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Internal Structure and Dynamics of Dilute Linear Polymers

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ABSTRACT: We report measurements of the internal structure and dynamics of a dilute high molecular weight polymer in good and Θ solvents, with a special emphasis on the form of the decay of internal modes. Intermediate elastic light scattering measurements show that the static structure exhibits the expected self-avoiding walk and random-walk fractal dimensions in good and Θ solvents, respectively. Quasielastic light scattering studies of the relaxation of internal "Zimm" modes demonstrate the universal q^3 dependence of the initial decay rate on the scattering wavevector. However, the primary goal of this work, to observe the expected stretched exponential time decay $\exp[-(t/\tau)^b]$ with the Zimm exponent $b = 2/3$, was difficult to achieve, even though we used the $\lambda = 331.6$ nm UV line of an argon ion laser to monitor relaxations on length scales much smaller than the polymer radius. In a good solvent we obtained $b \cong 0.72$, and in a Θ solvent we obtained $b \cong 0.71$. We compare these results to extant experimental and theoretical work.

Introduction

We find it odd that after many years of using elastic and quasielastic light scattering to study such complex systems as polyelectrolytes, ternary polymer solutions, sol–gels, colloidal aggregates, micelles and microemulsions, phase transitions, and even carbonated methanol, we are finally studying linear polymers in dilute solution. What can possibly be so interesting about dilute linear polymers after so many years of experimental and theoretical research? The theory of the structure and dynamics of linear polymers in dilute solution is dignified by a tradition of elegant papers of impenetrable complexity that are most assuredly correct, and some fine experimental work has substantiated most, if not all, of the theoretical predictions. For example, the fractal dimensions of polymers in good and Θ solvents have been measured in elastic scattering experiments, and these have adequately demonstrated the self-avoiding and random-walk universality classes. Likewise, the dynamics of the internal normal modes has been studied by examination of the dependence of the Rayleigh line width on the momentum transfer and by the stretched exponential line shape of the decay. However, the results for the dynamics are not quite as satisfying, since the expected exponents have never *quite* been observed. In this paper we are especially interested in understanding the asymptotic dynamics from a strictly experimental perspective, without appeal to nonasymptotic functional forms. In general, we try to avoid merely demonstrating consistency with known theoretical results; instead, we attempt to extract exponents directly from the data, with a minimum amount of analysis. Proving consistency is often dangerous, since theories usually fix key exponents, while providing a number of floating parameters that can be used to fit data.

A primary motivation for this paper is the surprising ubiquity of stretched exponential decay functions in nature. Stretched exponential decays are commonly observed in glassy materials, virtually regardless of what property is under study. We have recently observed stretched exponential decays, of the form $S_2(q,t) \sim \exp[-(t/\tau)^b]$, in quasielastic scattering (QELS) experiments from randomly branched polymers formed near the sol–gel transition. (Here $S_2(q,t)$ is the "homodyne" dynamic structure factor and $q = 4\pi \sin(\theta/2)/\lambda$ is the scattering wavevector, where θ is the scattering angle and λ is the wavelength in the scattering medium.) The experimental data are compelling, leading us to speculate on why we observe certain values of b. However, the family of stretched exponential decays is large, and it is nearly true that any monotonically decreasing, slightly noisy, data can be adequately fit with some value of b, especially if one is not too concerned about small discrepancies. However, on theoretical grounds alone we feel that we have observed the "wrong" values of b in our silica sol–gels, and we are thus inclined to distrust our ability to measure b accurately. It therefore seems reasonable to study a system that should give a stretched exponential decay with a known exponent, in order to discover whether we actually can observe the "correct" value of b. Linear polymers in dilute solution are expected to give $b = 2/3$, so this seemed an ideal choice, especially in light of the fact that the theory of b is relatively well-founded in this system. However, our best efforts to observe the expected line shape fell slightly short of the mark, as we shall see.

In the first part of this paper we report elastic light scattering measurements of the internal structure, i.e., fractal dimension, of high molecular weight linear polystyrene at the Θ point in cyclohexane and in the reasonably good solvent toluene. The observed fractal dimensions 1.62 and 1.95 agree reasonably well with the expected values of $\sim 5/3$ and 2. We then describe QELS measurements of the q-dependence of the initial decay rate Γ of the normal modes of polystyrene in the regime $qR \gg 1$ and find excellent agreement with the theoretical expectation $\Gamma \sim q^d$, where d is the dimension of space. In good solvents we obtain $d = 3.00$ and in Θ solvents $d = 2.88$. (Since the dimension of space should be independent of solvent quality, we prefer the good solvent number.) Finally, we report tedious UV laser measurements of the decay of $S_2(q,t)$ in the limit $qR \gg 1$. The relaxation of Zimm modes leads to the prediction $b = 2/3$, whereas we measure $b = 0.71$ in the θ solvent and $b = 0.72$ in the good solvent.

Experimental Section

Sample preparation: The polystyrene was obtained from Polysciences and had a nominal molecular weight of 48 000 000. Our static light scattering intensity measurements are in good agreement with this molecular weight. Polystyrene samples were prepared by dissolving the sample in an 0.2-μm-filtered solvent in a Class 10 laminar flow clean bench and centrifuging the solution at 30 000g for 1–2.5 h after complete dissolution. Samples were then transferred to Burchard scattering cells in the clean bench and placed in a continuously-filtered index-matching vat filled with n-propanol. Samples prepared in this fashion were

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absolutely dust free, as required for the difficult line-shape measurements.

Scattering measurements: Elastic scattering measurements were made with an NEC 60-mW He–Ne laser operating at the conventional 632.8 nm. Measurements on the toluene background indicated an intensity base-line error of less than $\pm 1.0\%$ from 10 to 135° of scattering angle. This is important since at high angles the solvent background was $\sim 50\%$ of the total scattering for the most dilute polystyrene/toluene sample. The scattered intensity was measured at many 5-s intervals at each angle, and any anomalously high readings were discarded, based on standard statistical procedures. This part of the experiment was simplified by the extremely rapid relaxation times of the polystyrene internal modes.

