subject, of course, to the approximations already introduced], application of the theory to systems in which ΔS_{mix} is not solely conformational, and so forth. This last explicit relation suggests that for systems adhering to Ehrenfest formalism there can be a universal relation for the pressure dependence of pure components, viz., $\mathrm{d} \ln T_g/\mathrm{d}P$ = constant.

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The Influence of Side Groups in Polymer Chain Dynamics. Alternative Comparisons of Viscoelastic Data and Dilute Solution Theory

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ABSTRACT: Extensive high-frequency studies of viscoelastic properties of dilute polymer solutions have been reported by Ferry and associates. Every system examined has shown a finite limiting value η'_∞ for the real part η' of the complex viscosity coefficient η^*, contrary to the predictions of simple bead-spring model theories. Further, η'_∞ is sensitive to the specific side group incorporated in the polymer. Initially the data were fitted with the Peterlin theory which was the only treatment available that predicted a nonzero η'_∞; approximate eigenvalues of the hydrodynamic interaction matrix were used but excellent fits were obtained. Recently an exact solution has been given by Peterlin and Fong; inclusion of exact eigenvalues substantially alters the theoretical predictions so that fits to the data are no longer possible. In addition, more detailed and realistic bead-rod models have been analyzed by Fixman and coworkers; they calculate nonzero values for η'_∞ which are several orders of magnitude smaller than those measured. At present there is no theory which predicts the observed viscoelastic properties, and the physical origin of η'_∞ is not clear. An empirical data modification procedure has been applied to the viscoelastic data in which the high-frequency limiting behavior is subtracted from the measured properties. The modified data plot shapes that results are essentially independent of concentration, molecular weight, and polymer species and correspond to Zimm theory predictions for very small values of hydrodynamic interaction; i.e., a unique master curve shape is obtained by this procedure for all data examined. However, the simple modification apparently does not result in the entire chain dynamics contribution being displayed. A molecular weight dependence of the intrinsic limiting value of η'_∞ appears for polystyrene solutions at molecular weights below 10 000, indicating that up to 100 monomer units may be involved in whatever motions are responsible for η'_∞; side groups may play an important role. Additional experimental evidence on a variety of different molecules as well as a more complete and general theory of chain dynamics will be required in order to understand the role of conformational dynamics in the viscoelastic properties of polymer solutions.

Extensive effective high-frequency studies of the linear viscoelastic properties of dilute polymer solutions have been reported over the last several years by Ferry and collaborators;[1–4] measurements were carried out over a wide effective frequency range utilizing the modified Birnboim apparatus.[5] The systems which have been studied are monodisperse atactic polystyrenes and poly(α-methylstyrenes) of various molecular weights and chain topologies, as well as some poly(2-substituted methyl acrylates) in two chlorinated biphenyl (Aroclor) solvents; all of the polymers examined to date in this laboratory have contained large side groups. The high-frequency regime, which reflects the contributions of fairly local motions to these properties, has been of particular interest since η', the real part of the complex viscosity coefficient η^*, reaches a finite limiting value of η'_∞ which is substantially greater than the solvent viscosity η_s contrary to the predictions of simple bead-spring model theories.[6–8] Here η'_∞ denotes the value of η' for the first high-frequency plateau although there is some evidence for a second plateau at much higher frequencies;[2,9] to this extent the subscript ∞ is somewhat arbitrary. These prior studies showed that η'_∞ is independent of molecular weight for linear polystyrene or poly(2-substituted methyl acrylates) with molecular weights of 19 800 or greater and for branched structures (polystyrene stars and combs) for which the branch lengths were substantial (100 or more monomer units). Further, the value of

$$[\eta']_\infty = \lim_{c \to 0} \frac{\eta'_\infty - \eta_s}{\eta_s c} \qquad (1)$$

(solution concentration c in grams/milliliter) is sensitive to the specific side groups on the chain; for example, Table I lists values of $[\eta']_\infty$ for polystyrene, poly(α-methylstyrene), poly(methyl-2-n-butyl acrylate), poly(methyl-2-ethyl acrylate), poly(methyl-2-phenyl acrylate), and poly(methyl methacrylate). $[\eta']_\infty$ may reflect the degree to which large side groups are held normal to the main chain backbone direction and their motional freedom restricted rather than simply the size of a given side group or chain. In addition, η'_∞/η_s is independent of solvent viscosity, indicating that the solvent plays an important role in whatever process is responsible for η'_∞ and that time–temperature superposition can be employed; plots of log (η'_∞/η_s) vs. concentration are straight lines over the range of concentrations studied.[4]

Finite concentration viscoelastic data and properties ob-

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tained by extrapolation to infinite dilution were initially fitted with the Thurston–Peterlin formulation[10] of the Peterlin theory,[11] a modification of the bead-spring model of Zimm,[7] which includes an additional mode dependent energy loss mechanism, the internal viscosity. Excellent fits were obtained for all monodisperse systems studied; the theoretical parameters N (number of submolecules), h^* (hydrodynamic interaction parameter), and ϕ/f (ϕ is the internal viscosity parameter and f the friction factor for a bead) all showed reasonable dependences on molecular weight and concentration.[2-4] In addition, earlier oscillatory flow birefringence studies of monodisperse polystyrene/Aroclor solutions were also fitted with the Peterlin theory;[12] these two substantially different experiments (one examines energy storage and dissipation while the other senses configurational rearrangements via optical polarizability fluctuations during cyclic defomation) both yielded the same values for the theoretical parameters for equivalent solutions. Thus it appeared that when a proper molecular explanation of the somewhat empirical ϕ factor was found, the polymer chain dynamics picture as revealed by viscoelasticity and oscillatory flow birefringence studies would be essentially complete. Peterlin suggested that ϕ described, in an approximate manner, the contributions from local chain rearrangements which have motional components not included in the bead-spring model.[13]

The chlorinated biphenyl solvents utilized exhibit an unusually strong dependence of viscosity on temperature, raising questions about the possible uniqueness of the measured properties to these specific polymer/solvent systems; however, high-frequency viscoelastic measurements by Cooke and Matheson on monodisperse polystyrenes and poly(α-methylstyrenes) in di(2-ethylhexyl)phthalate yielded values of $[\eta']_\infty$ in excellent agreement with those for the solutions utilizing biphenyl solvents.[14]

