The Glass Temperature of Polymer Rings

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Received September 9, 1986

ABSTRACT: The entropy theory of glass formation is used to predict the glass temperatures of a bulk polymer system consisting of noncatenated rings. It is found that the glass temperature of ring systems increases as the molecular weight is lowered, while the glass temperature of linear polymers decreases with decreasing molecular weight. Quantitative predictions for cyclic and linear poly(dimethylsiloxanes) and for cyclic and linear polystyrene are made and compared to experiment.

Introduction

There are three reasons why one might study the glass transition of bulk ring systems. First, melts of polymer rings have been recently studied because of the light that they shed on the reptation process.[1] The naive view of reptation of linear chains in the melt must be modified to account for motion of rings in the melt. In the study of the viscosity and of the diffusion of ring systems, the full curve of viscosity vs. temperature is obtained by the time–temperature shifting method. In analyzing the raw data, it is useful to know the glass transition temperature.

Second, ring or cyclic polymers also shed light on the entropy theory of glasses. Since the number of configurations of a ring is much less than that of a linear chain of equal length, we know that the configurational entropy, S_r, of a cyclic system will always be less than that of a linear system. This means that the glass temperature, T_g, of ring systems is always larger than that of an equal length linear system, since one must lower the temperature further in the linear system to reach the $S_r = 0$ point which defines the transition temperature.

Third, measurements of glass transition temperatures for cyclic poly(dimethylsiloxanes) exist and have not yet been explained by theory.[2] In this paper we will use the entropy theory of glasses to predict the glass temperature of ring polymers. We find that whereas linear chains always show a decrease in T_g as we lower the molecular weight, x, ring polymers either show a smaller decrease or more usually an increase in T_g. We apply the theory to two systems: cyclic polystyrene for which the material is made[3] but the glass temperatures are not yet systematically measured, and the dimethylsiloxanes for which glass temperatures are measured for both the cyclic and linear forms.[2] Polystyrene provides a very good test case because (1) the prediction for rings involves no additional parameters and (2) the data are not yet collected.

According to the entropy theory of glasses, the glass transition occurs when the configurational entropy reaches a critically small value.[4] If the Flory–Huggins lattice model of polymers is used to evaluate the partition function, a second-order transition in the Ehrenfest sense is predicted at finite temperatures and pressures. The configurational entropy equals zero along this transition line. If this (second-order) transition is identified with the glass transition, then good agreement with experiment is obtained.[5,6] The following classes of experiment have been compared with the theory: (1) T_g vs. molecular weight for linear polymers; (2) T_g vs. plasticizer content; (3) T_g vs. composition for copolymers; (4) T_g vs. composition for polymer blends; (5) T_g vs. pressure; (6) T_g vs. stretch ratio in a rubber; (7) T_g vs. cross-link ratio in a rubber; (8) the prediction of the specific heat discontinuity at the glass temperature. These predictions have been discussed elsewhere. The purpose of this paper is to predict the glass temperature of rings (cyclic noncatenated polymers) and to test the predictions with experiment. Although predictions for rings can be made in each of the seven above categories, we shall discuss only T_g vs. molecular weight.

Theory

The partition function, Q_l, for a linear system of N_x polymer molecules of length x with N_0 holes (volume fraction $V_0 = N_0/(xN_x + N_0)$) is

$$Q_l = \sum_{N_0,f} Q_l(x,V_0,f) \tag{1}$$

where f is the fraction of flexible bonds that are flexed out of their low-energy orientation. One can approximate the sum over f and N_0 by choosing f, N_0 (or equivalently f, V_0) to maximize the partition function. The number of holes (or V_0) and the fraction of bonds flexed are then viewed as order parameters. The two microscopic energies are the hole energy, E_h, and the flex energy, $\Delta\epsilon$, and they control the values of f and V_0. E_h is equal to the magnitude of the energy of a polymer–polymer van der Waals bond, and $\Delta\epsilon$ is the difference in the energy minima of the $(z - 2)$ high-energy wells and the low-energy well. Q_l has been evaluated in previous works. The functional form of Q_l when we use the Huggins site fraction rather than the Flory volume fraction and when we assume that the energy change on flexing is proportional to the number of flexes is