The quasielastic light scattering measurements were much more difficult. Several lasers were used to make measurements: An NEC 60-mW He–Ne laser was used for scattering at 632.8 nm; a 6-W Spectra-Physics 164 was used for scattering at 488 nm; a 4-W Coherent Innova 100 laser was used for scattering at 454.5 nm; and a 24-W Coherent Innova 200 laser was used for UV scattering at 331.6 nm. Obviously we did not run these lasers at full power, and do not get the wrong idea—we really do know how to change the wavelength of our lasers! It's just that we have two light scattering labs, and J.E.M. also acquired a new laser in the course of these measurements. Furthermore, because we were concerned with the possibility of UV degradation during signal averaging with the 331.6-nm line, we ran a He–Ne correlation function on the polymer before and after UV exposure; absolutely no changes were discerned even after 24 h of exposure to the UV line. This makes sense since the π–π^* styrene transition is down at 276 nm. We used two photomultiplier tubes, an RCA FW130 and an EMI 9863B/100, and these were run into separate 256-channel Langley–Ford correlators. Both of these detectors were carefully checked for afterpulsing as a function of the operating voltage, and the high voltage to the photomultiplier tubes (PMT's) was judiciously adjusted to effectively eliminate afterpulsing. A comparison between our two light scattering laboratories gave excellent agreement for all samples. We also used the new Brookhaven Instruments 8000AT "logarithmic" correlator with exponentially spaced channels and found good agreement with the Langley–Ford correlator.

Data analysis: The first cumulant of the intensity autocorrelation function was found by analyzing data *self-consistently*, to avoid any nonsystematic errors. Our basic approach is to do an nth-order cumulant analysis to $1/m\Gamma_1$ channels, where Γ_1 is the first cumulant expressed in terms of the number of correlator channels. For example, if we take a 256-channel correlation function and do a second-order cumulant analysis ($n = 2$), we might find that $1/\Gamma_1$ is 50 channels. If we then refit just these 50 channels ($m = 1$) with a second-order cumulant analysis, we might find $1/\Gamma_1$ is now 44 channels. We generally try different values of n and m before deciding what is best, but $n = 1$, $m = 2$ and $n = 2$, $m = 1$ usually work well. This process converges very quickly to a result that is quite independent of how the sample time is selected for the run. Since the correlation functions in the $qR \gg 1$ regime have a shape that is independent of q, this procedure leads to only systematic errors in determining Γ_1. This method, and the dust-free samples, accounts for the low noise in our data.

The stretched exponential curve fitting was accomplished using a nonlinear least-squares routine that fits the data in the logarithmic metric. Fitting in log space emphasizes the long-time tail where the curve should best be described by a stretched exponential decay. Obtaining these data is very difficult; we found that the calculated and measured base lines should agree within 0.05% in order to prevent serious errors in the exponent b.

Effect of polydispersity: A few comments should be made about the effect of polydispersity on static and dynamic light scattering measurements. In the Guinier regime, where $qR_z < 1$, polydispersity can certainly have quite an effect and so we have made some attempt to correct for this where necessary. However, in the intermediate scattering regime, where $qR_z > 1$, polydispersity has been shown[1] to have no effect on static and dynamic scattering exponents, except when extreme, power-law polydispersity is encountered,[2] of the form $N(m) \sim m^{-\tau}$ where $\tau > 1.5$. Although power-law polydispersity is indeed encountered in some systems, notably in gelation and reaction-limited aggregation, it does not occur in linear polymer systems. Thus the measurement of fractal dimensions and the q-dependence of the first cumulant are unaffected by the moderate polydispersity encountered in linear polymers. Later we will discuss the measurement of the stretched exponential intensity autocorrelation function, which is even more insensitive to polydispersity. It has recently been shown[3] that the stretched exponential exponent b remains unaffected even by the infinitely broad power-law polydispersity that occurs at the sol–gel transition, a truely surprising result!

Static Structure

Fractal dimensions: We first measured the radius versus mass exponent ν for polystyrene, in order to verify the proper intermediate scattering behavior. A comment on notation is needed here: although polymer scientists use ν for historical continuity, we prefer to talk in terms of the fractal dimension $D = 1/\nu$, because this dimension has a simple physical interpretation. Anyway, if one expresses things in terms of ν, one ends up writing $1/\nu$ all the time, so it probably easier to just write D.

Flory[4] was quick to understand that in good solvents, where the excluded volume of a polymer is uncompensated by attractive interactions, a polymer is described by a self-avoiding walk. Remarkably, Flory was able to accurately estimate the fractal dimension $D = 1.67$ for this case. Endless simulations, renormalization group calculations, and other lambrinthine formalisms have improved Flory's estimate to[5] $D \cong 1/0.5875 \cong 1.70$. As we shall see, it is doubtful that experiments will be able to resolve this small difference in the near future.

A far more subtle point is that, near the temperature at which the second virial coefficient vanishes, attractive interactions exactly balance excluded-volume interactions and a polymer acts like a random walk, the so-called ideal chain. This ideal chain limit seems reasonable if one makes an analogy to an ideal gas at the Boyle point, but it is really somewhat surprising, since one cannot take the zero density limit where $\langle \rho(0)\, \rho(r) \rangle$ vanishes, as one can for an ideal gas, and effectively eliminate three-body collisions. A polymer is a connected fractal blob, so the monomer–monomer correlation function is a slowly decaying power law and it is not obvious that three-body interactions allow a θ point. In fact, an ideal chain temperature does exist, where the random-walk dimension of 2 is expected, but it is not quite the temperature where the second virial coefficient vanishes.[6]

Good solvent: Light scattering measurements of polystyrene in toluene are expected to reveal the self-avoiding walk dimension of 1.70. In Figure 1 we show the raw He–Ne scattering data for three concentrations of polystyrene in toluene. Researchers accustomed to making scattering measurements in the Guinier regime, where $qR < 1$, may think these concentrations are somewhat high, but it is well to remember that, although $I/C \sim M_w$ in the Guinier regime, in the intermediate scattering regime where $qR \gg 1$, mass fractal scattering is independent of molecular weight and $I/C \sim M_w^0$. This molecular weight independence can be seen in the scattering data, since the large-q scattering is nearly the same at all correlation lengths. In fact, at the highest values of q the solvent background was a significant contribution, $\sim 50\%$, to the scattering data in the 0.1 mg/mL sample.