More recently, a new thin fluid layer oscillatory flow birefringence apparatus has been constructed to enable measurements at substantially higher effective frequencies; the results obtained for polystyrene solutions revealed high-frequency anomalies which cannot be described by the Peterlin theory or by any simple relaxation process theory of chain dynamics.[15] This led to a further examination of the viscoelasticity data which also show some anomalies. In addition, a recent analytical solution[16] of the eigenvalue problems in the original version of the Peterlin theory alters the theoretical predictions substantially; it no longer fits viscoelasticity data and does not provide unique fits for birefringence results. (Earlier theoretical fits to data from both experiments utilized approximate eigenvalues ν_p for the hydrodynamic interaction matrix **H**.[3,10,11]) Extensive theoretical work based on more realistic bead-rod models incorporating various bond length and bond angle restrictions as well as varying degrees of hydrodynamic interaction predicts values for $[\eta']_\infty$ which are independent of molecular weight but which are smaller than the measured values by several orders of magnitude; apparently reasonably complete simple models for treating chain backbone dynamics do not predict the high-frequency properties that are observed for these molecules.[17-19] Other theoretical efforts have been directed toward understanding the physical basis for the internal viscosity concept in polymer solutions.[20-23] At present there is no theory which fits the viscoelasticity data described here over the entire measurement frequency range; in addition, the physical basis for η'_∞ is not clear.

This paper presents and discusses the results of an empirical data modification procedure suggested by the anomalies mentioned above; when applied to the data of Ferry and collaborators,[1-4] unique master curves are obtained which have shapes that are essentially independent of concentration, molecular weight, and polymer species. At present it is unclear which aspects of polymer chain dynamics are being displayed by the modified data plots; however, the modified properties may provide a stringent test of future theoretical chain dynamics treatments. In addition, viscoelastic properties can be empirically predicted with high precision from measured values of η'_∞ and η_0, the steady flow low gradient solution viscosity.

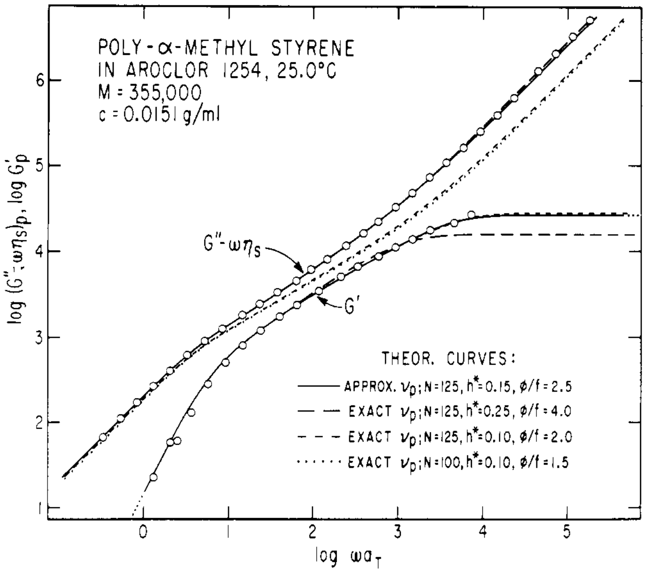

Figure 1. Storage (G'_p) and loss ($(G'' - \omega\eta_s)_p$) moduli, reduced to 25.0 °C, plotted logarithmically against frequency for poly(α-methylstyrene)/Aroclor solution noted in the figure. Curves drawn are various Peterlin theory predictions utilizing exact and inexact eigenvalues ν_p and values of N, h^*, and ϕ/f listed.

Data Modification Procedure

The data examined here are measurements obtained by various investigators at Wisconsin during the past seven years with the modified Birnboim apparatus and a computerized on-line data acquisition and processing system.[5] Measurements at various temperatures were reduced to 25.0 °C by time–temperature superposition.[8] Previous papers have examined the viscoelastic properties in terms of the reduced storage modulus $G'_p = (\rho_0 T_0/\rho T)G'$ and the reduced loss modulus $(G'' - \omega\eta_s)_p = (\rho_0 T_0/\rho T)(G'' - \omega\eta_s)$ plotted logarithmically against the reduced radian frequency ωa_T, where G' and G'' are the real and imaginary components of the complex shear modulus G^*. ρ and T are the solution density and absolute measurement temperature, respectively; the subscript zero refers to the reference temperature (25.0 °C), and η_s is the solvent viscosity. The shift factor a_T was obtained from the low-frequency limiting values of G'' where possible.[8] The polymer samples, solvents, and solutions are described in detail in previous papers.[1-4] Figure 1 illustrates the usual method of data presentation. The circles are the data obtained for the poly(α-methylstyrene) solution specified; the lines are various theoretical predictions of the Peterlin theory. The first power slope of log $(G'' - \omega\eta_s)$ for log ωa_T greater than 4 corresponds to the region in which η' has reached the frequency independent plateau denoted here as η'_∞. The various curves shown on the figure illustrate the substantial difference between theoretical curves generated with exact as opposed to inexact eigenvalues. Two sets of eigenvalues are involved in the Peterlin theory: the λ_p of the **HA** matrix (also appears in the Zimm theory[7]), and the ν_p of the **H** matrix.[11] Initially, approximate expressions for both the λ_p and ν_p were utilized;[1,2,12] more recent theoretical calculations incorporated exact eigenvalues[24] for the λ_p while the approximate ν_p were retained.[3,4,15,25,26] The use of exact λ_p results in substantially

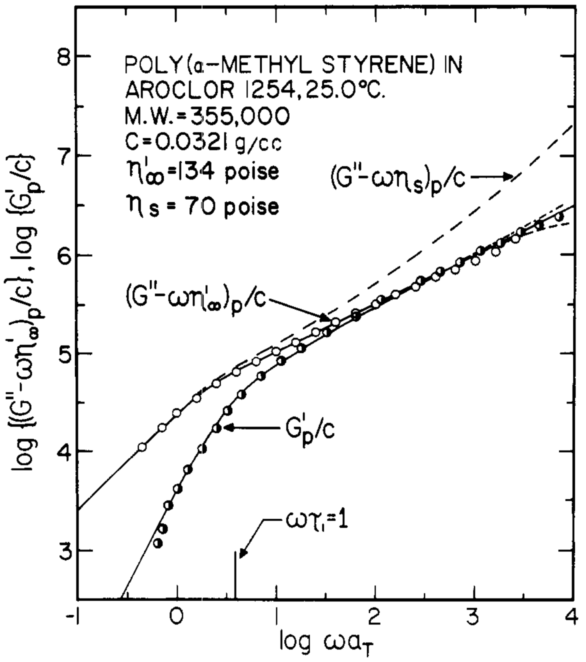

Figure 2. Plots of G'_p and modified loss modulus $(G''-\omega\eta'_\infty)_p$, divided by concentration c and reduced to 25.0 °C, for poly(α-methylstyrene)/Aroclor solution noted. Dashed line labeled $(G''-\omega\eta_s)$ /c corresponds to former unmodified data format. Solid lines are Zimm theory predictions for $h^*=0$, $N>1000$ (small arbitrary vertical shift). Chained and dashed lines shown at high frequencies correspond respectively to theoretical predictions for real and imaginary components of $(G^*-\omega\eta_s)$ for $N=100$.