$$Q_l = \mu_l'\lambda_l'$$

$$\mu_l' = \sum_{N_0}\left[\left(N!z^{xN_x}\left\{\frac{[(z-2)x+2]N_x+zN_0}{2}\right\}! \times (z-1)^{N_x}\exp(-zE_hN_0S_x/2kT)\right)\Big/(N_0!(zN/2)!2^{xN_x})\right]$$

$$\lambda_l' = \sum_f[((z-2)^{f(x-3)N_x}[(x-3)N_x]!\exp(-f(x-3)\Delta\epsilon/kT))/([(1-f)(x-3)N_x]![f(x-3)N_x]!N_x!)]$$

$$N = xN_x + N_0$$

$$S_0 = 1 - S_x = zN_0/([(z-2)x+2]N_x + zN_0) \tag{2}$$

z is the coordination number of the lattice. Formulas 2 use site fractions S_0 and S_x in place of volume fractions V_0 and V_x. These site fractions are measures of the numbers of neighbors to holes and polymer molecules, respectively, and result in more accurate expressions for the thermodynamic formulas.[7] Our point in writing eq 2 is that we can use it to derive the partition function, Q_r, for the cyclic system by concentrating on the differences between Q_l and Q_r. Let us begin with a completely flexible system ($\Delta\epsilon = 0$). The number of configurations associated with an individual linear chain is $(z - 1)^x$ where $(z - 1)$ is the freedom per monomer unit and is set equal to one less than the coordination number of the lattice since backstepping is not allowed, while for a ring the number of configurations is $(z-1)^x/(2\pi x/3)^{3/2}$. This simple formula is obtained by using the Gaussian distribution law for the end-to-end length and then setting the end-to-end length equal to 0. Obviously the difference in configurational entropy between the ring and the linear systems on a per monomer basis is

$$S_l - S_r = 3(\ln(2\pi x/3))/(2x) \tag{3}$$

This simple but approximate formula already tells us two things. First, at infinite molecular weight, the glass temperatures of ring and linear systems are the same. Second, the glass temperature of a ring system is always higher than a linear system because its configurational entropy is always less.

A more accurate estimate of the change in entropy between rings and linear glasses can be made if we include the effects of flexes. In this paper we shall consider two ways to estimate this. In one we estimate that the persistence length of a linear chain is inversely proportional to the fraction of bonds flexed, f. The formula for the number of configurations of a ring becomes

$$g = (z-1)^{fx}/(4\pi x/3f)^{3/2} \tag{4}$$

The extra factor of 2 multiplying π arises from the variance of the statistical length. We need to modify eq 2 to account for the fact that a certain minimum number of monomers are needed to form a loop. This number depends on the model of the polymer in question. We think six is a reasonable approximation. The $(x-3)$ that appears in the formula for the partition function Q_l arises from the fact that one needs to have a tetramer before one can have a bond to flex, so that the total number of flexible bonds in a linear system is $(x-3)N_x$. However, when we form rings the total number of flexible bonds is now $(x-6)N_x$ before a ring can be formed. The part of the partition function having to do with flexes now becomes for ring systems

$$\lambda_r' = \sum_f [((z-2)^{f(x-6)N_x}[(x-6)N_x]! \exp(-f(x-6)N_x\Delta\epsilon/kT))/([(1-f)(x-6)N_x]![f(x-6)N_x]!N_x![4\pi(x-3)/3f]^{3N_x/2})] \tag{5}$$

Another, different approximation is to use $(x-3)$ in eq 5 throughout. We can rationalize this as follows. If the energy to bend a bond through a small angle θ is $E = K\theta^2$ and we have x bends, then the total bending energy is $E_T = xK\theta^2$. But $\theta = 2\pi/x$ since we must bend the chain through an angle of 2π to form a ring. Thus, $E_T = K4\pi^2/x$ which is small. This suggests that the flexing that occurs in a linear chain is not dependent on what the end-to-end length of the chain is. This justifies the use of the permutation terms in eq 5 being the same as those in eq 2. Also, it suggests the Gaussian approximation

$$P(r) = \frac{\exp(-3r^2/2\langle r^2\rangle)}{(2\pi\langle r^2\rangle/3)^{3/2}} \tag{4A}$$

will give a proper estimate of the reduction in the number of configurations at $r = 0$ even though the chain has structure.

