the transition observed by DSC at 150° and is tentatively assigned to motions accompanying the glass transition of the "stereocomplex" postulated to occur in these polymers, composed of isotactic and syndiotactic chains.

The only previous report of activation energies for poly(methyl α-chloroacrylates) is for the "conventional" free-radical polymer which can be assumed to be reasonably syndiotactic.[13] The values quoted are 130 kcal/mol for the α relaxation and 26 kcal/mol for the β relaxation. The present results (Table II) are in qualitative agreement with these values. In general the activation energies for the α relaxations decrease with increasing ester side-chain length or bulkiness and the isotactic isomers have α relaxation activation energies about 35–50 kcal/mol lower than the comparable syndiotactic isomers.

Conclusions

(1) The T_g's of stereoregular poly(alkyl α-chloroacrylates) are strong functions of tacticity and can be rationalized, to a first approximation, on the basis of the previously proposed theory.[6]

(2) Evidence exists for the presence of a stereocomplex composed of a combination of isotactic and syndiotactic poly(methyl α-chloroacrylate).

(3) Crystallinity can be observed for the highly isotactic poly(alkyl α-chloroacrylates) and appears to be analogous to the behavior of isotactic poly(alkyl methacrylates).

(4) The relaxation behavior accompanying the glass transitions in stereoregular poly(alkyl α-chloroacrylates) is generally in accord with previous results on atactic polymers.

(5) The secondary or β relaxation, assigned to motions of the ester side group, is a minor feature dielectrically in contrast to the behavior of the poly(alkyl methacrylates).

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References and Notes

(1) B. Wesslen and R. W. Lenz, *Macromolecules*, **4**, 20 (1971).
(2) B. Wesslen, R. W. Lenz, W. J. MacKnight, and F. E. Karasz, *Macromolecules*, **4**, 24 (1971).
(3) B. Wesslen, R. W. Lenz, and F. A. Bovey, *Macromolecules*, **4**, 709 (1971).
(4) G. Dever, R. W. Lenz, W. J. MacKnight, and F. E. Karasz, *Macromolecules*, submitted for publication.
(5) G. Dever, R. W. Lenz, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, submitted for publication.
(6) F. E. Karasz and W. J. MacKnight, *Macromolecules*, **1**, 537 (1968).
(7) J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).
(8) S. Bywater and P. M. Toporowski, *Polymer*, **13**, 94 (1972).
(9) J. M. O'Reilly, F. E. Karasz, and H. E. Bair, *Bull. Am. Phys. Soc.*, **9**, 285 (1964).
(10) R. H. Marchessault, H. V. Hein, and G. P. Dever, in press.
(11) O. G. Lewis, "Physical Constants of Linear Homopolymers", Springer-Verlag, New York, N.Y., 1968, p 106.
(12) W. A. Lee, *Br. Polym. J.*, **5**, 3762 (1971).
(13) K. Deutsch, E. A. W. Hoff, and W. Reddish, *J. Polym. Sci.*, **13**, 565 (1954).
(14) H. Shindo, I. Murakami, and H. Yamamura, *J. Polym. Sci., Polym. Chem. Ed.*, **1**, 297 (1969).

Depolarized Rayleigh Spectroscopy Studies of Relaxation Processes of Polystyrenes in Solution

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ABSTRACT: Depolarized Rayleigh spectra and integrated intensities of atactic polystyrenes in solution have been measured as a function of molecular weight. All spectra (except at the lowest molecular weights) consisted of two components of roughly equal intensity. The relaxation time of the narrow component increased rapidly with molecular weight. This time is approximately equal to one-half the relaxation time of the longest wavelength mode of a Rouse–Zimm chain. The relaxation time of the broad component is roughly independent of molecular weight and can be related to the internal relaxation time of the individual phenyl groups on the chain. The total integrated depolarized intensities agree fairly well with those calculated by rotational isomeric state models (except for an excess intensity at high molecular weight).

I. Introduction

The study of the dynamics of macromolecules has long been an important branch of polymer science. Measurements of the translational and rotational motion of macromolecules have been important, for instance, in elucidating the structure of macromolecules in solution. The study of the intramolecular dynamics is not only important in studying macromolecular structure but is also of importance in determining viscoelastic and macroscopic mechanical properties of macromolecules. A knowledge of the intrachain dynamics at the molecular level would be invaluable in designing polymer systems with specific desired macroscopic properties. Unfortunately, however, there are few methods which may be used to probe these dynamic processes for macromolecules in solution, especially at high frequencies. Techniques such as dynamic viscosity and flow and electric birefringence are valuable at lower frequencies. Dielectric dispersion is currently the method most widely used over a wide frequency range, while NMR and EPR promise to be of great use. Clearly, complementary techniques for probing these motions are needed. In this article, we describe a new probe, depolarized Rayleigh scattering spectroscopy.

Rayleigh scattering total intensity measurements are routinely used to study equilibrium properties of polymers in solution. For instance, the isotropic Rayleigh component intensity is often measured to obtain molecular weights, radii of gyration, and solution virial coefficients of macromolecules.[1] More recently, the much weaker depolarized intensities have been used to study the local conformation of polymer chains.[2,3] Modern light beating and interferometric techniques have made it possible to study the spectral distribution of scattered light as well as integrated intensities.[4] The spectral distribution of the isotropic component of the scattered light from polymers is now regularly used to determine translational diffusion coefficients. For very large molecular weight samples, it is possible, by using both polarized and depolarized Rayleigh spectroscopy, to observe long wavelength intramolecular relaxations.[5,6] Despite the widespread use of various Rayleigh scattering techniques in polymer problems, however, there have been no studies of local intramolecular relaxation processes by depolarized Rayleigh spectroscopy. This article presents the first successful application of this technique to the study of fast local relaxation processes of flexible coil molecules in solution. We have also studied the slower long wavelength intramolecular relaxations.

Depolarized Rayleigh spectra have been measured for a wide variety of small molecules.[7-9] It has been found that the depolarized spectra of small molecules are primarily determined by overall molecular rotational motion. We might expect then, that the spectra of polymers in solution might also be dependent on overall tumbling times and in addition in the case of flexible polymers, on relaxations of long wavelength intramolecular modes. Since most polymer chains are composed of optically anisotropic subunits, the spectra may also be sensitive to local conformational changes that alter the laboratory-fixed polarizability. Since the relevant quantity in depolarized light scattering experiments is the laboratory-fixed optical polarizability, the depolarized spectra may be determined by overall molecular tumbling, or various intramolecular relaxation processes, or both, depending upon the coupling between the molecular relaxation processes and the molecular optical anisotropy and also upon the relative magnitude of the relaxation times of the various processes. For instance, if a particular intramolecular motion has no change in laboratory-fixed polarizability associated with it, it would not contribute to the depolarized spectrum. It is very difficult to predict the particular resultant depolarized spectrum for any given flexible polymer on the basis of existing dynamical models. The only detailed predictions of the depolarized spectra for flexible coils have been given by Ono and Okano for the familiar Rouse–Zimm chain model.[10] They found that the spectrum should consist of a sum of Lorentzians whose line widths are determined by the relaxation times of the normal modes. The Rouse–Zimm chain model, however, does not include local intramolecular relaxation processes, and, as we discuss below, the model does not agree with our experimental results for polystyrenes in solution.