different values for N and h^* and slightly different values of ϕ/f being required to generate theoretical curves that approximate closely those obtained with the approximate λ_p. Thus different values for the theoretical parameters were required, but good fits to data were still obtainable (not quite as good as with approximate λ_p). However, the incorporation of exact ν_p leads to drastically different results. Originally, the ν_p were approximated by $\nu_p \simeq \lambda_p/\lambda_{pf}$ where λ_{pf} denotes the values of λ_p for $h^*=0$ (free draining limit)[10,11] and the recent analytical solution gives $\nu_p=1$ for all values of h^*.[16] The solid lines of Figure 1 illustrate the excellent fits obtainable from the Peterlin theory when approximate ν_p are employed. The various dashed and dotted curves illustrate that, when exact ν_p are used, no fit is realized; values of N, h^*, and ϕ/f required to fit the $(G''-\omega\eta_s)$ curve do not fit G' and vice versa. Further, there is no unique set of parameters; substantial variations in N may be compensated by changing ϕ/f. This nonuniqueness is even more pronounced for birefringence properties.[27] Previous papers[1-4] have also listed values of G'_∞, the high-frequency limiting value of G', obtained by an extrapolation to higher frequency based on Peterlin theory fits to the data; since the value of G'_∞ is a fairly strong function of the theoretical parameters selected, these numbers are subject to question except for the one value[3] obtained from G'' measurements by an integration analogous to the Kronig–Kramers relations.[1]

Initial oscillatory birefringence measurements on polystyrene/Aroclor solutions utilizing the new thin fluid layer apparatus with extended high-frequency capability showed anomalous behavior at high frequencies.[15] The deviations appear to be caused by a high-frequency relaxation process(es) which has an intrinsic optical polarizability anisotropy of opposite sign to that for long-range conformational changes in polystyrene. The high-frequency relaxation process appeared to be caused by some type of phenyl group wagging motion or other highly localized motion in which the phenyl ring would tend to orient significantly in the principal stress direction.[15,27] Initially it was felt that the side group motion is quasi-independent of the chain backbone motions, and hence its contribution to the measured birefringence would be, to a first approximation, simply (tensorially) additive to the overall chain backbone dynamics contribution.[15] More recent work indicates that this picture is probably too simplified but that ring motions are intimately involved.[27] Interestingly, the anomalies in the birefringence experiment appear in the same frequency regime in which $(G''-\omega\eta_s)$ attains the high-frequency limiting slope for a given polymer solution, suggesting that there might be a common source for the optical anomaly and at least part of η'_∞. Since the initial birefringence data indicated to a first approximation that quasi-independent side group motions might be involved, it seemed possible that the contribution from such motions to η'_∞ might also be simply additive. There probably are various other contributions to η'_∞, including those from backbone motional restrictions,[17,18] rigid Einstein spheres,[30] internal viscosity,[20-22] etc. However, these contributions to η'_∞ may be small. Thus as a somewhat empirical first-order data modification procedure that might extract the chain dynamics contribution from measured viscoelastic properties one would plot $\log\,(G''-\omega\eta'_\infty)_p$ and $\log G'_p$ vs. $\log \omega a_T$. (Note that only the G'' term is modified; G' values are unchanged.) To remove the major concentration dependence for low solution concentrations the data are plotted herein as $\log\,(G''-\omega\eta'_\infty)_p/c$ and $\log G'_p/c$.

Figure 2 shows a typical result when this data modification procedure is utilized for solutions containing fairly monodisperse linear homopolymers. The circles correspond to the modified data points for the poly(α-methylstyrene) solution; the difference between the dashed line (the standard $(G''-\omega\eta_s)_p/c$ curve) and the circles illustrates the magnitude of the data modification. Surprisingly, the solid lines shown are the theoretical predictions of the Rouse limit ($h^*=0$) of the Zimm theory for large N (>1,000) with a small arbitrary vertical shift (0.06 on log scale) to compensate for finite concentration effects, while the (· - ·) and (- - -) curves (also arbitrarily shifted) correspond respectively to the real and imaginary $(G^*-\omega\eta_s)$ component predictions for the Rouse limit for $N=100$, the same value of N required to fit oscillatory flow birefringence data for this sample.[27] It is impossible to determine whether or not the finite N is more appropriate since the uncertainties in $(G''-\omega\eta'_\infty)$ are becoming significant at large values of ωa_T; modified data points for which the estimated uncertainty is greater than 20% have been discarded, but the three highest measurement frequencies shown probably have uncertainties between 10 and 20% since the difference between two nearly equal numbers is being plotted. This inability to distinguish between finite and large N applied to several of the solutions studied; large N curves are shown here for convenience. The G' data correspond more closely to the Rouse limit prediction than they do to the Peterlin theory with exact λ_p and inexact ν_p. The Rouse-like character of the G' data had been noted previously by Lamb and Matheson;[28] these investigators utilized an empirical correction viscosity η^*_s with their data so that $(G''-\omega\eta^*_s)$ and G' would both correspond to bead-spring model predictions for the Rouse limit of the Zimm theory. (Their measurements were not sufficiently extensive or precise to obtain η'_∞.) (Reference 2 indicated that the G' data could not be fitted well with the Zimm theory. This was correct for the approximate λ_p calculations available at that time but not for more recent exact λ_p results.) Figure 3 illustrates the surprising degree of concentration independence for the modified plots for poly(α-methylstyrene) solution concentrations differing by as much as a factor of 3; here again small vertical shift factors K (listed in Table I) are employed to superimpose the four individual curves. These shift factors

