estimation of the reduced partial molar combinatory entropy as incorporated in eq 8. However, so large an over-estimation, amounting roughly to half of the combinatory quantity whose value is $-^1/_2$ at $\varphi_2 = 0$, seems altogether implausible. Comparably large "entropy deficits" were found by Booth and Devoy[23] for benzene–polyoxyethylene and for benzene–polyoxypropylene. They attributed them to formation of weak charge-transfer complexes of benzene with the ether oxygens of the polymer chains. A corresponding explanation would be unfounded for the present systems.

Equally striking are the excess volumes which are consistently lower then predictions from theory by *ca.* 0.70×10^{-2}–1.0×10^{-2}, expressed as fractions of the total volume. Malcolm and Koh[6] likewise find excess volumes for the systems $CHCl_3$–PDMS and CCl_4–PDMS which are lower than values calculated similarly from theory, the discrepancies being of comparable magnitude to those found here. The benzene–poly(oxyethylene) system investigated by Booth and Devoy[23] does not share this discrepancy, good agreement having been found between observed and calculated excess volumes. For nonpolar solutions in general, the theory has been particularly successful in accounting for observed excess volumes. Solutions of PDMS in organic solvents appear to be exceptional in this regard.

One may plausibly assume the two discrepancies between experiment and theory, one in the entropy and the other in the excess volume, to be related. Peculiarities in the intermolecular force field may conceivably be responsible for both of them. Alternatively, an explanation may be found in the irregularity of the form of the PDMS chain, having pendant CH_3 groups spaced by comparatively long Si–O and Si–C bonds. Possibly the irregularity of the cross section of the chain obstructs efficient packing of the polymer chains in bulk. Effects of this nature should be ameliorated by molecules of the solvents here considered, which more easily fit into the irregularities. Such an accommodation of solvent molecules would entail a decrease of entropy as well as of volume.

Irrespective of the validity of the explanations suggested, it is to be hoped that more concrete generalizations will emerge from detailed investigations of a greater range of systems, with particular attention to the parameters p^* and T^* for the pure components and the exchange parameters X_{12} and Q_{12} for their mixtures.

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Dielectric Dispersion in Dilute Solutions of Poly(*p*-fluorostyrene), Poly(*m*-fluorostyrene), and Poly(*p*-chlorostyrene)[1]

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ABSTRACT: Dielectric loss tangents in dilute benzene solution at 25° have been measured from 10 to 150 MHz for three series of unfractionated halostyrene polymers, covering wide ranges of molecular weight. At sufficiently high molecular weights, the frequency of maximum loss is independent of molecular weight, but for molecular weights below about 2×10^4 it becomes gradually higher as the chain length decreases. This behavior can be quantitatively explained by the intrusion of overall rotatory diffusion as a mode of dipole relaxation competitive with local segmental motions. The slightly higher relaxation rate of poly(*m*-fluorostyrene) as compared to the para isomer is probably due to phenyl-group reorientation about the C_1–C_4 axis.

Polar groups in the repeat units of a polymer chain may conveniently be classified[2] into three types: (A) parallel to chain direction, (B) rigidly attached to chain backbone but perpendicular to chain direction, (C) on a flexible side chain. From a comparison between the experimental results[2,3] and the theoretical treatments,[4,5] it may be concluded that dielectric relaxation due to type A dipoles is well understood and that the existence of such a polar group in the repeat unit is a sufficient condition for a low-frequency dispersion with a molecular weight dependent relaxation time of the order of magnitude $\tau \cong M[\eta]\eta_0/RT$, where M is the molecular weight of the polymer, $[\eta]$ is the intrinsic viscosity of the polymer, η_0 is the viscosity of the solvent, R is the gas constant, and T is the absolute temperature.