In order to test the feasibility of using depolarized Rayleigh spectroscopy to study relaxation of polymers in solution and to determine the nature and magnitude of these relaxation times, we have measured the depolarized Rayleigh spectra of atactic polystyrenes in solution over the molecular weight range 2,200–2,000,000 using a spherical Fabry-Perot interferometer as a predetection filter. Depolarized correlation functions for the highest molecular weight samples were also measured using optical mixing techniques. We chose polystyrene for the following reasons: narrow fraction molecular weight samples are readily available; its monomer unit has a large optical anisotropy; and its physical properties have been studied in great detail. Physical techniques that have been used to study polystyrene include both isotropic[1] and depolarized light scattering integrated intensities, isotropic Rayleigh scattering spectral densities,[5] NMR relaxation,[11] EPR lineshapes,[12] dielectric relaxation (on substituted polystyrenes),[13,14] and acoustic absorption.[15,16] The solvents used in our study are CCl_4, 1,1,2,2-tetrachloroethane (TCE), and benzene. Spherical Fabry-Perot interferometry is the method of choice for determining line widths greater than 1 MHz.[17] Optical mixing was employed for line widths less than 100 kHz. In general the signal-to-noise ratio for interferometry was much higher than for the optical mixing techniques.

We have found that the depolarized spectra of the polystyrenes consist, in general, of the sum of two components: (1) a narrow molecular weight dependent component that can be associated with the relaxation time of a long wavelength intramolecular mode and (2) a broad, nearly molecular weight independent component which can be associated with a local relaxation. For the two lowest molecular weights, the overall tumbling is faster than the local conformation relaxation and only one component is observed. The relaxation time of the molecular weight dependent component is proportional to the product of the molecular weight, M, the intrinsic viscosity, $[\eta]$, and the solvent viscosity, η_0. This is in agreement with the molecular weight dependence predicted by normal coordinate theories.[18] The molecular weight independent component relaxation time is also proportional to η_0 and can be related to the relaxation times determined by NMR and EPR.

II. Theory

Pecora has formulated general expressions for the depolarized Rayleigh spectral distribution from dilute solutions of macromolecules composed of optically anisotropic monomer units in solvents consisting of optically isotropic molecules.[19] A summary of these results is presented to provide a framework for the discussion of our experimental results. For the scattering geometry of ref 7–9, the depolarized spectral distribution at frequency change ω, $I_{VH}(\omega)$, is given by

$$I_{VH}(\omega) = \frac{A\rho}{2\pi} \int \exp(-i\omega t) S_{yz}(t) \mathrm{d}t \qquad (1)$$

where A is a constant, ρ is the number density of polymer, and the correlation function $S_{yz}(t)$ is given by

$$S_{yz}(t) \equiv \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \alpha_{yz}{}^{i}(t)\, \alpha_{yz}{}^{j}(0) \exp\{i\mathbf{K}\cdot(\mathbf{r}^{i}(t) - \mathbf{r}^{j}(0))\}\rangle \qquad (2)$$

where n is the number of monomer units on a single chain and i and j are on the same chain, $\alpha_{yz}{}^{i}(t)$ is the yz component of the laboratory-fixed polarizability of monomer unit i at time t, $\mathbf{K}$ is the scattering vector, and $\mathbf{r}^{i}$ is the position of the ith monomer unit. Equation 1 assumes that the polymer is dilute enough that pair correlations between different polymer molecules are negligible. The $\mathbf{K}$ dependent term can be safely ignored because its relaxation is negligible over the time scale that $\alpha_{yz}{}^{i}(t)$ relaxes.

In general, calculation of $S_{yz}(t)$ is extremely difficult. We will evaluate two simple cases which serve to illustrate the main types of processes that may contribute to an actual spectrum. If the polymer is rigid in the sense that all intramolecular relaxation processes are slow compared to overall motion, or if the intramolecular motions do not change the laboratory-fixed polarizability, $S_{yz}(t)$ may be written

$$S_{yz}(t) = \langle \alpha_{yz}{}^{\mathrm{tot}}(t)\, \alpha_{yz}{}^{\mathrm{tot}}(0)\rangle \propto e^{-6\Theta t} \qquad (3)$$

where $\alpha_{yz}{}^{\mathrm{tot}}$ is the yz component of the total polarizability of the polymer and Θ is the macromolecular rotational diffusion coefficient. For this model we would predict that $I_{VH}(\omega)$ consists of one Lorentzian with a half-width at half-height of 6Θ. This rotational diffusion coefficient is a strong function of molecular weight. If, on the other hand, the monomer units of the polymer can reorient independently much faster than the overall tumbling time and if the different monomer units are uncorrelated with each other (the correlated case is treated in the Appendix), then $S_{yz}(t)$ may be written as

$$S_{yz}(t) = n\langle \alpha_{yz}^{\,i}(t)\,\alpha_{yz}^{\,i}(0)\rangle \propto e^{-t/\tau} \tag{4}$$

where τ is the correlation time for internal relaxation. Thus for this model, $I_{\mathrm{VH}}(\omega)$ consists of one Lorentzian with a molecular weight independent relaxation time τ. Of course neither of these models is very realistic for flexible polymers such as polystyrene. It could be possible to observe both types of relaxation in the same spectrum. This is because internal relaxation is often constrained to transitions between a few different configurations by barriers to internal rotation and there may not be large polarizability anisotropy changes associated with these motions. Thus the internal motion may not completely relax the laboratory-fixed polarizability. The residual anisotropy could be relaxed by some overall molecular tumbling.

The normal mode theories of Rouse and Zimm provide a framework for discussing relaxation times of polymers. The result of the Rouse-Zimm normal mode analysis is that there are m normal mode relaxation times in the polymer where m is the number of Kuhn statistical segments. The time autocorrelation function of the kth normal mode decays with time constant, τ_k,[18]

$$\tau_k = A_k \frac{M[\eta]\eta_0}{N_{\mathrm{av}}k_{\mathrm{B}}T} \tag{5}$$

where the A_k are constants. For the free draining model $A_1 = 0.608$ and $A_k = A_1/k^2$. For the nondraining model $A_1 = 0.422$. As mentioned in section I, Ono and Okano have calculated the depolarized Rayleigh spectrum of a free draining Rouse-Zimm chain. They predicted that the spectrum should consist of the sum of m equally intense Lorentzians where m is the number of normal modes of the chain. The relaxation time of each of the Lorentzians appearing in the spectrum is one-half the corresponding normal mode relaxation time given in eq 5. In section IV we point out that this prediction does not agree with the experimental results for polystyrene. There are, in addition, several theories which calculate "average" rotational diffusion relaxation times for flexible polymers. Kirkwood and Riseman[20] and Isihara[21] find that

$$\tau_{\mathrm{or}} = \frac{2}{3}\frac{M[\eta]\eta_0}{N_{\mathrm{av}}k_{\mathrm{B}}T} \tag{6}$$

Isihara has written eq 6 as follows

$$\tau_{\mathrm{or}} = \langle R_{\mathrm{g}}^{\,2}\rangle/9D \tag{7}$$

where D is the translational diffusion coefficient and $\langle R_{\mathrm{g}}^{\,2}\rangle$ is the mean square radius of gyration. The relationship between these "rotational" times and the light scattering spectrum is uncertain. In addition to the above theoretical calculations, Monte Carlo calculations have provided much information about polymer dynamics and structure.[22-24] We discuss some of these models in section IV.