To obtain the zero-concentration scattering function, it is necessary to extrapolate the scattering data to zero concentration. For reasons that are not entirely clear to us, the traditional Zimm method of extrapolating $1/I$ versus C works quite well at all scattering wavevectors. The resultant scattering function extrapolated to $C = 0$ appears in Figure 2.

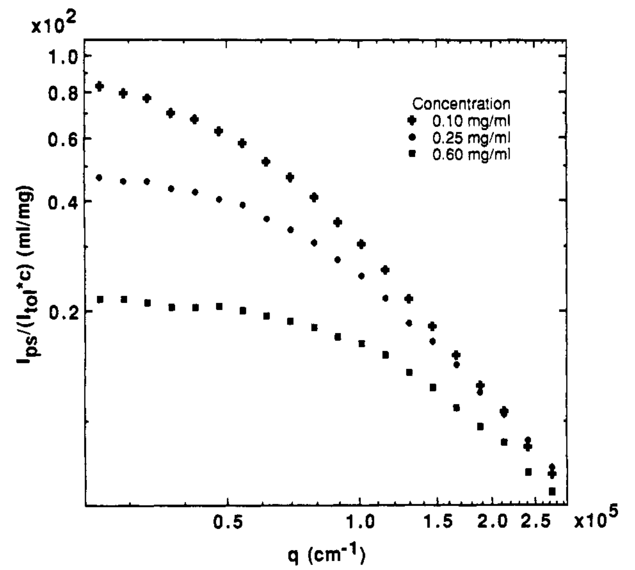

Figure 1. Scattered intensity per unit concentration of polystyrene in the good solvent toluene normalized by the scattered intensity of toluene for three concentrations of polystyrene. Data were taken with a He-Ne laser operating at $\lambda = 632.8$ nm. The significant concentration dependence of the low-q data indicates that the higher concentrations are in the coil overlap regime. The high-q, intermediate scattering data are very insensitive to sample concentration, since $qR_g \gg 1$.

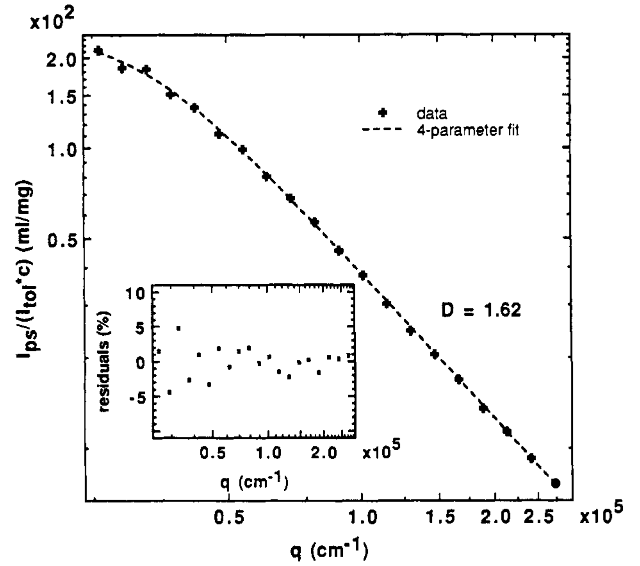

Figure 2. Polystyrene/toluene scattering data in Figure 1 linearly extrapolated to zero concentration by plotting the inverse intensity versus concentration for each value of q. A fit to the four-parameter function in eq 2 gives a fractal dimension of 1.62, in good agreement with the self-avoiding walk exponent of ~1.66–1.70. The intermediate scattering regime is quite extensive in this case, due to the large radius of gyration of the polymer.

The fractal dimension should be extracted from the zero-concentration scattering data by some sort of unbiased analysis; we certainly do not want to fit the data to a theoretical function, like a Debye function, that implicitly contains a fixed fractal dimension. One simple approach is to plot the data on logarithmic axes and draw a straight line through the high-q region. This is alright when one has at least a decade of intermediate scattering data. However, we resorted to nonlinear least-squares fitting with the four-parameter modified Fisher–Burford approximate

$$I/C = \frac{I(0)}{[1 + (4/3D)q^2R_g^{\,2} + bq^4R_g^{\,4}]^{D/4}} \tag{1}$$

This function looks terrible (and we hate to curve fit) but actually makes good sense. In the small-qR limit eq 1 reduces to the familiar Guinier expansion[7] $I/C = I(0)\ [1 - q^2R_g^{\,2}/3 + ...]$, and in the large-$qR$, or intermediate scattering, limit this gives $I/C = I(0)/b'(qR_g)^D$. Since $I(0) \sim M_w \sim R_g^{\,D}$ we obtain the molecular weight- and concentration-independent fractal scattering[8] $I/C \sim q^{-D}$ for $qR \gg 1$. (This fractal scattering law is readily understood: divide a fractal into N_q boxes of average mass m_q and size q^{-1}. The scattering at wavevector q is *coherent* on length scales smaller than q^{-1} and *incoherent* on larger length scales, so $I \sim N_q m_q^{\,2}$. Noting that $N_q m_q$ is the cluster mass M and $m_q \sim q^{-D}$ gives $I \sim Mq^{-D}$ or $I/C \sim q^{-D}$.) Thus, this form contains the smallest number of parameters needed to adequately *decouple* the Guinier and intermediate regimes. Anyway, the polymer itself has three real parameters, M, R_g, and D, so we have only introduced one "gratuitous" parameter that compensates for our uncertainty about the functional form.