Type B dipole moments, rigidly attached perpendicular to the direction of the chain contour, present a different and harder problem. For flexible chains, the vector sum of a sequence of such dipoles does not correlate with the end-to-end vector, so that the relevant modes of chain diffusion are usually short-range or local modes which cannot be meaningfully described by bead-and-spring models[4,5] except in a somewhat fictitious sense. Theoretically,[5,6] a true short-range mechanism within a flexible long chain must lead to a mean relaxation time independent of chain length, contrary to older predictions.[7-9] Experimentally it is in-

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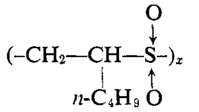
deed found that dielectric relaxation time for many pure type B polymers do not depend on molecular weight. In other instances, however, a molecular weight dependent relaxation has been reported. We may ignore the early data of Mead and Fuoss[10] on plasticized poly(vinyl chloride) as being too far from the dilute-solution state, but a few experiments by Davis[11] on poly(*p*-chlorostyrene) in the viscous solvent *o*-terphenyl revealed some dependence of τ on molecular weight, in contrast to the data for longer chains of the same polymers in benzene.[12] More strikingly, Ivin, Bates, and Williams[13] observed that the entire dipole relaxations in poly(hexene-1 sulfone) and poly(2-methylpentene-1 sulfone)



$$(\text{-CH}_2\text{—}\underset{n\text{-C}_4\text{H}_9}{\underset{|}{\text{CH}}}\text{—}\overset{\overset{\text{O}}{\downarrow}}{\underset{\underset{\text{O}}{\uparrow}}{\text{S}}}\text{-})_x$$

occurred at times corresponding to those of type A polymers, although the dipoles are essentially of type B. Since the equilibrium dilute-solution properties of these polymers are incontrovertibly those of random coils, the explanation of this result must be[2,13] that rotational diffusion of the entire macromolecule offers a more rapid route of relaxation than local conformational rearrangements. For structural reasons, local segmental motions in these polysulfone chains are unusually sluggish.

In general, the two processes may be considered as competitive. A simple analog is an equivalent circuit in which the local modes for relaxation of type B dipole orientation and the rotational diffusion mechanism are represented by two resistors in parallel. The observable relaxation rate is then the sum of those for the two separate mechanisms, and of course in most situations one of these will be sufficiently faster than the other to dominate the behavior. Since the rotational relaxation time is proportional to $M[\eta]$, the rotational diffusion process must always become too slow to compete with local motions for flexible chains at sufficiently high molecular weights. Our work was undertaken for the express purpose of exploring the dependence of dielectric relaxation time on molecular weight in the low molecular weight region, in the hope of observing the transition from local to overall rotational relaxation. As will be seen, this hope has been gratified, and the results can be quantitatively interpreted in terms of the picture just presented.

Experimental Section

Polymers. A number of unfractionated, essentially atactic polymers of *p*-chlorostyrene, *p*-fluorostyrene, and *m*-fluorostyrene were prepared by free-radical polymerization at 60°. The molecular weights were varied by the use of carbon tetrabromide as a transfer agent. From considerations of the polymerization mechanism, we believe that the chain-length distributions in these polymers were essentially of the exponential, "most probable" type. Molecular weights of the fluorostyrene polymers were determined by light scattering, and their characterization[14] will be reported elsewhere. The molecular weights of the poly(*p*-chlorostyrene) samples were obtained from their intrinsic viscosities by means of the published[15] viscosity-molecular weight relation.

Measurements. The dielectric properties of dilute benzene solutions of these polymers were measured over the frequency range between 10 and 150 MHz at the MIT Laboratory for Insulation Research under the guidance of W. B. Westphal. A bridge circuit was used to measure loss factors of polymer solutions at 10 MHz, and a resonant circuit[16] was used at 30, 48.5, and 101 MHz. Transmission-line methods[17] developed at MIT were used to measure the loss tangents of polymer solutions at 150 MHz. The dielectric loss tangent can be evaluated when the bridge (resonance) has been balanced with pure benzene in a sample cell and again after replacing solvent by solution. All measurements were for benzene solutions at room temperature (25 ± 1°), and at concentrations of 3% by weight or less.

Results

The observed dielectric loss tangents are recorded in Table I, where the abbreviations PPCS, PPFS, and PMFS stand for polymers of *p*-chlorostyrene, *p*-fluorostyrene, and *m*-fluorostyrene, respectively. The frequency f_{m} at which ϵ'' or $\tan \delta$ passes through its maximum was determined by graphical application of the empirical Fuoss-Kirkwood[18] relation

$$\epsilon'' = \epsilon''_{\max} \operatorname{sech} [\alpha \ln (f/f_{\mathrm{m}})] \tag{1}$$

where f is the frequency of observation and α is a parameter whose departure from unity measures the breadth of the loss peak. Since the solutions are dilute, the loss tangent, $\tan \delta = \epsilon''/\epsilon'$, is very nearly proportional to ϵ'' and can be used in place of the latter in eq 1. No strong concentration dependence of f_{m} (the frequency of maximum dielectric loss) is found, in agreement with earlier results[12,19] for such dilute solutions. Therefore, the values of f_{m} at infinite dilution could be taken from the dielectric loss curves of approximately 3% benzene solutions.