Integrated depolarized intensities are a measure of average local conformation. From eq 1 and 2, the total integrated intensity can be written as

$$I_{\mathrm{VH}} = A\rho \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \alpha_{yz}^{\,i}(0)\,\alpha_{yz}^{\,j}(0)\rangle \tag{8}$$

We define a quantity $1 + F$ which is a measure of the internal static pair correlations of the polymer chain

$$1 + F \equiv \frac{\sum_{i=1}^{n}\sum_{j=1}^{n}\langle \alpha_{yz}^{\,i}(0)\,\alpha_{yz}^{\,j}(0)\rangle}{n\langle \alpha_{yz}^{\,i}(0)\,\alpha_{yz}^{\,i}(0)\rangle} = \frac{\langle \gamma^2\rangle}{n\beta^2} \tag{9}$$

where $\langle\gamma^2\rangle$ is the mean-square optical anisotropy of the polymer and β is the anisotropy of the monomer. It is possible to measure this ratio directly without making absolute calibrations or refractive index corrections.[25] It is also possible to calculate the ratio $1 + F$ using rotational isomeric state (RIS) theory. A review of this theory has recently been given by Flory.[26] Briefly, one introduces monomer or bond anisotropies and various weighting factors involving the various polymer configurations into the theory and then calculates $\langle\gamma^2\rangle$. A usual result of RIS calculations for flexible coils is that $\langle\gamma^2\rangle/M$ approaches a constant for sufficiently large M. RIS theory calculates the "intrinsic" anisotropy of the polymer. Another type of anisotropy that can be important is "form anisotropy".[17] Form anisotropy arises in systems in which the refractive index of the polymer is different from that of the solvent and in which the polymer differs from spherical shape. The magnitude of the form anisotropy is proportional to the hydrodynamic volume of the polymer ($\propto M[\eta]$). Thus, form anisotropy becomes increasingly important as the molecular weight is increased.

Values of F much different from zero indicate that there are significant orientational pair correlations between different monomer units on the chain. The effects of this correlation on the light scattering spectrum can be calculated for a simple model using Mori's statistical mechanical theory of fluctuations.[27,28] We[8,29] and others[30] have already applied Mori theory to calculate the effect of pair correlations on the depolarized Rayleigh spectrum of liquids composed of "small" molecules (e.g., benzene and chloroform). These calculations can be easily extended to the case of correlated monomer units on a chain provided certain assumptions are made (see Appendix). The results are completely analogous to the small molecule case.[8] When the time displaced correlation between the time derivatives of the orientations of different monomer units is negligible, the "collective relaxation time", τ_{c}, is related to the "single monomer relaxation time", τ_{s}, by

$$\tau_{\mathrm{c}} = (1 + F)\tau_{\mathrm{s}} \tag{10}$$

Light scattering experiments measure the collective relaxation time. The single monomer relaxation time can be measured directly by other techniques (such as NMR and EPR). However, comparison of τ_{LS} ($=\tau_{\mathrm{c}}$) and τ_{NMR} ($=\tau_{\mathrm{s}}$) via eq 10 is meaningful only when the relaxation is isotropic or when the motion that relaxes the laboratory-fixed optical anisotropy also relaxes the C–H bond vector (which determines τ_{NMR} in ^{13}C NMR). When this condition is not satisfied, comparison of the two times (after correction for pair correlation) can be used to determine anisotropies in the internal motion.

Dielectric relaxation times are also collective relaxation times but the static pair correlation term that affects dielectric relaxation is different from the $1 + F$ that occurs for light scattering. Experimental results indicate that the ratio analogous to $1 + F$ is 0.5–1.0 for dielectric relaxation measurements on para-substituted polystyrenes.[31] Also since dielectric relaxation measures the relaxation of a first-order spherical harmonic while light scattering (and NMR and EPR) measures the relaxation of a second-order spherical harmonic, it is difficult to make meaningful conclusions from a comparison of these two times even in the absence of pair correlations. For example, it is predicted that for rotational diffusion, when no pair correlations are present, $\tau_{\mathrm{DR}} = 3\tau_{\mathrm{LS}}$, while for Rouse-Zimm relaxations $\tau_{\mathrm{DR}} = 4\tau_{\mathrm{LS}}$, and for some jump diffusion models when no pair correlations are present $\tau_{\mathrm{DR}} \approx \tau_{\mathrm{LS}}$.

III. Experimental Section

The general description of the interferometry apparatus used to obtain the depolarized spectra has been described previously;[7] however, due to narrow line widths and relatively weak signals in the depolarized scattering from the polystyrene solutions, a few modifications were necessary. The main modification was that for most of the spectra a set of spherical Fabry-Perot mirrors replaced the flat plates used in the previous work. The spherical mirrors had a radius of curvature of 10 cm (free spectral range = 750 MHz) and a reflectivity of 99.5%. The spherical mirrors were used because they are superior to the flat plates in light gathering power, resolution, and stability in this frequency range. Typical instrumental half-widths ranged from 5 to 7 MHz. At least half of this broadening is due to the line width of the laser. This width is probably caused by very fast fluctuations in the single mode frequency induced by mechanical vibrations from flow of the cooling water in the laser tube. There was also a slow drift in the laser frequency caused by temperature variations, but this was negligible over the duration of a typical experiment. The instrumental line width was extremely stable (over a period of hours) so that small broadenings (1 MHz) could be measured. The instrumental line shape could be accurately described by a Voigt function with a ratio of Gaussian to Lorentzian fraction of around 2. In order to determine the true spectral width, the experimental spectrum had to be deconvoluted from the instrumental line shape. This was done by convoluting a typical instrumental line shape with a set of Lorentzians of varying widths and constructing a table relating the measured and theoretical half-width. For the $M = 2200$ sample the spectral line width was too broad for the spherical mirrors. For this sample the flat plates (set at a free spectral range of 4,100 MHz) were used. A finesse of 70 was obtained using a 200 μ pinhole in front of the photomultiplier tube. A filter centered at 4880 Å with a width of 100 Å and a maximum transmission of 40% was used to remove unwanted fluorescence and Raman scattering. Also various aperatures were used in the collection geometry to remove unwanted stray light. Typically rates on the photon counter were ≤1000 counts/sec.

Translational diffusion coefficients were measured using homodyne optical mixing at a scattering angle of 19.5°. This technique has been discussed by many authors (see, for example, Cummins and Swinney).[32] The output from the photomultiplier tube was preamplified and autocorrelated using a Saicor SAI-43A 400 point autocorrelator. Each correlation function fit well to one exponential, and diffusion coefficients could be measured to better than ±5%. The relaxation times of the molecular weight dependent components for the three largest molecular weights were also measured by optical mixing at a scattering angle of 2°. In order to ensure that scattering from the cell walls would not be significant, a 4 cm diameter cell and a series of pinhole aperatures and light traps were used. The 2° scattering angle was chosen because of the increased power per coherence area that is available at low scattering angles. Count rates of over 5×10^6 counts/sec could be achieved although all but ~5–15% of this intensity was due to some combination of solvent scattering, multiple scattering, and polarizer leakage. The effect of this extraneous scattering on the observed spectra is discussed in section IV. In order to increase the signal-to-noise ratio, the autocorrelator was operated in the clip mode.

Total integrated intensities were measured by focusing the scattered light (at a scattering angle of 90°) through the filter and polarizer directly on the photomultiplier tube. The intensity was read directly from the photon counter; the reported intensities are the average of several runs. All intensities were measured relative to the depolarized intensity of CCl_4 whose Rayleigh ratio (R_{VH}) at 4880 Å was taken to be 2.83×10^{-7} cm^{-1}. This number was obtained by interpolating the data of Patterson and Flory[2] to our experimental conditions. Rayleigh ratios are proportional to the integrated intensities given in eq 8 and 9. The polarized intensity (R_{VV}) of CCl_4 was also measured and the ratio of polarized to depolarized intensity was found to be 63 ± 3 in good agreement with the ratio calculated using previously determined values of R_{VV} and the above value of R_{VH} (61 ± 3). The intensities were corrected for multiple scattering and stray light by subtracting the number of photocounts obtained from the sample volume directly below or above the beam. This correction increased monotonically with increasing R_{VV} and was negligible for samples with $M \leq 37{,}000$. It was found in the spectra that there was an excess intensity in the wings over that due solely to the solvent (CCl_4). This excess intensity was found to be roughly 10% of the total excess intensity. We attribute this excess to collision induced scattering (see section IV). The corrected depolarization ratios range from 80×10^{-4} to $\sim 1 \times 10^{-4}$ and decrease monotonically with M. These were compared to depolarization ratios measured by comparing the polarized and depolarized spectra. There was good agreement provided it was assumed that the narrow and broad components had equal intensity (see section IV).