Table I
Parameters at Low and High Frequency Reduced to 25.0 °C from Modified and Unmodified Data for All Polymer/Aroclor 1254 Solutions Investigated (η_s = 70 P at 25.0 °C)

Polymer	$\overline{M}_w \times 10^{-3}$	$[\eta]_0$[a] mL/g	$[\eta']_\infty$, mL/g	$[\eta_m]_0$,[a] mL/g	$c \times 10^2$, g/mL	η_0, P	η'_∞, P	log K	$\tau_{1m} \times 10^2$, s
Polystyrene	19.8	15.6	14.3	1.3	7.57	358	196	+0.14	0.135
	51	27	14.3	13	7.56	660	215	+0.08	0.91
	82	37	14.3	23	5.09	455	143	+0.04	1.29
	267	76	14.3	62	2.74	440	100	−0.02	6.9
					5.54	1410	152	+0.05	18.2
	860	183	14.3	169	1.52[c]	19.8[c]	3.24[c]	−0.03[c]	26.9[c]
Poly(α-methylstyrene)	355	95[b]	22.2	73	1.51	270	96	+0.00	10.0
					2.38	554	115	+0.05	17.8
					3.21	941	134	+0.06	20.4
					4.62	2470	183	+0.14	55
Poly(methyl-2-ethyl acrylate)	459		18.5		1.15	187	83	−0.02	8.5
					2.11	367	95	+0.05	14.1
	687		18.5		1.60	349	91	+0.06	26.3
					2.88	775	116	+0.09	38.9
					4.28	1790	155	+0.14	74
	1000		18.5		1.41[c]	12.1[c]	3.21[c]	−0.01[c]	1.62[c]
Poly(methyl-2-*n*-butyl acrylate)	75.2		13.3		4.09	209	117	+0.06	0.44
	235		13.3		1.86	163	87	−0.10	1.62
					2.30	188	91	−0.10	1.74
					2.74	216	96	−0.09	2.04
					3.96	359	114	−0.06	2.95
Poly(methyl-2-phenyl acrylate)	65		18.5		4.21	267	144	+0.14	0.59
	263		18.5		1.94	168	91	−0.02	2.24
					3.23	304	116	+0.09	4.07
Poly(methyl methacrylate)	1500[d]		22.8						

[a] Steady flow intrinsic results are for various Aroclors (1232, 1248, or 1254); solvent powers of these are nearly identical. [b] Data shown are for mol wt 349 000. [c] Results in A-1248 solvent (η_s = 2.57 P at 25.0 °C). [d] Broad distribution sample; viscosity average molecular weight.

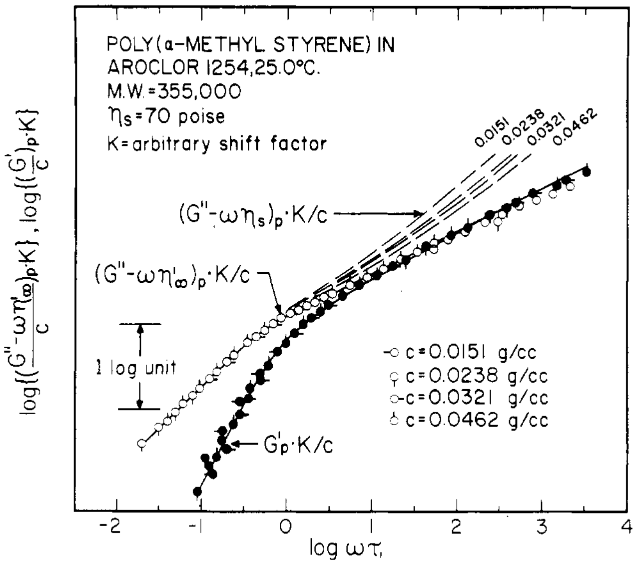

Figure 3. Plots of G'_p/c and $(G'' - \omega\eta'_\infty)_p/c$, reduced to 25.0 °C, plotted logarithmically against $\omega\tau_1$, for four poly(α-methylstyrene)/Aroclor solution concentrations noted in the figure. Dashed lines again correspond to unmodified $(G'' - \omega\eta_s)_p/c$ data. Small vertical shift factors K have been employed (see Table I) to superimpose data on Zimm theory predictions (solid curves) for $h^* = 0$, $N > 1000$.

are simply the ratio of the experimental ordinate position to that calculated from the Rouse ($h^* = 0$) limit of the Zimm theory assuming large N. Since the theory strictly applies for infinite dilution conditions, K should approach unity as c approaches zero. The solid lines again are Zimm theory curves for $h^* = 0$, N large. Note that the largest data modification occurs for the lowest solution concentration since the low-frequency properties are much more strongly dependent on concentration than are those at high frequency;[29] this indicates that extrapolation of the modified high-frequency data to obtain infinite dilution properties will only be possible with very precise measurements since the difference between two similar numbers is being plotted. The same superposition yielding the Rouse limit master curve shape is obtained for polystyrene solutions although the available data do not cover as extensive a concentration range.

Figure 4 shows the molecular weight independence of the shape of the modified plots for polystyrene solutions having molecular weights ranging from 19 800 to 860 000; there appear to be small downward deviations at the highest measurement frequencies for each molecular weight which may be the onset of finite N effects, but the modified plot uncertainties at the highest measurement frequencies again make it impossible to unequivocally answer the finite N question. (Birefringence measurements show that N must be finite and directly proportional to molecular weight.[12,15,27]) The longest relaxation time τ_{1m} obtained from these curves is a strong function of molecular weight, of course. Since the modification procedure results in significantly different low-frequency values for molecular weights below 267 000 (see Figure 4), the dependence of τ_{1m} shown in Table I differs somewhat from the unmodified data τ_1 values reported previously, particularly at low molecular weights.[1-4]

Figure 5 presents intrinsic modified viscoelastic properties obtained by extrapolation to zero concentration of the quantities shown in the square brackets. As noted earlier, this extrapolation becomes more difficult as measurement frequency is increased. Considering the uncertainty of the data for values of log ω greater than 3.0 it is not clear that the values of h^* required to generate the Zimm theory fit shown (solid curve) are quantitatively significant to better than ±0.025; h^* appears to lie between 0.025 and 0.05, however. The solid lines