The breadth parameter α of eq 1 was in the neighborhood of 0.8, as in earlier work[19] on similar polymer solutions. In this paper we will not be concerned with deviations from ideal Debye dispersion. Recent discussions of models to account for such deviations in polymer systems are given by Clark and Zimm[20] and by Williams.[21]

The derived values of f_{m} are plotted against weight-average molecular weights M_{w} on a double-logarithmic scale for the three polymer systems in Figures 1, 2, and 3. Filled circles denote the present results, while open circles are from earlier investigations. It is seen that in each case the expected increase in f_{m} occurs at low molecular weights. The various curves in the figures are calculated as explained below. At high molecular weights, the results for PPCS and PPFS are in good agreement with previous published work.[12,19,22,23]

Discussion

It is seen that for each series of polymers the value of f_{m} reaches a constant level at molecular weights greater than

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TABLE I
LOSS TANGENTS ($\times 10^3$) IN BENZENE SOLUTION

Sample	$M_w \times 10^{-3}$	Concn, wt %	Frequency, MHz						Log f_m, Hz
			10	30	48.5	101	150	300	
PPCS									
13	2.03	3.01	1.32	2.39	3.51	4.11	4.15	3.89	8.15
14	4.60	2.99	3.30	5.04	5.86	5.96	5.52	3.93	7.86
15	11.1	3.11	3.85	5.50	5.96	5.42			7.73
16	21.1	3.02	4.31	6.31		5.33	5.05	3.65	7.63
		1.51	2.75	4.30	4.66	3.44			7.62
		0.75	1.77	2.93	3.21	2.30			7.62
17	38.8	3.02	4.90	5.76	5.96	5.38	4.55	3.03	7.58
									7.53[a]
PPFS									
24	2.04	2.71		1.64	2.52	2.95	2.73	2.04	7.99
25	4.13	3.10	2.20	4.46	5.95	5.97	5.52	4.02	7.90
26	7.73	3.10	3.21	5.16	5.99	5.30		4.13	7.84
27	14.9	3.16	3.47	5.84	6.10	5.30		3.60	7.68
28	26.9	3.08	3.65	5.96	5.91	4.87			7.59
29	48.8	3.12	3.46	5.44	5.55	4.12			7.58
30	157	2.79	4.50	6.08	6.01	4.74			7.57
		1.40	2.06	3.33	3.30	2.48			7.57
PMFS									
13	2.80	2.37	1.12	2.00	2.61	2.93	2.63	2.02	7.99
12	4.09	3.05	2.40	4.51	6.02	6.80	6.32	4.66	7.96
11	10.6	3.19	3.45	5.95	6.50	6.45	5.71	4.21	7.82
10	21.8	3.07	3.12	5.70	6.25	5.88	5.30	4.01	7.78
4	38.7	3.07	3.61	5.62	6.06	5.60			7.75
6	88.5	2.97	3.66	5.55	6.78	5.86			7.72
7	161	3.09	3.75	5.89	6.67	5.88			7.72

[a] Reference 3a.

about 2×10^4, indicating the complete predominance of local segmental motion as the relaxation mechanism in long chains. From the curves we take $f_m^{(\infty)}$ = 34 MHz for PPCS, 37 MHz for PPFS, and 54 MHz for PMFS, with uncertainty of about 10%. The corresponding relaxation times, $\tau_\infty = {}^1/_{2\pi f_m^{(\infty)}}$, are 4.7, 4.3, and 3.0 nsec, respectively. The influence of the chain structure is evident enough, as the observed relaxation times for liquid chlorobenzene and fluorobenzene are[24] only 7 and 3.3 psec. The small but definite difference in the behavior of PPFS and PMFS suggests that reorientation of aromatic rings about the C_1–C_4 axis contributions to dielectric relaxation in the latter polymer.