The polystyrene samples were obtained from Pressure Scientific Co. They were prepared by anionic polymerization.[33] The ratio M_w/M_n ranged from <1.06 to <1.20. Solutions were filtered through 0.2 μ Alpha Metrecel filters to remove dust. Intrinsic viscosities were measured in a Cannon-Ubbelohde viscometer and were extrapolated to infinite dilution. They were reproducible to ±3%. Temperatures at which spectra were obtained were controlled to ±1° by a Lauda temperature bath.

IV. Results and Discussion

The molecular weight dependence of the intrinsic viscosity and translational diffusion coefficients in CCl_4 are shown in Figure 1. The experimental data fit the following equations

$$\begin{aligned}
[\eta] &= 0.0174 M^{0.69}\ \mathrm{cm^3/g} && M \geq 19{,}800 \\
[\eta] &= 0.103 M^{0.51}\ \mathrm{cm^3/g} && M < 19{,}800 \\
D &= (1.91 \times 10^{-4}) M^{-0.55}\ \mathrm{cm^2/sec} && M > 19{,}800 \\
D &= 8.31 \times 10^{-5} M^{-0.48}\ \mathrm{cm^2/sec} && M \leq 19{,}800
\end{aligned} \tag{11}$$

These values are typical for flexible coils in a good solvent like CCl_4. Both determinations give similar values for R_g when the theoretical values for ζ and ζ_f (see Tanford[34]) are used, except for the smallest M where R_g determined from diffusion is larger than that determined from intrinsic viscosity.

The corrected excess polarized and depolarized scattering intensities for the polystyrene solutions are given in Table I along with the $1 + F$ values. Cumene was used to estimate the scattering intensity of the monomer unit. The scattering from the 14% cumene solution in CCl_4 was corrected for collision induced scattering[35] (roughly 45% of the excess scattering is due to collision induced scattering). Due to the uncertainties in the refractive index correction[25] we have reported the absolute values of $\Delta R_{VH}/c$ at 4880 Å. These values are proportional to $\langle \gamma^2 \rangle / n$ which is the usually reported quantity. Fourche and Jacq reported values of $\Delta R_{VH}/c$ from 30 to 40% higher than ours at each value of M.[3] They failed to correct for collision induced scattering (10% of the excess scattering). The rest of the discrepancy could be due to Raman scattering, fluorescence, polarizer leakage, multiple scattering, and calibration errors. Our values of $1 + F$ can be compared to those calculated by Tonelli and Flory using RIS theory.[36] Their calculations indicate that $1 + F$ is a constant between 2.5 and 3.0 for $M > 5000$. Our experimental values level off around $M = 19{,}800$ at ~3.0 and increase further for $M \geq 390{,}000$. Much of this increase at high M could be due to experimental errors such as failure to correct completely for multiple scattering. Some of this increase could also be due to the increasing importance of form anisotropy at high M. Thus, after accounting for the large experimental error at high M and the possibility of form anisotropy, the experimental values of $1 + F$ are reasonably similar to those obtained from RIS calculations.

All of the spectra measured by interferometry in CCl_4 and TCE except those for $M = 2200$ and 4000 were found to fit well to the sum of two Lorentzians convoluted with the instrumental line shape. The narrow component is highly molecular weight dependent while the broader component has a relaxation time that is fairly independent of M. The values of the relaxation times in CCl_4 and benzene are given in Table II. Although there was qualitative evidence for the presence of a broad component in the spectra

Table I
Integrated Intensities

$M \times 10^{-3}$, g/mol	$C \times 10^2$, g/cm^3	$(\Delta R_{vv}/c) \times 10^2$,[a] cm^2/g	$(\Delta R_{VH}/c) \times 10^5$, cm^2/g	$1 + F$
0.12[b]	11.6		0.335 ± 0.015	1.0
2.2	5.94	0.103	0.85 ± 0.05	2.2 ± 0.2
4.0	2.99	0.174	0.86 ± 0.05	2.2 ± 0.2
10.0	1.99	0.44	0.94 ± 0.1	2.4 ± 0.3
19.8	0.99	0.89	0.10 ± 0.15	2.85 ± 0.4
37.0	1.00	1.40	1.20 ± 0.15	3.1 ± 0.4
97.2	0.99	2.47	1.15 ± 0.15	2.95 ± 0.4
390.0	0.403	8.2	1.5 ± 0.3	3.8 ± 1.0
670.0	0.301	11.5	1.8 ± 0.5	4.5 ± 1.5
2000.0	0.103	33.5	2.5 ± 1.0	3.8–9.0

[a] Reproducible to better than ±5%. [b] Cumene.

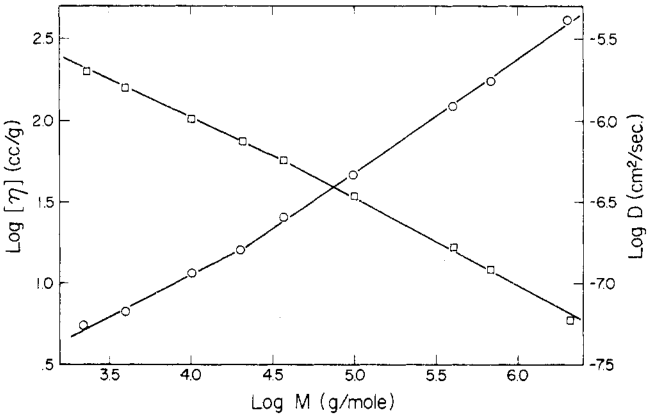

Figure 1. Log $[\eta]$ (○) and log D (□) vs. log M. The lines are least-squares fit to the data at high and low molecular weights.

Table II
Relaxation Times[a]

$M \times 10^{-3}$, g/mol	τ_1, nsec	A[b]	τ_2^{int},[c] nsec	$(1 + F)\tau_s$, nsec
2.2	1.2 ± 0.1	0.26 ± 0.02		2.6 ± 0.7
4.0	2.6 ± 0.3	0.26 ± 0.03		2.6 ± 0.7
10.0	10.5 ± 2.0	0.23 ± 0.04	3.2 ± 1.0	2.9 ± 0.8
19.8	29.0 ± 3.0	0.24 ± 0.02	3.5 ± 0.5	3.4 ± 1.0
19.8[d]	20.0 ± 3.0	0.27 ± 0.04		
37.0	78.0 ± 15	0.22 ± 0.04	3.6 ± 1.0	3.7 ± 1.0
97.2	≥250	≥0.15	4.5 ± 1.0	3.5 ± 1.0
97.2[d]	≥170	≥0.15		
390.0	~4.5[e]	~0.24	5.7 ± 2.0	4.6 ± 1.8
670.0	~10.0[e]	~0.24	5.7 ± 2.0	5.4 ± 2.5
2000.0	~73.0[e]	~0.24	5.0 ± 1.5	4.0–12
2000.0[d]	≥170			

[a] In CCl_4 unless otherwise noted. [b] $\tau_1 = A(M[\eta]\eta_0/N_{\mathrm{av}}k_BT)$. [c] $1/\tau_2^{\mathrm{int}} = (1/\tau_2) - (1/\tau_1)$. [d] In benzene. [e] In μsec; see text for further discussion.

of the polystyrenes in benzene, it was impossible to determine quantitatively a line width for this component because of the strong depolarized background scattering from benzene. A typical spectrum with the two best fit components is shown in Figure 2. The line width of the broad component was determined by fitting the wings of the experimental spectrum (where the narrow component is negligible) to one Lorentzian. The spectra for $M = 2200$ and 4000 fit well to one Lorentzian because the molecular weight dependent relaxation time (which can be associated with an overall tumbling time) has become shorter than the second relaxation time. The second relaxation time in Table II, τ_2^{int}, has been corrected for the broadening caused by overall tumbling (or slow intramolecular relaxation) by the following expression: $1/\tau_2^{\mathrm{int}} = (1/\tau_2) - (1/\tau_1)$, where τ_2 is the experimentally determined relaxation time of the broad component and τ_1 is the relaxation time of the narrow component. This is in general a small correction compared to the experimental error in τ_2. The temperature and viscosity dependence of τ_2^{int} is shown in Table III. The error limits reported in Tables II and III are conservative estimates made by varying the fitted parameters to the spectra.