The formula for f is obtained by maximizing the partition function with respect to f. If we approximate $\exp(-3/2(x-3))$ by the first three terms of its power series expansion, we obtain

$$f \cong [A + 3/2(x-6)] \times [1 + (1 - 18(1+A)/(3 + 2A(x-3))^2)^{1/2}]/2(1+A)$$
$$A = (z-2)\exp(-\Delta\epsilon/kT) \tag{6}$$

In solving our equations for numerical results, we actually used the more accurate procedure of maximizing eq 5 on a computer to determine f rather than using the slightly less accurate formula 6. This is to be contrasted to the formula for f in linear systems which reads

$$f = A/(1+A) \tag{7}$$

The formula for the configurational entropy of the ring system becomes

$$S_r/kxN_x = \frac{z-2}{2}\ln\left(\frac{V_0}{S_0}\right) + \frac{N_0}{xN_x}\ln(V_0^{(z-2)/2}/S_0^{z/2}) + \frac{\ln([(z-2)x+2](z-1)/2)}{x} + \frac{x-6}{x}[f\ln(z-2) - (1-f)\ln(1-f) - f\ln f] - \frac{3}{2x}\ln\left(\frac{4\pi(x-3)}{3f}\right) \tag{8}$$

which differs from linear systems only by the presence of the last term and the use of $(x-6)$ rather than $(x-3)$ in the denominator of the next to the last term. The formula obtained by maximizing with respect to N_0 (or V_0) is unchanged and reads

$$\ln(V_0^{(z-2)/2}/S_0^{z/2}) - zE_hS_x^2/2kT = 0 \tag{9}$$

Equation 9 and $S_r = 0$ can now be used to determine T_g vs. x, provided that we know the energies $\Delta\epsilon$ and E_h.

The above method used the maximum term method for f as described in eq 9 of the original Gibbs–Di Marzio paper.[4] It is also possible to sum over f and obtain a partition function for each chain as in their eq 7. This can be done and we obtain for λ'

$$\lambda_r' = (N_x)!\prod_i\frac{(q_i)^{n_i}}{(n_i)!} = (\sum_i q_i)^{n_x} = q^{N_x} \tag{10}$$

Now there is no sum over f. We have for linear chains

$$q = (1 + (z-2)\exp(-\Delta\epsilon/kT))^{x-3} \quad \text{linear molecules} \tag{11}$$

while for rings we use eq 4A to obtain

$$q = (1 + (z-2) \times \exp(-\Delta\epsilon/kT))^{x-3}/\left(\frac{2\pi\langle r^2\rangle}{3}\right)^{3/2} \quad \text{ring molecules} \tag{12}$$

The value of $\langle r^2\rangle$ needs to be estimated for a model of a chain with flexes. The simple isomeric state[7] model with nearest-neighbor energies and tetrahedral valence angle gives

$$\langle r^2\rangle \cong 2nl^2\left(\frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle}\right) \equiv 2x\frac{(1 + ((z-3)/2)\exp(-\Delta\epsilon/kT))}{((z-1)/2)\exp(-\Delta\epsilon/kT)} \tag{13}$$

where

$$\langle\cos\phi\rangle = \frac{(1-\exp(-\Delta\epsilon/kT))}{(1+(z-2)\exp(-\Delta\epsilon/kT))} \tag{14}$$

is the expected value of the cosine of the bond rotation angle, ϕ. Here the zigzag configuration corresponds to $\phi = 0$ and has the weight 1. The other $(z-2)$ angles are equally spaced $2\pi/(z-1)$ rad apart and have the weight $\exp(-\Delta\epsilon/kT)$. For large z the coefficient multiplying $2x$ in eq 13 is equal to $1/f$, and in this limit the direct sum and the maximum term methods give identical results.

For linear molecules it is easy to verify that eq 11 gives the same result for the entropy as the use of λ_l' in eq 2 with

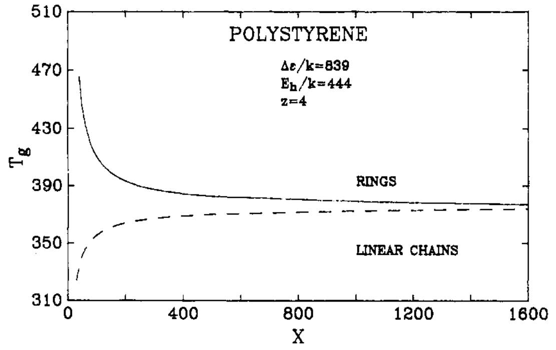

Figure 1. (lower curve) Both a theoretical prediction and a fit to experiment for linear polystyrene (see ref 4). (upper curve) Prediction for rings which uses only the parameters used to obtained the lower curve. The maximum term method was used.

