the data is excellent.

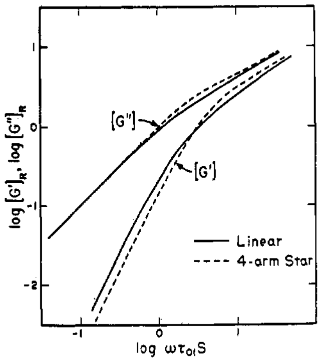

Figure 4. Logarithmic plots of $[G']_R$ and $[G'']_R$ against $\omega\tau_{01}S = \omega[\eta]\eta_s M/RT$, from Figures 2 and 3, to show comparison of frequency dependence.

Thus each type of polymer, linear and star, has a characteristic frequency dependence of viscoelastic properties, the shape of which (exclusive of high frequencies[11]) is independent of molecular weight and solvent viscosity, and the absolute values of the viscoelastic properties are correctly predicted by theory with only one adjustable parameter, $h^*$. The fact that $h^*$ is slightly less for the branched than for the linear polymer may be associated with a higher density of polymer segments in the former. The difference between the forms of the frequency dependence can be seen more clearly in Figure 4, where the reduced viscoelastic functions are plotted logarithmically against $\omega\tau_{01}S$; inclusion of the factor $S$ makes $[G'']_R$ coincide at low frequencies for the two types. The star polymer shows the following characteristics: (a) closer approach of $[G']_R$ and $[G'']_R$ in the "power-law" region at the higher frequencies shown, superficially resembling the effect of partial free draining; (b) small "bumps" in both $[G']_R$ and $[G'']_R$, especially the latter, resembling an incipient appearance of the plateau region which characterizes entangled polymer systems; (c) lower values of $[G']_R$ at the lowest frequencies. The last feature is associated with a low value of steady-state compliance $J_e{}^0$. For example, the reduced steady-state compliance parameter $J_{eR}{}^0 = J_e{}^0RT/Mc[\eta]^2$, which in the bead–spring theories ($c \rightarrow 0$) is given by $\Sigma\tau_p{}^2/(\Sigma\tau_p)^2$, is 0.257 for the linear and 0.148 for the four-arm star with the values of $h^*$ used in Figures 2, 3, and 4. The strong dependence of $J_e{}^0$ on branching suggests its use for detection and gauging of long-chain branches.

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[11] D. J. Massa, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **4**, 210 (1971).