To treat the data quantitatively, we adopt a model admitting two different local motions in addition to rotational tumbling of the whole polymer molecule in solution: α, reorientation of the aromatic ring about the C_1–C_4 axis, and β, precession of the C_1–C_4 axis in a plane perpendicular to the chain backbone. With the utmost simplicity, we here take each of these motions to be an independent stochastic process within each repeat unit of the polymer chain. This assumption is particularly vulnerable to criticism for motion β, which is the relevant one for strictly type B dipoles as in the para-substituted polymers; all physically reasonable models of such motions involve some coupling to the motions of neighboring units,[25,26] and this is of course a basic reason for broadening of the dispersion region in polymers.[7,20,21] However, results obtained with the bead-and-spring model for an approximate type B structure show[5] that the broadening effect is probably minor, and the gain in simplicity is great.

In addition, we take the overall rotational tumbling of the chain to be independent of the local motions. This assumption has often been made, *e.g.*, in treatments of dielectric relaxation,[21,27] magnetic relaxation,[28,29] and fluorescence depolarization[29] involving small local motions on a larger rigidly rotating structure. Of course it cannot be strictly valid, since a local rearrangement must almost always produce some change in the rotational friction tensor, and indeed it is not at all consistent with the common bead-and-spring model (see below), in which rotations and large-scale deformations of chain shape occur at essentially the same rate.

It is a simple matter to calculate the dipole correlation function[21] for the above model. For each repeat unit, it is

$$\langle \boldsymbol{\mu}(t)\cdot\boldsymbol{\mu}(0)\rangle/\mu_0^2 = \exp(-t/\tau')\cos^2\theta + \exp(-t/\tau'')\sin^2\theta \quad (2)$$

where θ is the angle between the carbon–halogen bond dipole moment and the C_1–C_4 axis of the aromatic ring, μ_0 is the magnitude of the moment, and the two relaxation times are given by

$$1/\tau' = \tau_\beta^{-1} + 2D_{\text{rot}}$$
$$1/\tau'' = \tau_\alpha^{-1} + \tau_\beta^{-1} + 2D_{\text{rot}} \quad (3)$$

in which τ_α and τ_β are the correlation times for the two local motions described above, and D_{rot} is the rotatory diffusion coefficient of the molecule, here taken as spherically symmetric. Extension to nonspherical rotational diffusion is considered later.

Since we deal only with dilute solutions in a nonpolar solvent, molecular field problems[21] do not plague us, and the

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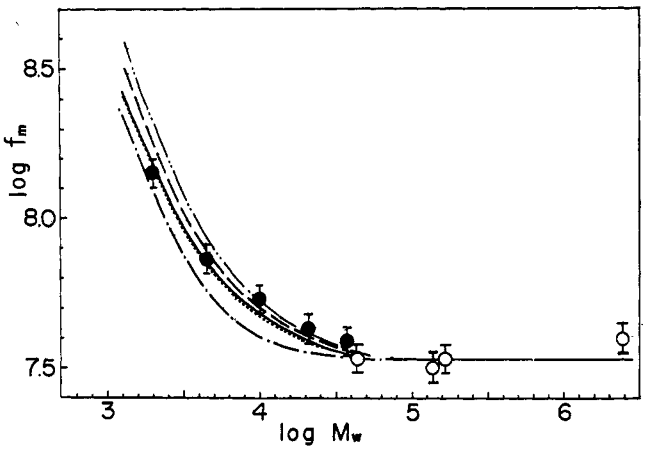

Figure 1. Frequency of maximum dielectric loss against weight-average molecular weight for poly(*p*-chlorostyrene) in benzene at 25°: (●) present results, (○) previous results (ref 12, 19); vertical bars represent estimated experimental uncertainty. Curves calculated as described in text for monodisperse spherical coils (—·—), polydisperse spherical coils (···), polydisperse nondraining ellipsoidal coils (——), polydisperse free-draining ellipsoidal coils (- - - -), and polydisperse impenetrable spheres (-···-).

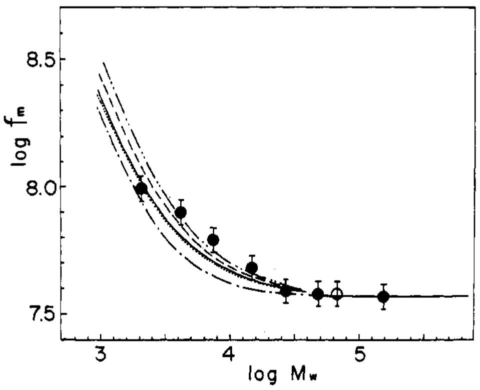

Figure 2. Frequency of maximum loss against weight-average molecular weight for poly(*p*-fluorostyrene) in benzene at 25°: (●) present results, (○) ref 19. Curves as in Figure 1.