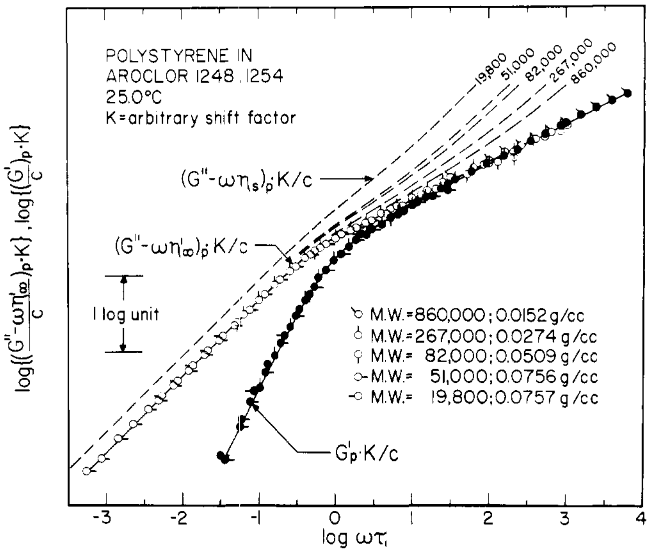

Figure 4. Plots of G'_p/c and $(G'' - \omega\eta'_\infty)_p/c$, reduced to 25.0 °C, plotted logarithmically against $\omega\tau_1$, for five different molecular weight polystyrene/Aroclor solutions. Dashed lines correspond to $(G'' - \omega\eta_s)_p/c$ data. Small vertical shift factors K employed to superimpose data on Zimm theory curve ($h^* = 0$, $N > 1000$) are listed in Table I.

are theoretical curves calculated from the Zimm theory for $N = 381$ (based on studies of the molecular weight dependence of oscillatory flow birefringence for polystyrene solutions[27]) and $h^* = 0.05$, indicating that the hydrodynamic interaction parameter is close to the Rouse free-draining limit, again demonstrating that the modified plot curve shape is at most very weakly dependent on concentration. The theoretical curves of Figure 5 are not arbitrarily positioned to provide best curve shape fits but are absolute fits; the small cross corresponds to the theoretical ordinate value of log (RT/M) and the abscissa value of log ω for which $\omega\tau_{01m} = 1$ (τ_{01m} is the infinite dilution limiting value of τ_{1m}). τ_{01m} is calculated from the known molecular weight, the steady flow intrinsic viscosity $[\eta]_0$, the solvent viscosity η_s, and $[\eta']_\infty$ by [29]

$$\tau_{01m} = [\eta_m]_0 \cdot \frac{M\eta_s}{RT} \cdot \frac{1}{\sum\limits_{p=1}^{N} \lambda_1/\lambda_p} \tag{2}$$

which is the Zimm theory expression for τ_{01} with $[\eta]_0$ replaced by a modifed intrinsic viscosity $[\eta_m]_0$ defined as

$$[\eta_m]_0 \equiv \lim_{c \to 0} \frac{\eta_0 - \eta'_\infty}{\eta_s c} = [\eta]_0 - [\eta']_\infty \tag{3}$$

where η_0 is the steady flow solution viscosity. Table I lists $[\eta]_0$, $[\eta']_\infty$, and $[\eta_m]_0$ for the polymer/Aroclor solutions that have been investigated.[1-4] Very recently, more precise intrinsic modified viscoelastic properties of monodisperse 860 000 molecular weight polystyrene in both α-chloronaphthalene and Aroclor 1232 solvents (solvent powers similar to Aroclor 1248) obtained with the multiple lumped resonator apparatus have been examined; again, good fits to the Zimm theory are obtained for $N = 381$ and $h^* \leq 0.05$.[29]

Figures 6 through 9 illustrate the modified viscoelastic properties for various poly(2-substituted methyl acrylate)/Aroclor solutions. Figures 6 through 8 are for samples that have $M_w/M_n \leq 1.05$ so that good Zimm theory curve shape fits are obtained for a given molecule with one value each of N (same as in ref 4) and h^*; Figure 9 presents data for a broad distribution commercial poly(methyl methacrylate) solution for which an integration of the properties for an appropriate range of N values would be necessary to generate the proper theoretical curve shape. The solid lines correspond to arbitrarily positioned Zimm theory curves for the parameter values shown on the figures; for the broad distribution sample of Figure 9 the theoretical curve shown is that for a large value of N and is strictly speaking appropriate only for log (ωa_T) greater than zero (high-frequency slope is to a good approximation independent of the molecular weight distribution). The N values selected to generate the theoretical curves for the methyl acrylate derivatives (Figures 6 through 9) are somewhat arbitrary;[4] N values are normally assigned on the basis of oscillatory flow birefringence results which are not yet available for these samples. Again for this family of polymers the h^* required to match theory to experiment is close to the free-draining limit.

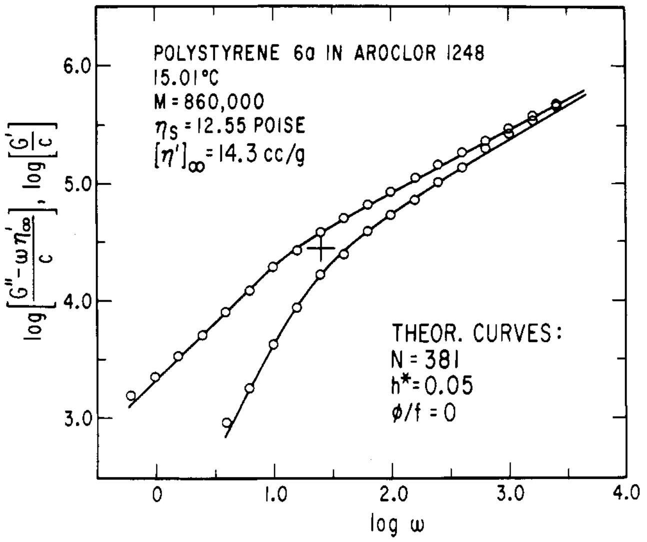

Figure 5. Infinite dilution viscoelastic properties (modified format) for polystyrene/Aroclor solution at 15.01 °C. Theoretical curves are Zimm theory predictions for N and h^* values listed, with no arbitrary curve shifting.