The experimental ratio of intensity in the narrow to that in the broad component ranged from 1:1 at low M to 4:1 at the high M. We have already noted that at the higher M, multiple scattering becomes more important. Both this scattering and stray laser light and polarizer leakage contribute solely to the narrow component. We have noted that the depolarization ratio as determined by the integrated intensities and the spectra agree if we assume that the intensities in the two components are roughly equal at all values of M. The effect of this multiple scattering on the spectra at high M is to make it more difficult to determine τ_2^{int}. This is reflected in the larger errors reported in τ_2^{int} at high M. At high M (>97,200) the relaxation time of τ_1 becomes so long that it is impossible to resolve it interferometrically from the instrumental line shape. These slow relaxation times of the narrow component were measured by optical mixing for the three highest M samples. A typical correlation function obtained in 2 hr of data sampling is shown in Figure 3. The signal-to-noise ratio can be seen to be much lower than for the spectra obtained in a few minutes by interferometry. Of course the amount of depolarized scattering, ΔR_{VH}, was smaller at high M because of the lower concentrations used.

Narrow Component. The molecular weight dependent component has a single relaxation time that can be described accurately by eq 5 (for all $M \leq 97{,}200$). The value of the constant A is 0.24 ± 0.02 as shown in Table II. This value of A falls between one-half of the free draining and nondraining limits of the longest wavelength Rouse–Zimm relaxation time (0.21–0.31).

According to Isihara,[21] eq 6 and 7 are equivalent; however, our data indicate that eq 7 is more successful in predicting τ_1. Equation 6 predicts values of τ_1 about a factor of 2 too long while eq 7 predicts values that are essentially within experimental error. Our experimental value of A agrees well with the value (0.2–0.3) determined by Huang and Frederick by isotropic light scattering for a polystyrene

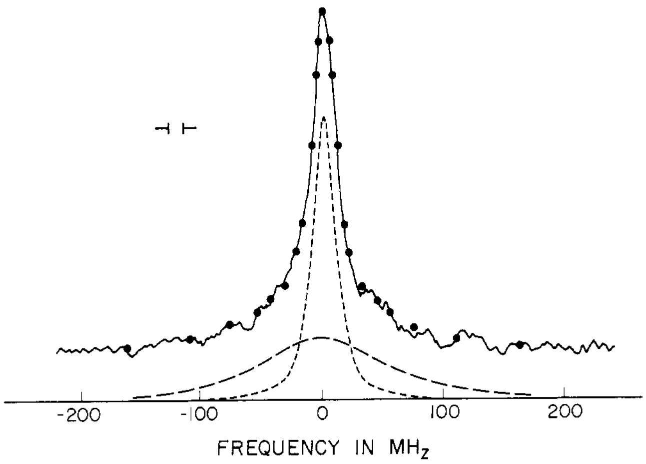

Figure 2. Experimental spectrum of 1% solution of M = 19,800 polystyrene in CCl_4. The narrow component is given by - - - , broad component by – – –, and the dots are the best fit sum of the narrow and broad component. The instrumental full width is given by ⊣ ⊢.

with $M = 27 \times 10^6$.[5] It also agrees with the value (0.26 ± 0.02) determined by EPR at very low molecular weight.[12]

The depolarized autocorrelation functions of the three highest M samples as measured by optical mixing consist in general of three components: a spike at zero time; a molecular weight dependent component with relaxation times ranging from 4 to 50 μsec; and an extremely slow component (>1 msec). The spike at zero time is due primarily to the scattering from the broad component and the depolarized solvent scattering which together make up about 70% of the total depolarized scattering. Since the spectral distribution of these components is very broad, the correlation function is a spike at zero time. This spike and instrumental distortion at very short times made it impossible to determine the autocorrelation function at times <2 μsec. The very slow relaxations are probably due to multiple scattering or polarizer leakage and are highly sensitive to optical alignment and polarizer setting. These slow relaxations act as local oscillators. Thus the observed spectra will consist of the sum of heterodyne and homodyne components. By measuring the intensities of the molecular weight dependent component and the very slow component it is possible to estimate the fraction of heterodyne component. This fraction varied from 0.0 to 0.6 depending on the sample and the optical parameters mentioned above. If $\langle\alpha_{yz}(t)\alpha_{yz}(0)\rangle$ relaxes as a single exponential (with decay constant τ), then the observed spectrum should consist of the sum of two exponentials whose decay constants are τ (heterodyne) and $\tau/2$ (homodyne). The spectra for M = 390,000 and 670,000 fit well to such a sum when τ is given by eq 5 with $A = 0.24$ in agreement with the value of A found for the lower M by interferometry. Thus the molecular weight dependent components of depolarized spectra are determined predominately by the relaxation of the longest wavelength Rouse–Zimm mode. Although the spectrum for $M = 2 \times 10^6$ could also be fit to this sum, there was an excess intensity observable at short time (<15 μsec) in this spectrum. This will be discussed further below. Due to the poor signal-to-noise ratio and the difficulty in estimating the fraction of heterodyne component, it was impossible to determine A to better than ±30% for these molecular weights.

The experimental result that the molecular weight dependent component of the spectrum is dominated by one relaxation time is in apparent disagreement with the prediction of Ono and Okano who predicted an equally weighted sum of several Lorentzians.[10] None of the spectra could be fit to an equally weighted sum of several Lorentzians. The experimental values of the slow relaxation times are, however, approximately equal to one-half the Rouse–Zimm relaxation times in agreement with their prediction.[10] This discrepancy in the form of the spectrum is surely due to the choice of the Kuhn–Grün expression for the optical anisotropy of a Rouse submolecule in the Ono and Okano calculation.

Table III
Viscosity and Temperature Dependence of τ_2^{int} for M = 19,800

Solvent	T, °C	η, cP	τ_2^{int}, nsec	τ_2^{int}/η, nsec/cP
CCl_4	22	0.94	3.5 ± 0.5	3.7 ± 0.5
TCE[a]	22	1.84[b]	6.5 ± 0.5	3.53 ± 0.3
TCE	35	1.39[b]	4.5 ± 0.5	3.23 ± 0.3
TCE	50	1.13[b]	3.0 ± 0.5	2.65 ± 0.3
TCE	65	0.95[b]	2.5 ± 0.5	2.63 ± 0.3

[a] TCE ≡ 1,1,2,2-tetrachloroethane. [b] E. D. Washburn, Ed., "International Critical Tables", Vol. III, McGraw-Hill, New York, N.Y., 1928, p 213.

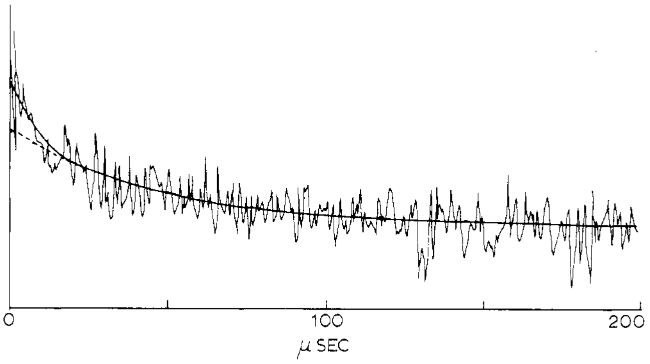

Figure 3. Experimental autocorrelation function of 0.1% solution of $M = 2 \times 10^6$ polystyrene in CCl_4. The — is the best fit to eq 12 with $\tau_1/2$ = 73 nsec (A = 0.24). The - - - is the fit with $m = n = 1$ term only.