A fit of eq 1 to the scattered intensity data produces the curve in Figure 2, which has fairly small residuals, especially at high q. The observed fractal dimension is 1.62, in substantial agreement with theoretical expectations, which are in the range 1.67–1.70. We would not write the Nobel committee about the discrepancy, since other curve-fitting schemes, such as the *three-parameter* Fisher–Burford function, $I(q) = I(0)/[1 + (2/3D)q^2R_g^{\,2}]^{D/2}$, give a fractal dimension closer to 1.7. We cannot give precise uncertainties for this fractal dimension, since a number of experimental factors incur larger systematic uncertainties than the small statistical uncertainties of the fit. However, on the basis of our experience with a variety of systems, we would estimate that the fractal dimension is in the range of 1.6–1.7. By comparison, Tsunashima and Kurata[9] measured $D = 1.72$ for PS in toluene by plotting intermediate light scattering data logarithmically and fitting with a straight line. Because much of the data are in the intermediate scattering regime, the radius of gyration was not reliably extracted; however, a Zimm analysis gave a z-average radius of gyration of 354 nm and a weight-average molecular weight of 5.0×10^7. These numbers could probably be improved on a low-angle light scattering instrument, but intermediate scattering is the primary focus of this paper.

Although the intermediate scattering data give a fractal dimension that agrees with our expectation, we decided to try an alternate approach to D that takes advantage of the fact that some of the samples are in the coil overlap regime. According to the concentration blob model, the solution can be described as a system of blobs of concentration-dependent radius ξ and average mass $M_\xi \sim \xi^D$. We used Zimm analysis to obtain ξ and M_ξ at each concentration and coplotted the resultant data in Figure 3, to obtain a fractal dimension of 1.63. The agreement with the intermediate scattering estimate $D = 1.62$ may be somewhat fortuitous since plotting the radius against the concentration yields $R_g \sim c^{-0.5}$, which disagrees with the concentration scaling prediction $R_g \sim c^{-0.75}$, indicating that we are close to the overlap concentration.

Θ solvent: The elastic scattering data for polystyrene in cyclohexane at the Θ temperature of 35 °C, extrapolated to zero concentration, are shown in Figure 4. The three-parameter Fisher–Burford approximate $I(q) = I(0)/[1 + (2/3D)q^2R_g^{\,2}]^{D/2}$ fits the data quite well, so we did not use the four-parameter fit, nor did we fit to the Debye function, since this implicitly contains the random-walk dimension $D = 2$. The three-parameter fit gives $D = 1.95$, in good agreement with 2, and $R_g = 174$ nm, a size that is about half that of the good solvent chain. Since the intermediate scattering regime is about half the size of the good solvent case, we will not be able to collect dynamics data as far

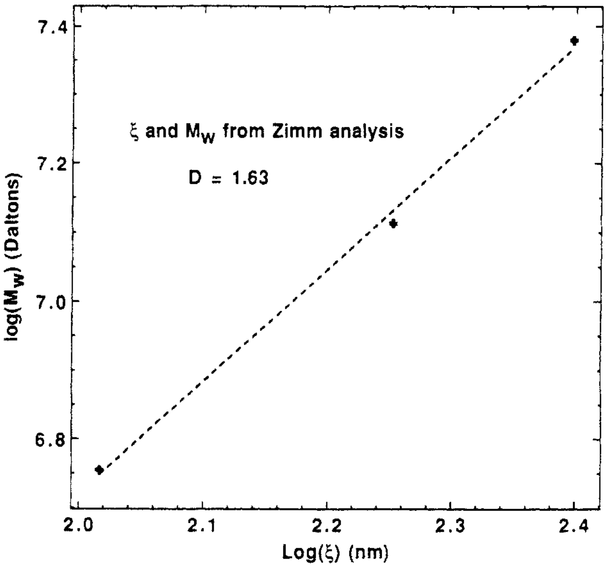

Figure 3. Static correlation length and mass, taken from the data in Figure 1. Coplotted to obtain the "blob" fractal dimension 1.63, which is in very good agreement with the zero-concentration, intermediate scattering dimension of $D = 1.62$. It is expected that the dilute polymer dimension and the blob dimension are identical, due to the free overlap of the flexible coils.

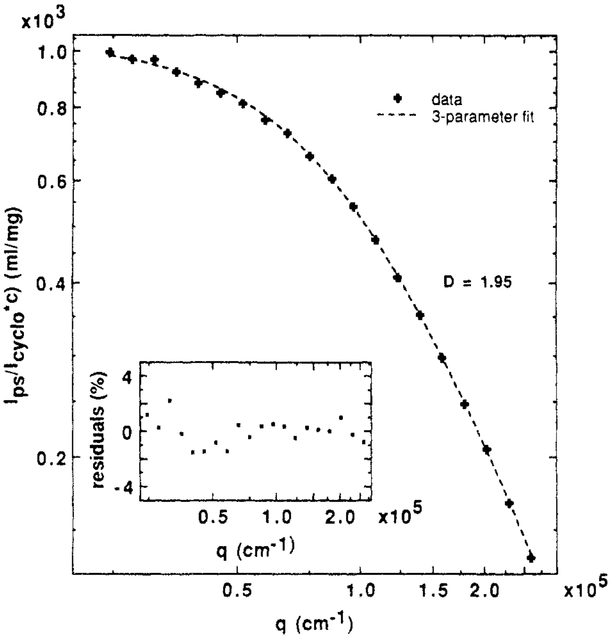

Figure 4. Normalized Θ point scattering data for polystyrene in cyclohexane at 35 °C indicate a fractal dimension of 1.95, in good agreement with the random-walk dimension of 2.0. Data were taken with a He-Ne laser operating at $\lambda = 632.8$ nm. Note that the relatively small Θ radius leads to a poorly defined intermediate scattering regime compared to the good solvent data in Figure 2.

into the intermediate scattering regime as in the good solvent case.