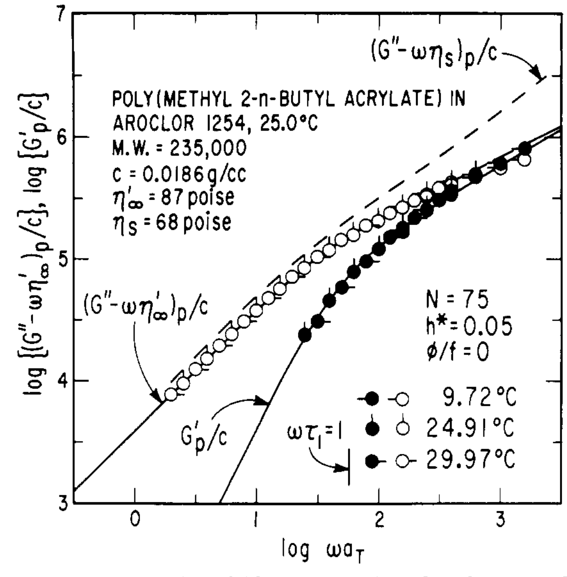

Figure 6. Plots of G'_p/c and $(G'' - \omega\eta'_\infty)_p/c$, reduced to 25.0 °C, for poly(methyl-2-n-butyl acrylate)/Aroclor solution. Solid curves are Zimm theory predictions for N and h^* shown (small arbitrary vertical shift employed).

Table I lists the polymer species, molecular weights, solution concentrations, η'_∞, the unmodified steady flow solution viscosity η_0, the longest relaxation time τ_{1m} from the modified

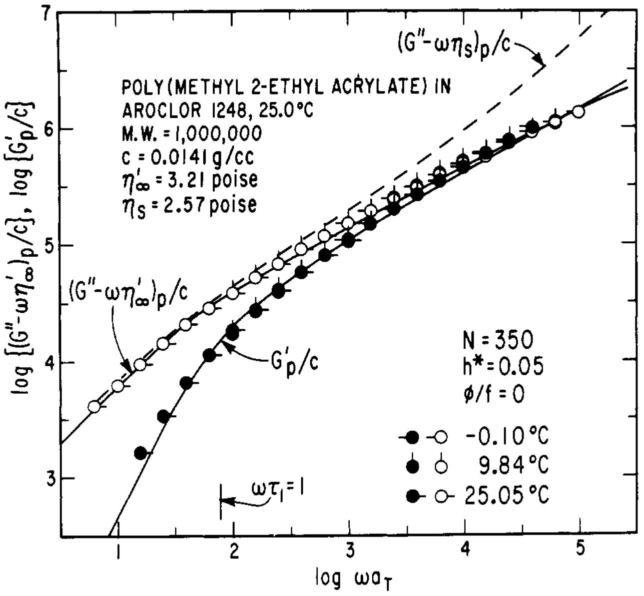

Figure 7. Plots of G'_p/c and $(G'' - \omega\eta'_\infty)_p/c$, reduced to 25.0 °C, for poly(methyl-2-ethyl acrylate)/Aroclor solution. Solid curves are Zimm theory predictions for N and h^* shown (small arbitrary vertical shifts employed).

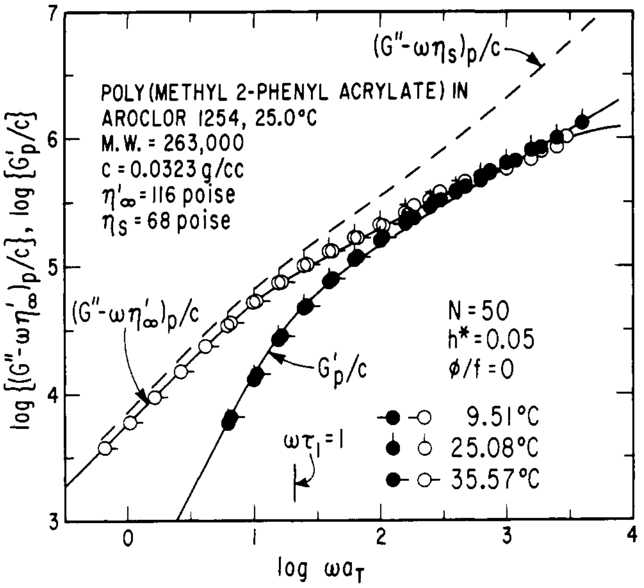

Figure 8. Plots of G'_p/c and $(G'' - \omega\eta'_\infty)_p/c$, reduced to 25.0 °C, for poly(methyl-2-phenyl acrylate)/Aroclor solution. Solid curves are Zimm theory predictions for N and h^* shown (small arbitrary vertical shift employed).

plots, and the small ordinate shift factors K required to superimpose the modified data and theory in addition to the intrinsic limiting properties noted previously.

Discussion

As Figure 1 indicates, the Peterlin theory[10,11] does not fit viscoelastic data when exact eigenvalues λ_p and ν_p are incorporated. Thus at this point in time there appears to be no theory capable of fitting the measured properties over the experimentally accessible frequency range. However, modified versions of the Peterlin theory are in preparation which have different mode number dependences than the original formulation for the additional energy dissipation and should correspond more closely to the predictions of the theory when inexact ν_p were used.[30] Also, a new chain dynamics theory has been developed by Fixman and Evans which treats η'_∞ in terms of resonant energy transfer between local and global modes of motion in a polymer chain; preliminary calculations exhibit the basic character displayed by the data.[31] It is clear that an appropriate theory must mimic the frequency dependence predictions of the Peterlin theory with approximate ν_p and λ_p.

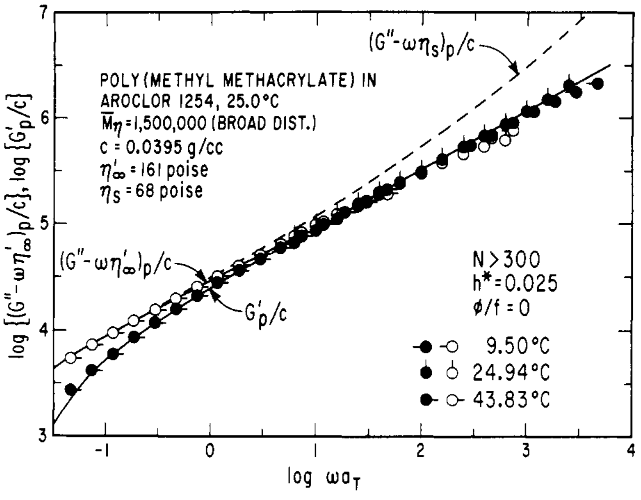

Figure 9. Plots of G'_p/c and $(G'' - \omega\eta'_\infty)_p/c$, reduced to 25.0 °C, for poly(methyl methacrylate)/Aroclor solution. Solid curves are Zimm theory predictions for N and h^* shown (small arbitrary vertical shift employed).