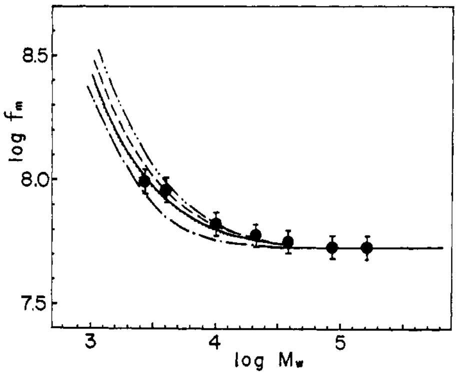

Figure 3. Frequency of maximum loss against weight-average molecular weight for poly(*m*-fluorostyrene) in benzene at 25°; (●) experimental results. Curves as in Figure 1.

dielectric loss factor corresponding to eq 2 is just

$$\epsilon''(\omega) = \phi(\omega\tau')\cos^2\theta + \phi(\omega\tau'')\sin^2\theta$$

$$\phi(\omega\tau) = (\text{constant})\ \omega\tau/(1 + \omega^2\tau^2) \qquad (4)$$

For long enough chains, the contribution of D_{rot} to the relaxation rate becomes negligible. For the para polymers, where $\theta = 0$, we can therefore identify τ_∞ with τ_β, which is quite similar in the two systems. In PMFS, however, we have $\theta = \pi/3$, and if we assume that τ_β is the same in this case as for PPFS we find $\tau_\alpha \cong 7$ nsec, somewhat slower than the β motion. Conformational energy considerations[30] indicate that this motion should encounter sizeable steric barriers between the two stable minima for which the ring plane is perpendicular to the chain backbone. Indeed, Allerhand and Hailstone,[31] in a recent ^{13}C nmr study of polystyrene in tetrachloroethylene, consider that the α motion is too slow to be significant. We believe, on the contrary,[32] that their data can be interpreted to indicate an α motion with a correlation time that is at least consistent with our dielectric result. A more serious but not hopeless discrepancy is found for the β motion. The Allerhand–Hailstone data yield[32] $\tau_\beta \simeq 0.8$ nsec, while our dielectric result for PPFS would correspond to about 3.5 nsec under their experimental solvent and temperature conditions. If the β motion, instead of involving locally independent jumps over substantial barriers between potential minima, were sufficiently coupled to neighboring groups to approximate one-dimensional rotational diffusion, a factor of 4 between the magnetic and dielectric values of τ_β could be admitted, thus effectively reconciling the two experimental findings. Other evidence regarding the local motions is furnished by acoustic,[33,34] esr,[35] and fluorescence depolarization[36] measurements on solutions of polystyrene or appropriately labeled derivatives. These results are discussed elsewhere.[32]

Let us now treat more quantitatively the contribution of rotational diffusion to relaxation at different molecular weights. From eq 3 we have

$$f_{\text{m}}/f_{\text{m}}^{(\infty)} = \tau_\infty/\tau = 1 + 2D_{\text{rot}}\tau_\infty \qquad (5)$$

and we may consider alternative expressions for D_{rot}. According to Riseman and Kirkwood[37] or Isihara[38] the rotatory diffusion coefficient for a rigidly rotating spherically symmetric random coil is given by

$$D_{\text{rot}} = RT/4M[\eta]\eta_0 \qquad (6)$$

and this relation holds for all degrees of hydrodynamic interaction from free draining to complete shielding. Direct substitution of the measured intrinsic viscosities and weight-average molecular weights then produces predicted curves of f_{m} against M_{w} which fall somewhat below the experimental results (lowest curves in Figures 1–3).