Stockmayer and Šolc and coworkers have found that flexible chains in solution are, on the average, highly nonspherical.[22] (This might explain the apparent presence of form anisotropy.) Stockmayer and Verdier and coworkers have calculated some dynamical properties of a chain constrained to lie on a cubic lattice.[23,24] They found that the mean square end to end length $\langle l^2\rangle$ relaxation is dominated by the longest wavelength Rouse–Zimm mode with weaker contributions from the odd shorter wavelength modes. For a free draining Rouse–Zimm chain

$$\langle l^2(t)\, l^2(0)\rangle \propto \sum_{m,n=\text{odd}} \frac{1}{m^2n^2} \exp[-(n^2 + m^2)t/\tau_1] \quad (12)$$

where τ_1 is given by eq 5. This is in substantial agreement with the Monte Carlo results. Roughly 75% of the intensity is in the $m = n = 1$ term. Hence the relaxation is roughly one-half of the relaxation time of the longest wavelength mode. For this lattice changes in l^2 and α_{yz} are closely related. In order to show this we have calculated $\langle\alpha_{yz}(t)\alpha_{yz}(0)\rangle$ and $\langle l^2(t)l^2(0)\rangle$ for a $n = 6$ chain on a cubic lattice using the technique of Kranbuehl et al.[24] For simplicity we have assumed that the polarizability of each bond is cylindrically symmetric. As can be seen from Figure 4 the two correlation functions are essentially identical for this chain. The experimental values of $\langle\alpha_{yz}(t)\alpha_{yz}(0)\rangle$ for the three highest M's are also in good agreement with eq 12. The correlation functions for the three highest M fit well to eq 12 when $A_1 = 0.48$ (thus the dominant $m = n = 1$

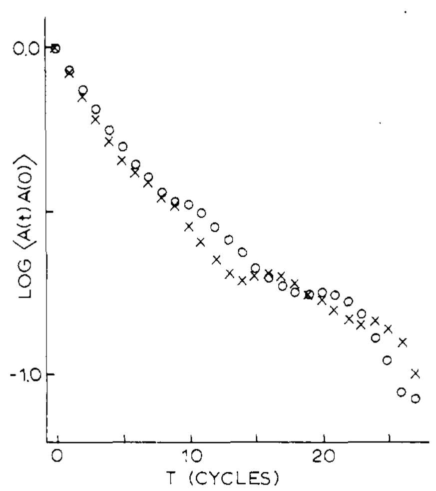

Figure 4. Monte Carlo autocorrelation functions $\langle A(t)A(0)\rangle$, $A = \alpha_{yz}$ (O), and $A = l^2$ (X) for an $n = 6$ chain on a cubic lattice. One thousand cycles were used to compute the functions.

term has a relaxation time given by eq 5 with $A = 0.24$). It should be noted that the higher order terms in eq 12 contribute significantly to the correlation function when $t > 2$ μsec only for $M = 2.0 \times 10^6$. The fit including the higher order terms is significantly better in this case (see Figure 3) than is the fit which includes only the $m = n = 1$ term. These higher order terms could be present in the lower M samples. Such a contribution would be very difficult to detect by interferometry for three reasons: (1) the presence of the broad molecular weight independent component; (2) the difficulty of deconvoluting these narrow lines from the instrumental line shape; and (3) the difficulty of fitting a spectrum with a weak broad component to more than one Lorentzian. The function as determined by optical mixing is more sensitive to a weak short relaxation time component in the presence of a strong slow component than is the spectral distribution as determined by interferometry, despite the superior signal-to-noise ratio of interferometry. Neither the Monte Carlo calculations nor Ono and Okano's calculation predicts the observed molecular weight independent part, although it would be an easy matter to include it in the Monte Carlo calculation by allowing jumps of more than one lattice point at a time.

Han and Yu have obtained spectra of isotactic polystyrene of molecular weight 3.5×10^6 over the frequency range 0 to 2 kHz by optical-mixing spectroscopy.[6] The signal-to-noise ratios in their spectra were such that they could each be fit equally well by one Lorentzian or by a sum of equally weighted Lorentzians with the Rouse–Zimm relaxation times. Thus, their experiments are not precise enough to distinguish between the various theories of relaxation that we consider here.

The relaxation time they obtained from their one Lorentzian fit to the spectrum of their most dilute sample is consistent with our value of τ_1. Han and Yu could not investigate fast local relaxation processes ($\tau < 10^{-5}$ sec) because of the limited frequency range of their apparatus.

Broad Component. The lack of a strong M dependence of the broad component observed in the spectra of $M > 4000$ is an indication that this component is due to some kind of local intramolecular motion. The dielectric relaxation experiments also measure a molecular weight independent relaxation time for para-substituted polystyrenes. It is found from these experiments that $\tau \propto \eta_0 e^{-\Delta H_c/kT}$. Values of ΔH_c ranged from 2.8 kcal/mol for the Cl substituent to 1.2 kcal/mol for the Br substituent.[14] As can be seen from Table III, τ_2^{int} is also proportional to solvent viscosity with $\Delta H_c \approx 1.5 \pm 1$ kcal/mol. This is in good agreement with the value (2.1 ± 0.5 kcal/mol) determined by EPR.[12] We can use known solvent viscosities and a $\Delta H_c \sim 2$ kcal/mol to calculate τ_s at 22° in CCl_4 ($\eta_0 = 0.94$ cP) from the quantities determined experimentally by NMR and EPR.[11,12] Correcting to the temperature and viscosity conditions used in our light scattering experiments gives $\tau_{\text{EPR}} = 1.1 \pm 0.2$ nsec and $\tau_{\text{NMR}} = 1.3 \pm 0.3$ nsec at all values of M. The average of these two numbers gives $\tau_s = 1.2 \pm 0.2$ nsec for these samples. Fluorescence depolarization measurements on polystyrenes substituted with 9,10-diphenylanthracene give results in qualitative agreement with ours.[37] In the Appendix we present a model that predicts that τ_{LS} (in this case τ_2^{int}) is equal to $\tau_s(1 + F)$. From Table II we note that τ_2^{int} is indeed approximately equal to $\tau_s(1 + F)$. This good agreement lends support to the results derived by use of the Mori formulation in the Appendix. It implies that the same motion that relaxes the NMR and EPR experiments also relaxes the optical anisotropy and it suggests that within experimental error the off-diagonal elements of $\dot{\mathbf{N}}$ (see eq A2) are negligible.

Finally we discuss the nature of this local intramolecular relaxation. Allerhand et al.[11] have concluded from NMR results that internal rotation about the C–phenyl bond is slow. In addition Tonelli has calculated that the barrier to phenyl rotation about this bond is rather high in most conformations.[38]

It is possible that we are observing "crankshaft" type motions. Helfand has shown that the relaxation times of crankshaft and similar motions are independent of M and exhibit a temperature dependence of the form $\tau \propto \eta_0 e^{-\Delta H_c/kT}$, provided that the friction coefficient is large enough that motion over the barrier is diffusional.[39] This type of motion is consistent with the light scattering results. A crankshaft motion would rotate the phenyl ring (which contains nearly all the optical anisotropy) 120°. This would alter the laboratory-fixed polarizability so that this rotation should contribute to the light scattering spectrum. In addition the phenyl groups stick out from the chain and upon rotation displace significant amounts of solvent. Thus, the motion should be diffusional and exhibit the viscosity dependence we have observed previously.[7-9] Although our results therefore indicate that the major contribution to the relaxation time of the broad component is due to rotation of the phenyl group about the main chain axis, we cannot rule out the possibility of contributions from rotations of the phenyl group about the C–phenyl bond axis.