The modified data plots, illustrated in Figures 2 through 9, correspond to the predictions of the Zimm theory for $h^* \leq 0.05$ (close to the free-draining limit) for all polymer/solvent systems studied here during the past 7 years. The fits obtained are excellent; they are equal or superior to those obtained originally with the approximate Peterlin theory.[1,2] Modified data for polystyrene when extrapolated to infinite dilution are fitted absolutely with essentially the same value of h^*, as Figure 5 demonstrates; the modified data format shows no or at most a very weak concentration dependence for the polystyrene and poly(α-methylstyrene) solutions studied, the only systems for which sufficient data exist to study dilution effects. Further, for polystyrene, the only system for which extensive molecular weight studies have been carried out, the superimposed modified data demonstrate that the same theoretical master curve shape fits these data very well also; it is not clear whether finite N (proportional to molecular weight) is necessary for optimal fits. Theoretically, the shift factors K given in Table I should approach one as concentration approaches zero; there is some scatter in the values shown, but the overall trend is for K to become somewhat less than one when extrapolated to zero concentration.

It is not clear what aspect of chain dynamics is being displayed by the alternate data format; however, it seems fairly certain that these modified plots do not correspond to the entire chain backbone dynamics contribution to the measured viscoelasticity as the simple quasi-independent side group motion picture mentioned initially would suggest. The small value of h^* required for theoretical fits does not correspond to that required to fit either modified or unmodified oscillatory flow birefringence data;[27] further, the birefringence vs. concentration results correspond to a substantial variation of h^* with concentration as is predicted by various theories.[15,27,33] Also, the dependence of $[\eta]_0$ on solvent power demonstrates hydrodynamic interaction effects.[33] However, the clearest demonstration of the inadequacy of the simple quasi-independent side group motion picture is shown in Figure 10; here $[\eta]_0$ values obtained from capillary viscometers

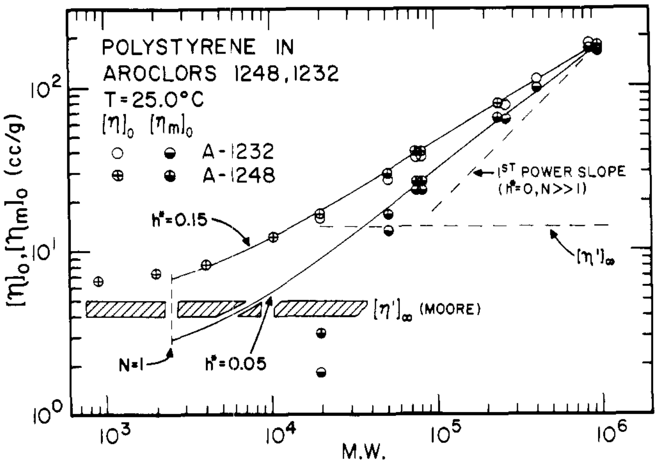

Figure 10. Plots of steady flow intrinsic viscosity $[\eta]_0$ and modified intrinsic viscosity $[\eta_m]_0$ vs. molecular weight for polystyrene/Aroclor solutions, 25.0 °C. Solid lines are Zimm theory curves for values of h^* shown. $[\eta']_\infty$ shown as horizontal dashed line. Very high-frequency $[\eta']_\infty$ values (Moore and collaborators[9]) are also shown (broad shaded band).

(Aroclor 1232 solvent)[34] and from a concentric cylinder apparatus (Aroclor 1248 solvent)[12] are plotted logarithmically against weight average molecular weight for monodisperse polystyrene solutions. Also shown as a horizontal dashed line is $[\eta']_\infty$ for the polystyrene/Aroclor system.[2,4] Note that $[\eta']_\infty$ was determined only for $\overline{M}_w$ of 19 800 or larger; extrapolation of $[\eta']_\infty$ to lower molecular weights results in an obvious inconsistency since $[\eta']_\infty$ must be less than $[\eta]_0$ unless the only motions possible are those giving rise to $[\eta']_\infty$. Further, if $[\eta']_\infty$ is the result of very local and quasi-independent motions, it should be independent of molecular weight to small values; from the figure $[\eta']_\infty$ would vary with $\overline{M}_w$ for values below 10 000. Two Zimm theory (exact λ_p) curves for the molecular weight dependence of $[\eta]_0$ are shown (solid lines); the curve corresponding to $h^* = 0.15$ fits the $[\eta]_0$ data for $\overline{M}_w \geq 2000$ ($\overline{M}_w \simeq 2000$ is where an N of 1 is required to fit oscillatory flow birefringence data). The success of this fit is remarkable considering that the Zimm theory strictly applies for θ solvent conditions; this fit illustrates again that non θ solvent data may be fitted readily by utilizing an appropriate value of h^*.[35] Also shown is the Zimm prediction for $h^* = 0.05$; it corresponds reasonably closely to $[\eta_m]_0$ data shown for $\overline{M}_w > 50\,000$. Thus the simple subtractive procedure results in a reasonably consistent picture only at high molecular weights. A dashed line (first power slope) illustrates the molecular weight dependence predicted for $h^* = 0$ and moderate to high molecular weights; $[\eta_m]_0$ and the intrinsic viscoelastic properties for polystyrene both correspond to theoretical curves for $h^* \simeq 0.05$ (low $\overline{M}_w$ data excluded). The broad shaded band of Figure 10 corresponds to the very high frequency $[\eta']_\infty$ measured by Moore;[9] these data obtained at 23.0, 40.0, and 98.94 MHz with di-*n*-butyl phthalate as solvent suggest that at very high frequencies the value of $[\eta']_\infty$ is substantially less than the value obtained in the studies discussed here. Note that Moore's data falls below $[\eta]_0$ for $\overline{M}_w$ as low as 900 as would be expected if $[\eta']_\infty$ results from either very local side group motions or the physical processes treated in such theories as those of Fixman and co-workers.[17,18] Based on the evidence obtained to date it appears that the first plateau value denoted as $[\eta']_\infty$ herein is a result of somewhat localized motions, but motions not described by simple bead-spring model theories that may involve chain segments up to approximately 100 monomer units in length for atactic polystyrene. Further, the nature of the polymer side groups seems to play an important role in these motions as evidenced by the variation of $[\eta']_\infty$ with side group. For polystyrene solutions with molecular weights below 20 000 $[\eta']_\infty$ is a substantial fraction of $[\eta]_0$ indicating that a proper understanding of the physical origin of $[\eta']_\infty$ may be required before simple steady flow properties are understood from a chain dynamics viewpoint, at least for low molecular weights.