the substitution afforded by eq 7. However, for rings the use of λ_r' from eq 5 with the substitution afforded by eq 6 gives somewhat different result than eq 12. There is a slight inconsistency in eq 5 because the term accounting for rings assumes the same value for f for all rings, while the remaining part of the expression allows permutations of flexed and unflexed bonds that result in different values of f for different rings. On the other hand, eq 12 is a simplification. It relies on the notion that the fraction of flexes, f, in a chain is not a function of the end-to-end length, r. Both of these statements are rigorously valid only for large x where the flex and end-to-end length distributions are decoupled. See the discussion surrounding eq 4A.

For small x the approximations afforded by eq 5 and 10 differ slightly, and we will display both results.

The simple nearest-neighbor model that we have used for the chain energy can be generalized by using an isomeric state model with a more accurate description of the energies as, for example, in Flory's book,[8] but this would be premature since there are so little data to explain.

Discussion of Results

The glass temperature of linear polystyrene was predicted in 1958. The lower curve of Figure 1 which agrees with experiment was calculated by using a $\Delta\epsilon/k$ of 839.3 K and $2E_h/k$ of 887.7 K. The value of E_h was chosen to fit the break in the thermal expansion coefficient at the glass temperature, while $\Delta\epsilon$ was chosen to fit the glass temperature for infinite molecular weight. Thus, the fit to the data is essentially a one-parameter fit. The degree of polymerization, x, was chosen to be the number of carbon atoms in the backbone of the polymer, the rule used being that only rotations about bonds that result in changes in the shape of the molecule are to be counted. Since the rotation about the benzene ring does not result in a distinguishable shape, there are two flexible bonds per monomer unit. Because we have used our parameters in fitting to the lower curve, the prediction for rings is a no-parameter prediction.

The upper curve can be understood as a result of two competing effects. The first effect is a delocalization entropy. If we take a chain of length x and cut it in half, then there is a larger entropy because now there are two centers of mass to place in space rather than just one. This effect occurs in both the ring and linear systems and results in a decrease in T_g (whatever raises the configurational entropy lowers T_g). To understand the steep upswing in the curve, compare the number of configurations in a ring of size x and two rings each of size $x/2$.

$$z^x/(4\pi x/3)^{3/2} > (z^{x/2}/(4\pi x/6)^{3/2})^2 \qquad (15)$$

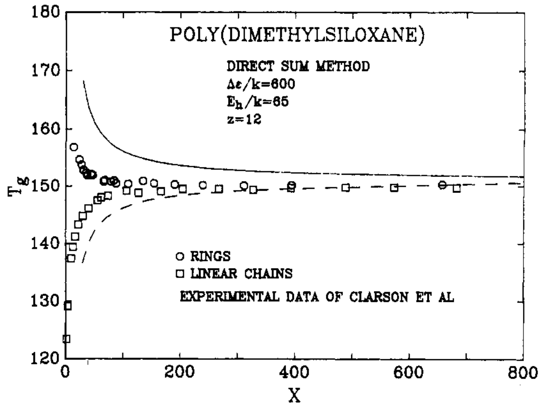

Figure 2. Direct sum method for poly(dimethylsiloxane). Circles and squares are the data points, and the curves are the theoretical predictions. Although the qualitative behavior is correctly predicted, one can obtain quantitative predictions only if the number of flexible bonds per monomer is lowered to below 1 rather than the value 2 which we have used.

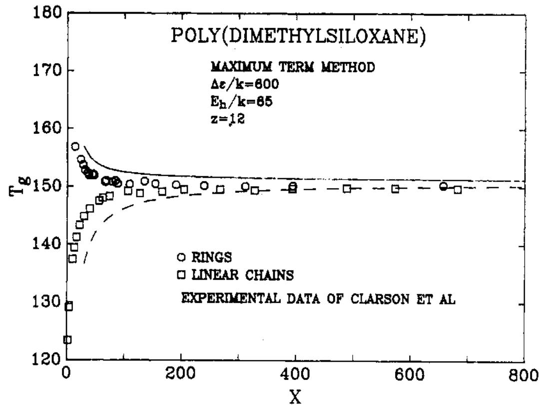

Figure 3. Comparison of theory to experiment for poly(dimethylsiloxane). Maximum term method.