The dielectric relaxation times for p-Cl- and p-F-substituted polystyrenes corrected to 22° and a viscosity of 0.94 cP are 6 and 4 nsec, respectively.[31] Assuming that the diffusion equation applies and that the quantity analogous to $1 + F$ is between 0.5 and 1.0 for dielectric relaxation in these polymers, the dielectric relaxation time values listed above are in reasonable agreement with the other results. Mashimo et al. have observed a high frequency dispersion in the dielectric relaxation of these polymers.[14] As we show in the Appendix it is unlikely that this dispersion is due to the collective nature of the dielectric relaxation process. Such a dispersion should show up as non-Lorentzian behavior in the broad light scattering component. However, due to signal-to-noise problems and the presence of the narrow component, no such behavior could be observed in the depolarized spectra.

V. Conclusion

We have measured the depolarized Rayleigh spectra of atactic polystyrene in solution in the molecular weight range 2.2×10^3 to 2.0×10^6. The spectra of the two smallest molecular weights fit well to one Lorentzian whose line width is related to the longest wavelength Rouse–Zimm relaxation time. The spectra of the other samples contained two components of roughly equal intensity. The line width of the narrow component is again related to the longest wavelength Rouse–Zimm relaxation time, while the broad component is roughly independent of molecular weight. The integrated intensity measurements agree reasonably well with RIS calculations. The corrected relaxation time of the broad component, τ_2^{int}, is approximately equal to the product of τ_s and the integrated intensity ratio $1 + F$ in agreement with the results calculated using the Mori formulation. It is clear from these results that depolarized Rayleigh spectroscopy can be a valuable tool for studying the chain dynamics of polymers in solution.

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Appendix

Since the application of Mori's statistical mechanical theory of fluctuations to collective orientational relaxation has been discussed elsewhere,[7,29,30] only the basic assumptions and results will be presented. We assume that the only relevant slowly relaxing variables are the set of orientation tensors, ζ, associated with each of the individual phenyl groups of a single chain. The overall tumbling time (or slow long wavelength intramolecular relaxation time) is assumed to be much slower than the relaxation times of the individual phenyl groups which are all taken to be equal (τ_s). Thus, the slowest relaxation processes are assumed to be so slow compared to the those of the local phenyl group motions that they do not relax at all on the time scale considered. For simplicity we assume that the time displaced correlations between the first time derivatives of the orientation tensors of the different phenyl groups are negligible (see eq A2). Later we will relax this assumption. Finally we assume that the chains are in dilute solution so that there are no correlations between the chains.

We define the static overlap matrix **N**

$$N_{ij} \equiv \langle \zeta_i \zeta_j \rangle \qquad \text{(A1)}$$

and note that

$$1 + F = (1/n) \sum_{i=1}^{n} \sum_{j=1}^{n} N_{ij}$$

where n is the number of phenyl groups on a single chain. We next define the matrix $\dot{\mathbf{N}}$

$$\dot{N}_{ij} \equiv \int_0^\infty \langle \dot{\zeta}_i(t) \dot{\zeta}_j(0) \rangle^\dagger \, \mathrm{d}t \qquad \text{(A2)}$$

where $\dot{\zeta}_i(t)$ is the time derivative of $\zeta_i(t)$ and † indicates that $\dot{\zeta}_i(t)$ propagates with the modified propagator.[28] We have assumed that $\dot{\mathbf{N}}$ is diagonal and that $\dot{N}_{ii} = 1/\tau_s$. The equation of motion is given by

$$\mathrm{d}\boldsymbol{\zeta}/\mathrm{d}t = -\boldsymbol{\Gamma}\boldsymbol{\zeta} \qquad \text{(A3)}$$

where $\boldsymbol{\Gamma} = \dot{\mathbf{N}}\mathbf{N}^{-1}$. The equation of motion can best be solved by taking Laplace transforms, with Laplace variable s of both sides of eq A3. We find

$$\boldsymbol{\zeta}(s) = (s\mathbf{1} + \boldsymbol{\Gamma})^{-1} \cdot \boldsymbol{\zeta}(0) \qquad \text{(A4)}$$

We define the matrix $\mathbf{A}(s)$,

$$\mathbf{A}(s) = (s\mathbf{1} + \boldsymbol{\Gamma})^{-1} \cdot \mathbf{N} \qquad \text{(A5)}$$

The sum of all the elements in **A** is the Laplace transform of the collective correlation function. We can determine the spectral density by setting $s = i\omega$ in eq A5 and taking the real part of the result. The problem then is to determine the matrix $\mathbf{A}(s)$ from eq A5.

We show how this can be done by working out an example which is somewhat unrealistic in our case but does serve to illustrate the procedure. We assume that **N** is given by

$$\begin{aligned} N_{ii} &= 1 \\ N_{i,i\pm1} &= a \\ N_{ij} &= 0 \ (\text{where } j \neq i,\ i \pm 1) \end{aligned} \qquad \text{(A6)}$$

where a may be interpreted as the static orientational correlation between nearest neighbor phenyl groups. This matrix is equivalent to the Hückel Hamiltonian for the electronic wave functions of a noncyclic conjugated system. It may be shown (see, for example, Kauzmann[40]) that there is a similarity transform, **Q**, which diagonalizes **N**, where

$$Q_{kl} = \left(\frac{2}{n+1}\right)^{1/2} (-1)^{k+l} \sin \frac{kl\pi}{n+1} \qquad \text{(A7)}$$

The roots of the matrix **N** are $X_k = 1 - 2a \cos (k\pi/n + 1)$. It is easy to show that

$$\sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} = \sum_{k=1}^{n} \frac{X_k}{s + (1/\tau_s X_k)} \sum_{i=1}^{n} \sum_{j=1}^{n} Q_{ik} Q_{kj} \qquad \text{(A8)}$$

where

$$\begin{aligned} \sum_{i=1}^{n} \sum_{j=1}^{n} Q_{ik} Q_{kj} &= \frac{2}{n+1} \tan^2 \frac{k\pi}{2(n+1)} \quad n - k = \text{even} \\ &= 0 \quad n - k = \text{odd} \end{aligned} \qquad \text{(A9)}$$

After converting the Laplace transform, $A/(s + 1/b)$, to its corresponding Fourier transform we obtain a Lorentzian with a half-width $1/b$ and an intensity A. Thus the spectral distribution in this case is the sum of n Lorentzians; however, from eq A8 and A9 it is easy to see that for reasonably large n the only components that contribute significantly are those for which $k \sim n$. Thus, to a good approximation for large n the spectrum consists of one Lorentzian whose relaxation time is given by $\tau_s X_n$ which from eq A6 may be shown to be nearly equal to $\tau_s(1 + F)$.

Equation A8 is, in fact, true in general provided that there exists a matrix **Q** which diagonalizes **N**. It is possible in this general case to show that the only components which contribute significantly to the spectra are those for which $k \sim n$ by analogy with molecular orbital theory. The quantity Q_{kl} is the probability amplitude for the lth atom in the $(n - k)$th energy level (n is the lowest energy level). The lower energy levels in general have the fewest nodes with the nth level having no nodes. Thus in the double sum in eq A8 all but the $k = n$ level will consist of the sum of positive and negative terms which will tend to cancel. Thus only the nth level will contribute significantly and it follows that

$$\tau_{\mathrm{LS}} \approx \tau_s X_n \approx \tau_s(1 + F) \qquad \text{(A10)}$$

It is possible to calculate the spectra when $\dot{\mathbf{N}}$ is not diagonal provided that the same matrix **Q** that diagonalizes **N** also diagonalizes $\dot{\mathbf{N}}$. When this is true, it can be shown that for sufficiently large n, the spectrum consists of essentially one Lorentzian with a relaxation time given by

$$\tau_{\mathrm{LS}} = \tau_s[(1 + F)/(1 + G)] \qquad \text{(A11)}$$

where $1 + G$ is given by

$$1 + G = \tau_s \cdot (1/n) \sum_{i=1}^{n} \sum_{j=1}^{n} \dot{N}_{ij} \qquad \text{(A12)}$$

In section IV we use eq A10 to relate the light scattering broad component relaxation time to the EPR and NMR relaxation times.