Relaxation of Internal Modes

Apparent hydrodynamic radius: The dynamics of the internal modes of linear polymers is a subject of longstanding interest. Early efforts involved calculations of the normal modes and relaxation times for ideal chains without hydrodynamic interactions,[10] but the relaxation times were subsequently shown to be greatly modified by hydrodynamic interactions.[11] These calculations indicate that in some sense a flexible polymer is dynamically self-similar. In fact, much of the dynamics of linear polymers is universal and should describe all flexible fractal clusters.

The key to understanding the dynamics of flexible clusters is that the relaxation times of the internal modes can be rendered length-scale-independent by dividing each relaxation time by the time it takes the cluster to diffuse its own radius R. Specifically, a flexible cluster of fractal dimension D and radius R will have a spectrum of normal modes that range from the time τ_0 it takes a cluster-entrained monomer to diffuse its own radius to the time $\tau_R \sim R^2/D_t(R)$ it takes the cluster to diffuse its own radius, where $D_t(R)$ is the translational diffusion coefficient. Dynamic light scattering in the regime $qR \gg 1$ measures the relaxation rate as a function of the length q^{-1}. The longest relaxation time of a chunk of the cluster the size q^{-1} should be independent of the overall size of the flexible cluster in which it is embedded, so this longest relaxation time is $\tau_q \sim q^{-2}/D_t(q^{-1})$, and the relaxation rate is just $\Gamma_q \sim q^2 D_t(q^{-1})$. Without hydrodynamic interactions, the diffusion coefficient is inversely proportional to the mass $M_q \sim q^{-D}$, which gives the Rouse prediction[12] $\Gamma_q \sim q^{2+D}$. In the so-called Zimm limit of strong hydrodynamic interactions, the diffusion coefficient $D_t(R) \sim kT/\eta_0 R^{d-2}$ leads to the remarkably universal, and therefore uninformative, result[13] $\Gamma_q = Cq^d kT/\eta_0$, which should describe all flexible fractal clusters. Although this result was first obtained by preaveraging the Oseen interactions, more sophisticated calculations show that only the constant of proportionality C depends on preaveraging,[14] solvent quality,[15] and combinations thereof.[16] In fact, this general result apparently holds for all systems with a single length scale and hydrodynamic interactions, including liquid consolute points, etc., so studies of the q-dependence of the mean relaxation rate merely allow one to measure the dimension d of space, in case there is any real uncertainty about that.

Experiments on linear polymers[17] often give results like $\Gamma_q \sim q^{2.8}$, leading to speculation on why the relaxation rate exponent is not quite 3. Our measurements indicate that the problem is one of reaching the asymptotic limit $qR \gg 1$. We prefer to express relaxation rates in terms of the apparent hydrodynamic radius, which we define through $R_{app} = q^2 kT/6\pi\eta_0\Gamma_q$. *In the diffusion regime* $qR \ll 1$ we expect $R_{app} = \xi_h$, the hydrodynamic correlation length of the solution, whereas for $qR \gg 1$ we expect the universal result $R_{app} \sim q^{-(d-2)}$. Of course, in the limit $C \rightarrow 0$ the hydrodynamic correlation length becomes R_h, the hydrodynamic radius of a single chain.

Good solvent: We first attempted to verify the universal "q-cubed" regime for the initial decay rate of polystyrene in toluene. The q-dependence of the apparent hydrodynamic radius of polystyrene in toluene was determined for samples at the three concentrations 0.1, 0.25, and 0.6 mg/mL. The apparent hydrodynamic radius at each value of q was linearly extrapolated to zero concentration, and the results are plotted in Figure 5. As for the elastic scattering data, we fit R_{app} to the four-parameter form

$$R_{app} = \frac{R_h}{[1 + a(qR_h)^2 + b(qR_h)^4]^{(d-2)/4}} \qquad (2)$$

where d, properly the spatial dimension, is treated as a floating parameter. The resulting fit in Figure 5 is quite good and neatly yields $d = 3.00$; thus, $R_{app} \sim q^{-1.00}$ for large qR. This is something of an improvement on attempts to extract this universal behavior from directly fitting intermediate QELS data on log-log axes, which tends to give $d = 2.8$. The plot in Figure 6 greatly expands the small deviations in the universal regime. The quality of fit is quite good, and the high-qR data level off in a convincing manner. Previous light scattering studies[17-22]

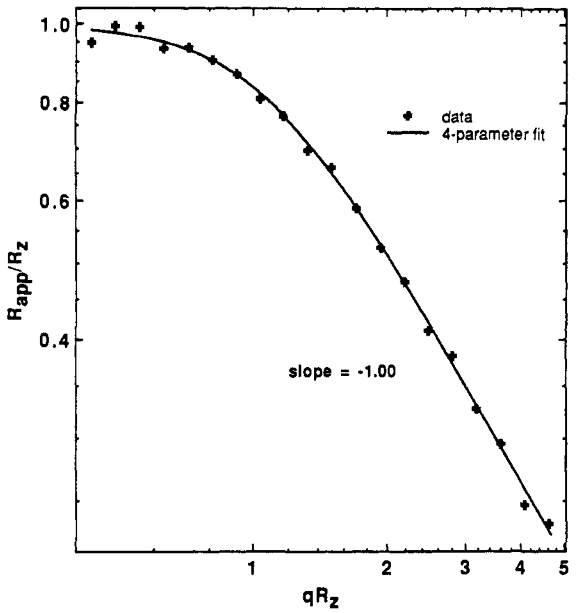

Figure 5. q-dependence of the apparent hydrodynamic radius of polystyrene in toluene on logarithmic dimensionless axes. Here R_z is the hydrodynamic radius extrapolated to $C = 0$ and $q = 0$. A four-parameter fit to the data gives $R_{app}/R_z \sim (qR_z)^{-1.00}$ in the intermediate scattering regime, providing direct experimental evidence that the dimension of space is $2 + 1.00 = 3.00$. This indicates that at high qR internal modes of relaxation dominate the dynamics.