The predictions are noticeably improved if the polydispersity of the polymer samples is taken into account. Substituting the Mark–Houwink relation, $[\eta] = KM^\nu$, into eq 6, we have for a given polymer species

$$\tau_\infty/\tau = 1 + BM^{-a}$$

$$B = \tau_\infty RT/2\eta_0 K \qquad a = 1 + \nu \qquad (7)$$

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For polydisperse para-substituted polymers (and essentially also for PMFS), we may then write

$$\epsilon''(\omega) = \int_0^\infty \phi(\omega\tau)w(M)\mathrm{d}M =$$

$$(\text{constant}) \int_0^\infty \left[\frac{\omega\tau_\infty(1 + BM^{-a})}{\omega^2\tau_\infty{}^2 + (1 + BM^{-a})^2}\right]w(M)\mathrm{d}M \quad (8)$$

where $w(M)$ is the weight-fraction molecular-weight distribution function. Adopting a "most probable" molecular-weight distribution[39]

$$w_x = x(1 - p)^2p^{x-1}$$
$$p = (M_\mathrm{w} - M_0)/(M_\mathrm{w} + M_0) \quad (9)$$

where x is the degree of polymerization and M_0 the molecular weight of a repeat unit, we replace the integral in eq 8 by a sum over integers, evaluate it on a digital computer for a range of values of the variable $\omega\tau_\infty$, and locate its maximum value, which corresponds to $\omega_\mathrm{m}\tau_\infty = f_\mathrm{m}/f_\mathrm{m}{}^{(\infty)}$. The results[14] of this calculation, for various weight-average degrees of polymerization, produce the dotted curves in Figures 1-3. It is seen that substantial agreement with the experimental trends has been achieved.

Still other models for the rotational diffusion may be explored. For example, hard impenetrable spheres give

$$D_\mathrm{rot} = 5RT/12M[\eta]\eta_0 \quad (10)$$

which displaces the curves upward from those of random coils; again with the "most probable" chain-length distribution, we obtain the results given in the topmost curves of Figures 1-3. This model represents a retrograde step, but we remark that it still yields a tolerable imitation of the experiments. Apparently even the crudest model of rotational diffusion suffices to demonstrate the reality of the effect.

We also tried a somewhat broader molecular weight distribution, corresponding to $M_\mathrm{w}/M_\mathrm{n} = 3$, but this resulted in almost imperceptible further changes. As the ultimate in refinement, we considered anisotropic rotatory diffusion. It was recently shown[40,41] that the most probable shape of a random coil is not spherical but more or less ellipsoidal with principal moments of inertia in the ratio 3.9:3.4:1, not far from an ellipsoid of revolution. In the free-draining limit, the corresponding components of the rotational friction tensor are in the same ratio, while in the nondraining limit we can adapt Perrin's treatment[42] of impenetrable ellipsoids. Skipping the details,[14] we see in Figures 1-3 that the introduction of anisotropy causes little further change; but it is pleasing that the best model from a physical point of view (polydisperse sample, anisotropic nondraining rotational diffusion) does seem to give as good a fit as any.

It may be asked whether other types of motion should also be considered. For example, internal rotation about a single chain-skeletal bond, with attendant relative displacement of the two pendant chain portions, was directly considered by Kuhn[9] and is implicit in the dielectric relaxation theories of Kirkwood.[7,8] Recently Paul and Mazo[43] calculated the rates of this kind of process. For internal rotation hindered by a threefold symmetrical barrier of height U_0, their treatment leads to

$$1/\tau = 27N_\mathrm{A}U_0 \exp(-U_0/kT)/4\pi M[\eta]\eta_0 y^{1/2}(1 - y)^{1/2} \quad (11)$$

where N_A is Avogadro's number and y is the fractional distance of the bond from an end of the chain. Using the observed[19] barrier height of about 13 kJ/mol for polystyrenes, we then find that even at a molecular weight of 2×10^3 this process is slower than the observed τ_∞ for all except the bonds very near a chain end. We therefore conclude that overall rotational diffusion, rather than the above hybrid motion, is the dominant competitor to local modes at low molecular weight.

Finally, it should be clearly stated that the observed molecular-weight effect cannot be accommodated by present versions of the bead-spring model. Recent high-frequency viscoelastic measurements by Ferry and his collaborators[44] on dilute polystyrene solutions are very well correlated by the bead-spring model with an internal viscosity and a finite number of Gaussian subchains.[45] However, in this formulation the normal coordinates (of the model without internal viscosity) are preserved from the start,[46] and this feature eliminates the possibility that rotational diffusion of the entire chain could be faster than the quickest local segmental motion. We must await the development of a more general but also tractable theory of chain dynamics, from which the internal-viscosity model and the treatment of this paper may emerge as alternative well-defined approximations.

Acknowledgments. We thank W. B. Westphal for his encouragement and tutelage, Professor A. R. von Hippel for the privilege of making the measurements at MIT, and Gary Brehm and Francois Gény for helpful discussions.

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