References and Notes

(1) See, for instance, M. Kerker, "The Scattering of Light and Other Electromagnetic Radiation", Academic Press, New York, N.Y., 1969.

(2) G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1098 (1972).

(3) G. Fourche and M.-T. Jacq, *Polym. J.*, **4**, 465 (1973).

(4) R. Pecora, *Annu. Rev. Biophys. Bioeng.*, **1**, 257 (1972).

(5) W. H. Huang and J. E. Frederick, *Macromolecules*, **7**, 34 (1974).

(6) C. C.-C. Han and H. Yu, *J. Chem. Phys.*, **61**, 2650 (1974).

(7) G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **58**, 5570 (1973).

(8) G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **59**, 5310 (1973).

(9) G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **59**, 5321 (1973).

(10) K. Ono and K. Okano, *Jpn. J. Appl. Phys.*, **9**, 1356 (1970).

(11) A. Allerhand and R. K. Hailstone, *J. Chem. Phys.*, **56**, 3718 (1972).

(12) A. T. Bullock, G. G. Cameron, and P. M. Smith, *J. Phys. Chem.*, **77**, 1635 (1973).

(13) W. H. Stockmayer, *Rev. Pure Appl. Chem.*, **15**, 539 (1967).

(14) S. Mashimo and A. Chiba, *Polym. J.*, **5**, 41 (1973).

(15) K. Ono, H. Shintani, O. Yano, and Y. Wada, *Polym. J.*, **5**, 164 (1973).

(16) M. A. Cochran, J. H. Dunbar, A. M. North, and R. A. Pethrick, *J. Chem. Soc., Faraday Trans. 2*, **70**, 215 (1974).

(17) S. B. Dubin, N. A. Clark, and G. B. Benedek, *J. Chem. Phys.*, **54**, 5158 (1971).

(18) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).

(19) R. Pecora, *J. Chem. Phys.*, **49**, 1036 (1968).

(20) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **17**, 442 (1949).

(21) A. Isihara, *J. Chem. Phys.*, **47**, 3821 (1967).

(22) (a) K. Šolc and W. H. Stockmayer, *J. Chem. Phys.*, **54**, 2756 (1971); (b) K. Šolc, *ibid.*, **55**, 335 (1971); (c) W. Gobush, K. Šolc, and W. H. Stockmayer, *ibid.*, **60**, 12 (1974).

(23) P. H. Verdier and W. H. Stockmayer, *J. Chem. Phys.*, **36**, 227 (1962).

(24) P. E. Kranbuehl, P. H. Verdier, and J. M. Spencer, *J. Chem. Phys.*, **59**, 3861 (1973).

(25) The experimental intensity is related to $\langle\gamma^2\rangle$ by a complicated function of the refractive index. (See, for example, A. K. Burnham, G. R. Alms, and W. H. Flygare, *J. Chem. Phys.*, **62**, 3289 (1975), and the discussion in ref 29.)

(26) P. J. Flory, *Macromolecules*, **7**, 381 (1974).

(27) H. Mori, *Prog. Theor. Phys.*, **33**, 423 (1965); **34**, 399 (1965).

(28) H. C. Andersen and R. Pecora, *J. Chem. Phys.*, **54**, 2584 (1971).

(29) D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, to be published.

(30) T. Keyes and D. Kivelson, *J. Chem. Phys.*, **56**, 1057 (1972).

(31) B. Baysel, B. A. Lowry, H. Yu, and W. H. Stockmayer, "Dielectric Properties of Polymers", F. E. Karasz, Ed., Plenum Press, New York, N.Y., 1972, p 329.

(32) H. Z. Cummins and H. L. Swinney, *Prog. Opt.*, **8**, 133 (1970).

(33) D. P. Wyman, L. J. Elyash, and W. J. Frazer, *J. Poly. Sci., Part A*, **3**, 681 (1965).

(34) C. Tanford, "Physical Chemistry of Macromolecules", Wiley, New York, N.Y., 1961, p 345.

(35) W. M. Gelbart, *Adv. Chem. Phys.*, **26**, 1 (1974).

(36) A. E. Tonelli, Y. Abe, and P. J. Flory, *Macromolecules*, **3**, 303 (1970).

(37) D. Biddle and T. Nordstrom, *Ark. Kemi*, **32**, 359 (1970).

(38) A. E. Tonelli, *Macromolecules*, **6**, 682 (1972).

(39) E. Helfand, *J. Chem. Phys.*, **54**, 4651 (1972).

(40) W. Kauzmann, "Quantum Chemistry", Academic Press, New York, N.Y., 1957, pp 49 and 50.

Scattered Intensity by a Polymer Chain in a Sample with External Constraints

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ABSTRACT: The configuration of a deformed polymer coil is described by a general distribution function, depending on three parameters. The scattering law is given as a function of momentum transfer and parameter value. The relation between external constraint and parameter value is discussed and a clear interpretation from the scattering law diagram in the intermediate momentum range is predicted.

The fact that in the amorphous state polymer chains have random "Gaussian" configurations is now well established[2a] when no external constraint is applied. Obviously the observation of polymer configurations from neutron scattering experiments by mixtures of deuterated and protonated chains is feasible as well with external constraints on the sample as without. It is therefore of real interest to determine how the scattering law is modified by the onset of constraint and to find a formulation which is general enough to cover most cases of interest.

In order to do so we consider the following expression[2b] for the distribution function of the distance $\mathbf{r}$ between segments i and j of a chain in the deformed state

$$f_{ij}(\mathbf{r}) = \mathfrak{N}_{ij}\exp\left\{\frac{-3/2}{|i-j|l^2}\left(\frac{(X-X_{ij}^0)^2}{\lambda_X^2} + \frac{(Y-Y_{ij}^0)^2}{\lambda_Y^2} + \frac{(Z-Z_{ij}^0)^2}{\lambda_Z^2}\right)\right\} \qquad (1)$$

$$\mathfrak{N}_{ij} = \frac{(\lambda_X\lambda_Y\lambda_Z)^{-1}}{((2\pi/3)|i-j|l^2)^{3/2}}$$

where X, Y, Z are the components of vector $\mathbf{r}$, and l^2 is the mean squared length of the elementary step in the chain without constraint. The principal axes of the deformation are the $\hat{X}$, $\hat{Y}$, $\hat{Z}$ axes. The constraint factors are λ_X, λ_Y, λ_Z. The lengths X_{ij}^0, Y_{ij}^0, Z_{ij}^0 are the coordinates of the average end-to-end distance $|i-j|$. The random "Gaussian" chain corresponds to the case where

$$\lambda_X = \lambda_Y = \lambda_Z = 1$$

and

$$X_{ij}^0 = Y_{ij}^0 = Z_{ij}^0 = 0$$

For the purpose of carrying out the calculations in the next paragraph, we assume that the λ_α ($\alpha = X, Y, Z$) are independent of the pair i,j and that

$$\begin{aligned} X_{ij}^0 &= (i-j)b_X \\ Y_{ij}^0 &= (i-j)b_Y \\ Z_{ij}^0 &= (i-j)b_Z \end{aligned} \qquad (2)$$

These hypotheses correspond in fact to classical modes of deformation, which are discussed in the last paragraph. In