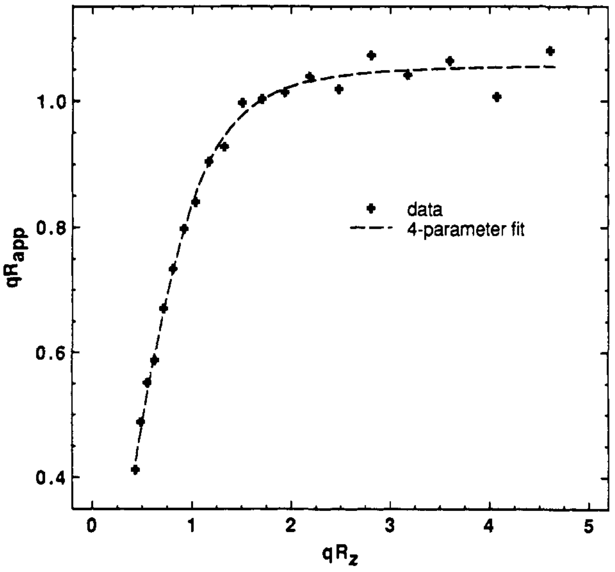

Figure 6. Data and fit in Figure 5 replotted on linear dimensionless axes qR_{app} versus qR_z in order to better resolve the intermediate scattering regime, where we expect $qR_{app} \sim (qR_z)^0$. The deviations from q^3 behavior are relatively small in this case.

have shown good consistency with the universal q-cubed law but have not been able to conclusively extract this result from the data.

Since the curve fit provides a value of R_h, we thought it might be interesting to determine the universal ratio $\rho = R_g/R_h$. Our best estimate was obtained by extrapolating ρ to zero concentration; ρ is relatively insensitive to concentration, so this is more accurate than extrapolating R_g and R_h individually to $C = 0$ and taking the ratio. After reducing ρ by 1.12 to correct for polydispersity, we obtain $\rho = 1.44$. Polydispersity corrections were based on the Schulz distribution[7] and the stated polydispersity of the sample, obtained from gel permeation chromatography. In a Θ solvent ρ is predicted to be[7] $8/3\sqrt{\pi} \cong 1.50$, and this ratio is expected to be somewhat larger in a good solvent. Our value is lower than expected, which is consistent with previous experiments.

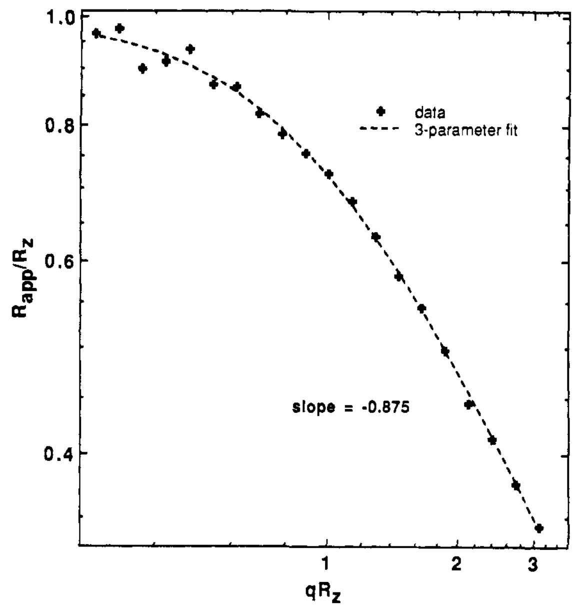

Figure 7. q-dependence of the apparent hydrodynamic radius of polystyrene in cyclohexane at the θ point. A three-parameter fit to the data gives $R_{app}/R_z \sim (qR_z)^{-0.88}$ in the intermediate scattering regime, probably due to the fact that the smaller radius gives a more limited large qR regime than in a good solvent.

Θ solvent: In the Θ solvent cyclohexane the hydrodynamic radius was only 118 nm, so with the He–Ne laser we were not able to obtain large values of qR. Still, the three-parameter function $R_{app} = R_h/[1 + a(qR_h)^2]^{(d-2)/2}$ fits the data in Figure 7 quite well and gives $d = 2.88$, in good agreement with the expected value of $d = 3$. The small discrepancy in this case is probably due to a poorly defined $qR \gg 1$ regime. After correcting for polydispersity, we obtain $R_g/R_h = 1.32$, in contrast to the predicted Θ value of 1.50. The discrepancy may be due to the importance of three-body interactions at the Θ point or may be due to the slow molecular weight convergence of the hydrodynamic radius to its expected value. In any case, the ratio R_g/R_h is usually smaller than predicted.

Stretched exponential decay: The reader has probably realized that investigating the q-dependence of the line width Γ is not a particularly illuminating way to investigate the dyamics of a linear polymer: There's certainly such a thing as "too much universality". However, the shape of the correlation function contains much more information and so is of greater interest. There are two alternative approaches to studying the shape. One can attempt to extract the spectrum of decay times from the observed decay—an ill-conditioned inverse transform problem that only clever researchers can beat into submission—or one can simply describe the decay by some meaningful family of functions with a few parameters. We have had terribly discouraging experiences with ill-conditioned inverse transform algorithms (they only seem to work when you know the answer anyway) and do not trust them at all, so we adopted the latter approach. Fortunately, the dynamic structure factor for the Zimm model is expected to behave in a very simple way in the large qR, large Γt limit. The complete functional form of $S(q,t)$ is complex for the Zimm model,[18] but $S(q,t)$ is a function of the single variable $\Gamma_q t$ at all times and at large times is the stretched exponential decay[13,18]

$$S(q,t) = Ae^{-a(\Gamma_q t)^{2/3}} \tag{3}$$

where A and a are constants[18] (in a Θ solvent $a \cong 1.35$). The exponent $^2/_3$ is a consequence of the long-ranged hydrodynamic interactions and so is expected to be relatively universal for all flexible clusters, regardless of their fractal dimension or connectivity. Thus, eq 3 should apply to Θ chains and good solvent chains, even though calculations are for the ideal chain. Finally, we again point out that the exponent b is insensitive to polydispersity.