An earlier paper[2] also discussed the viscoelastic properties of some of the same polystyrene and poly(α-methylstyrene) solutions analyzed here. Some conclusions were drawn based on fits of the inexact eigenvalue Peterlin theory to the data; the exact results together with recent birefringence data lead to somewhat different conclusions. It still seems clear that $[\eta']_\infty$ does not arise from an additional purely dissipative mechanism (independent of molecular weight) since $[\eta_m]_0$ exhibits an anomalous molecular weight dependence at low molecular weights. However, it is no longer correct to say that existing G' curves cannot be fitted precisely by the addition of a constant viscosity term to the Zimm theory.[2] Also, previous conclusions based on the evaluation of the number of modes from the high-frequency limiting value of G' are suspect since this value was obtained from Peterlin theory extrapolations which are now subject to considerable uncertainty.[2] The previous paper suggested that a very local fast relaxation mechanism such as a side group motion could be responsible for $[\eta']_\infty$. Again, Figure 10 suggests that the motions involved are not that localized.

Other experiments utilizing quite different force fields also suggest that there are motions involving from 10 to 100 monomer units in polystyrene solutions that perhaps play a role in what is observed at high frequency in the shear excited viscoelasticity experiment as well. For example, Raman light-scattering results show that the reorientation correlation time for phenyl groups has a substantial dependence on molecular weight for $\overline{M}_w < 10^4$, indicating that some cooperative motions involving several rings may be present.[36] Dielectric measurements on halostyrene polymers also show a substantial dependence of the frequency of maximum loss on molecular weight for $\overline{M}_w < 20\,000$.[37] Ultrasonic absorption also suggests moderately local motions involving a few monomeric units.[38] Perhaps such motions play a role in some type of global-to-local mode energy transfer process as suggested by Fixman and Evans.[31] Clearly extensive theoretical and experimental work is needed to clarify the origin of η'_∞ and its role in polymer chain dynamics. We are now attempting to obtain viscoelastic measurements for polymers with very small side groups or with bulky groups in the chain backbone (polyphenylene oxide, for example), as well as data for isotactic polystyrene and lower molecular weights of atactic polystyrene to clarify experimentally the role of side groups in polymer motions; a more general theory of chain dynamics will also be essential to understand the role of chain dynamics in the viscoelastic properties of dilute polymer solutions.

The data modification procedure outlined here has yielded one useful empirical result; given measured values of η_0 and η'_∞ for a linear homopolymer of sufficiently high molecular weight one can predict to within better than 5% the viscoelastic properties that would be exhibited over a wide frequency range by combining these values with a Zimm theory curve for small h^*.

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Spin Relaxation and Local Motion in Solutions of Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: The spin–lattice relaxation time of the methyl protons of poly(2,6-dimethyl-1,4-phenylene oxide) dissolved in $CDCl_3$ was measured as a function of molecular weight, temperature, and concentration. At a given temperature and concentration, the molecular weight dependence of the spin–lattice relaxation times was interpreted in terms of correlation times for motions likely in this polymer. Motions considered include overall rotatory diffusion, three-bond crankshaft motions, anisotropic internal rotation of the phenyl group, and anisotropic internal rotation of the methyl group. According to the interpretation, spin relaxation at high molecular weights is dominated by anisotropic phenyl group rotation characterized by correlation times from 0.2 to 0.4 ns. The three-bond crankshaft motions also contribute to relaxation and the corresponding correlation times range from 1 to 15 ns. The rapid phenyl group rotation accounts for the unusual presence of minima in some of the plots of spin–lattice relaxation times vs. molecular weight. Methyl group rotation is too fast to significantly contribute to relaxation and only serves to partially average the dipole–dipole interactions. The apparent activation energy for phenyl group rotation is 5 kJ, and the apparent activation energy for the three-bond crankshaft motion is 25 kJ. The correlation time for the three-bond crankshaft motion is strongly dependent on concentration while the phenyl group rotational correlation time is only weakly dependent on concentration.

Local motion in poly(2,6-dimethyl-1,4-phenylene oxide) abbreviated here as M_2PPO is expected to be quite different from other polymers recently studied in solution by NMR such as polystyrene,[1-4] polyoxymethylene,[5] and polyisobutylene.[6-9] In polymers containing carbon–carbon single bonds and carbon–oxygen single bonds, backbone rearrangements of the general crankshaft type have been proposed as the dominant local motion although rotation of substituent groups attached to the backbone is also observed.[1-9] In M_2PPO, the backbone is composed of rigid phenyl groups between oxygen atoms and in addition to crankshaft type motions, internal rotation of the phenyl group composing the backbone could be an important local motion.[10] This latter motion has been proposed as the major contributor to the high impact strength of M_2PPO.[10]

To probe local motion in M_2PPO, proton spin relaxation was observed as a function of temperature, concentration, and molecular weight. The dependence of T_1 of the methyl protons vs. molecular weight served as the primary basis for interpretation. The unusual local chain dynamics in M_2PPO is immediately apparent in the relaxation data since minima are present in the plots of T_1 vs. molecular weight under a variety of experimental conditions. An earlier ^{13}C NMR study[11] of one high molecular weight sample of M_2PPO found T_1 of all carbons in the repeat unit to be nearly independent of temperature which is also atypical for synthetic polymers in solution. A similar temperature dependence is observed for the ^1H relaxation times at high molecular weight, and indeed extensive data including molecular weight dependent data are required for the interpretation. The greater sensitivity of ^1H NMR expedited the acquisition of a large body of data.

The interpretation given here employs a specific motional model presented by Jones and Stockmayer[12] which includes local motions caused by backbone rearrangements and in-

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