There are a number of important experimental considerations in attempting to observe a stretched exponential decay. We had to try many times to get really good data, and we found this measurement to be at least a decade harder than the elastic scattering or initial decay rate experiments. First, it is necessary to take data at large values of qR, where the scattered intensity is quite small, and since polymers just get so big, this requires a short laser wavelength. We used the 331.6-nm line of our Coherent argon ion laser, since this is as short as possible without continuous-wave frequency doubling and running into photodegradation problems with the polystyrene. Second, the stretched exponential decay occurs at large correlation times, where the amplitude of the correlation function is small. Since the incoherent base line must be subtracted from the coherent scattering to obtain $S(q,t)$, we must observe a very small difference between two large numbers. This requires large signal-averaging times, so the scattering samples must be immaculately dust-free in order that the calculated base line agrees with the base line obtained from the 16 delayed channels. This latter point is the real bugaboo in this experiment, since, if one does not really know the incoherent base line, it is impossible to extract the stretched exponential exponent. We made repeated measurements on several samples before we were able to get the required base-line agreement of less than ~0.05%! A difference this small is easy for strong scatterers, but for the weak intermediate scattering of low-concentration polystyrene solutions, where the coherent signal at zero time is only ~10% greater than the base line, this is quite difficult. Finally, in order to observe the rapid decay of short-wavelength normal modes of polymers, it is necessary to set the correlator channel time to ~0.1–1.0 μs. Because of this, photomultiplier tube afterpulsing can seriously compromise the early time behavior of the intensity autocorrelation function. We effectively eliminated afterpulsing by judiciously selecting the PMT voltage.

Good solvent: We made a variety of measurements on the PS/toluene sample in order to obtain the expected stretched exponential decay exponent of $^2/_3$. We first checked the concentration dependence of the correlation function at $q^{-1} = 36.5$ nm with a 60-mW He–Ne laser and found none in the range 0.1–0.6 mg/mL. This is reasonable since 36.5 nm is always smaller than a correlation length. At this value of q a nonlinear stretched exponential fit to the data gave $b = 0.746$, where the data were fit in the logarithmic space in order to emphasize the long-time tail where the stretched exponential form is expected. Measurements with an argon ion laser operating at $\lambda = 331.6$ nm ($q^{-1} = 18.2$ nm, or $qR_g \cong 19.0$), shown in Figure 8, gave $b = 0.72$ after 24 h of signal averaging. Thus, our attempts to find the expected $^2/_3$ were close but not quite successful. This may be due to the fact that the asymptotic-time regime where the exponent $^2/_3$ should be observed is experimentally inaccessible because the amplitude of the correlation function is too small at very large times or because we cannot get to large enough qR. In fact, the theoretical analysis of Akcasu et al.[18] has demonstrated that the asymptotic-time regime is difficult to access and that measured stretched exponential exponents will generally be too large.

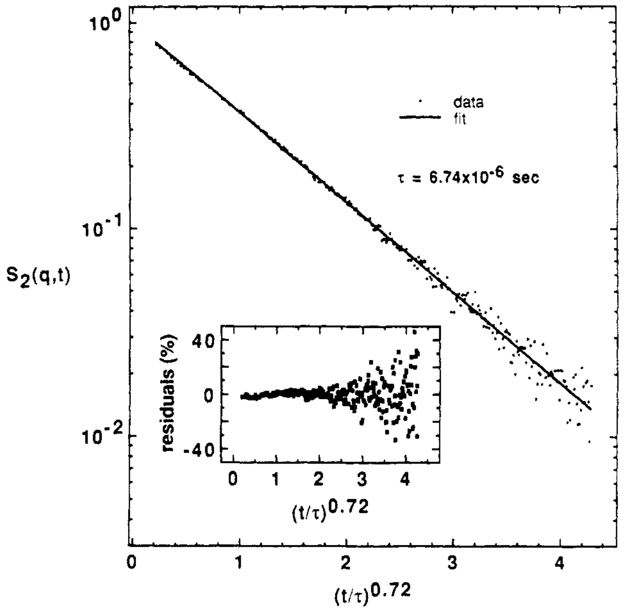

Figure 8. Normalized homodyne intensity autocorrelation function $S_2(q,t)$ for polystyrene in the good solvent toluene showing a stretched exponential decay with $b = 0.72$, in reasonable agreement with the expected theoretical value $b = {}^2/_3$. The decay time of 6.7 μs was obtained from the nonlinear stretched exponential fit. These data were taken with a UV argon ion laser operating at 333.6 nm and $q^{-1} = 18.3$ nm, for $qR_g \cong 19.0$.

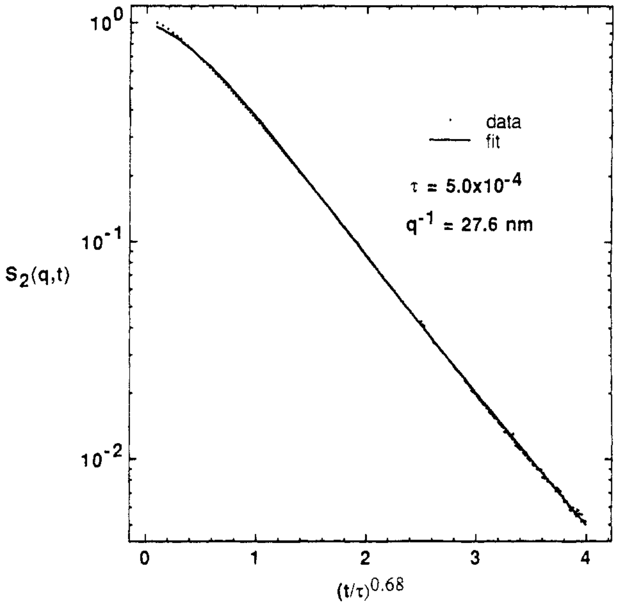

Figure 9. Autocorrelation function $S_2(q,t)$ for polystyrene in the Θ solvent cyclohexane showing a stretched exponential decay with $b = 0.68$, in good agreement with the expected theoretical value $b = {}^2/_3$. The decay time of 50 μs was obtained from the nonlinear stretched exponential fit. These data were taken with an argon ion laser operating at 454.5 nm and $q^{-1} = 27.6$ nm, for $qR_g \cong 6.3$.

Θ *solvent*: The results for polystyrene in cyclohexane were even more surprising. Using an argon ion laser operating at 454.5 nm for $q^{-1} = 27.6$ nm, we were able to obtain a correlation function with only a 0.01% difference between the calculated and measured base lines. However, careful analysis of this correlation function indicates that it is not well described by a stretched exponential decay. In fact, it is not possible to extract the asymptotic-time behavior of the decay by any simple means, so we resorted to fitting the decay to the three-parameter function

$$S_2(q,t) = e^{-\Gamma t/[1+c(\Gamma t)^2]^{(1-b)/2}} \tag{4}$$

At eary times this gives the exponential decay $e^{-\Gamma t}$, and at large times this crosses over to the stretched exponential decay $\exp[-a(\Gamma t)^b]$ where $a = c^{(b-1)/2}$. A nonlinear least-squares fit to the data is shown in Figure 9 and yields $b = 0.68$ and $a = 1.35$. These parameters are in quite good agreement with the theoretical predictions[18] $b = 0.67$ and $a = 1.35$; however, the validity of these exponents requires further comment.

A more critical analysis of the correlation function can be made by defining the time-dependent exponent

$$b(t) \equiv \frac{\mathrm{d} \ln [-\ln (S_2(q,t))]}{\mathrm{d} \ln (t)} \qquad (5)$$

In principle, experimental data can thus be differentiated to find the asymptotic value of $b(t)$. In practice, differentiating data produces too much noise, so it is best to first smooth the data. The function in eq 4 accurately smooths and interpolates the data, and this function can be differentiated within the actual time domain of the experimental data to evaluate $b(t)$. Note that we are not using any of the fit parameters in this method of noise reduction. When this is done, it is found that $b(t)$ decreases from 1.0 at small times to $b = 0.71$ at the largest experimentally accessible time. Of course, our fit to the data indicates that $b(\infty) = 0.68$, but it is not really legitimate to quote this extrapolated value, so we prefer to quote $b = 0.71$ as the measured value.

Previous light scattering experiments on the shape of the dynamic structure factor have not accessed sufficiently large times to extract the stretched exponent b from the data itself. Rather, consistency has been shown by fitting the available data to the theoretical form.[17,19] This can be inconclusive if the asymptotic-time behavior is not being tested in the fit. On the other hand, quasielastic neutron scattering experiments using the spin–echo technique have yielded noisy correlation functions[23,24] from which it is not even possible to demonstrate consistency with any presumed line shape. The measurements described herein indicate that the stretched exponential decay can be deduced from the data and that the measured value is in good agreement with the Zimm model.

Discussion

These experiments confirm the expected intermediate elastic light scattering behavior of linear polymers in both good and Θ solvents, with fractal dimensions of 1.63 and 1.95, respectively. Clearly, the improvements on the original Flory estimate of the self-avoiding walk dimension are inconsequential, since even the best measurements and data analysis have an uncertainty of at least ±0.05 in the measured fractal dimension. Much of the uncertainty derives from the nonasymptotic nature of the experimental data, so it is quite meaningless to quote errors in D based on the fit residuals from one method of data analysis.

Intermediate quasielastic light scattering measurements of the Rayleigh line width adequately demonstrate the jejune q^3-dependence of the initial decay rate of the correlation function for both good and Θ solvents, with measured exponents of 3.00 and 2.88, respectively. However, measurements of the line shape demonstrate a stretched exponential decay, but with an exponent that is greater than ${}^2/_3$—specifically 0.72 for good solvents and 0.71 for Θ solvents. However, it is difficult to obtain data with sufficiently little noise to obtain these exponents.

Several previous studies of the dynamics of linear polymers have been reported, although the main subject of interest has always been the q-cubed prediction for the line width. Adam and Delsanti[17] studied the q-dependence of the line width of polystyrene/benzene and found $\Gamma_q \sim q^{2.85\pm0.05}$ by plotting data log–log and fitting with a straight line. Our data analysis improves on this result somewhat and removes any doubt about the q-cubed law. Adam and Delsanti comment that they were able to fit their $S(q,t)$ quite well with the Dubois-Violette[13] function, but no details were given. A more detailed line-shape analysis was later given by Han and Akcasu[19] on polystyrene/toluene; however, the data were fit to the expected functional form, so b was not allowed to freely vary. Furthermore, the signal-averaging was only sufficient to obtain ~1.7 decades of clearly defined decay, so a critical determination of the long-time decay was not possible from these data.

Finally, there have been a number of efforts to study single-chain dynamics with spin–echo neutron scattering.[23,24] However, the noise in the correlation functions is so great that, although a nonexponential decay can be discerned, it cannot be quantified, and the length scales are sufficiently short that measurements are near the segment diffusion limit. Furthermore, the correlation functions decay over only a fraction of a decade in amplitude, so a line-shape analysis is not possible in an experiment of this technical difficulty.

In summary, these light scattering measurements substantiate many of the theories of the static and dynamic properties of linear polymers in solutions and demonstrate that asymptotic internal dynamics is experimentally observable with some effort. It has been possible to extract exponents directly from the data in all cases, so we have made an improvement on showing consistency with existing ideas.

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