The x^3 term in the denominator of the right-hand side dominates the $x^{3/2}$ term in the denominator of the left-hand side. Thus, small ring systems have a lower entropy than large ring systems from this effect. The T_g is raised (whatever lowers the configurational entropy raises the glass temperature).

For the $\Delta\epsilon$ and E_h values for polystyrene, the glass temperature difference between rings and linear chains is predicted to be 10.3 °C at $x = 500$, 23.4 °C at $x = 200$, 44.8 °C at $x = 100$, and 85.9 °C at $x = 50$.

Recently Clarson et al.[2] have measured the glass temperatures of both ring and linear poly(dimethylsiloxanes). Figures 2 and 3 display the data as well as the predictions of the theory. We have used $\Delta\epsilon = 600$ and $E_h = 65$ (direct sum method) in Figure 2 in order to achieve a reasonable fit to the data, and $\Delta\epsilon = 600$ and E_h 65 for the two-parameter model (maximum term method for both N_0 and f). Clearly, the qualitative features of the data are correctly predicted.

Figure 4 is an attempt to display the full possibilities of T_g vs. $1/x$ variation when different values are chosen for $\Delta\epsilon$ and E_h ($R = 2E_h/\Delta\epsilon$). More generally $R = zE_h/(2\Delta\epsilon)$, but the curves depend only weakly on z. Although the curves for linear systems are always monotonically decreasing, the curves for ring systems show a maximum provided the ratio of E_h to $\Delta\epsilon$ is small enough. However, for small R, ring systems show values of V_0 that we judge to be too large. The glass temperature of a ring system must always be larger than that of the corresponding linear system. One notices that the T_g vs. 1/MW curve is a

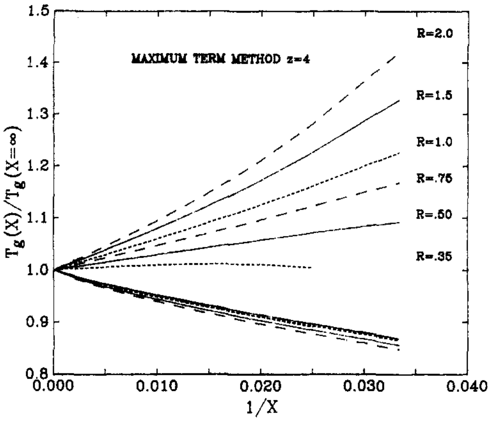

Figure 4. $T_g(x)/T(\infty)$ vs. $1/x$ for various values of $R = 2E_h/\Delta\epsilon$. The lower curves for linear systems are insensitive to the value of R, while the upper curves for rings are sensitive.

strong function of R for rings but depends weakly on R for linear systems.

At first sight the fact that the prediction of T_g for rings involves no additional parameters would seem to provide a critical test of the theory. For this reason it may be useful to list those factors that we have glossed over and which may under certain circumstances modify our predictions.

(1) Our determination of $\Delta\epsilon$ for polystyrene by use of the break in the thermal expansion coefficient at the glass temperature assumes that the holes are the same size as the empty cells. However, it has been argued that the holes can be smaller.[9] Use of a smaller size hole would allow us to fit the experimental thermal expansion coefficient with a smaller R value. Also, the weak dependence of the T_g-vs.-x curve on R for linear systems means that a correct prediction of T_g vs. x for linear systems (see Figure 4) does not establish the E_h value with any degree of certainty.

(2) The simple nearest-neighbor model of the chain we have used may not be adequate. In the more general version of our original treatment, we specifically allowed for a general dependence of chain energy on chain shape.[10] Thus, for example, one could use the isomeric state model to treat the poly(dimethylsiloxanes). It would seem that this polymer has more than one kind of energy associated with rotations around flexible bonds. The poor modeling of this polymer by the nearest-neighbor approximation may be the source of the need to stretch the data points along the x axis (Figures 2 and 3).

(3) Even the simplest models of closed rings with energies that are functions of the number of flexes have not been solved.[11] The simplest model which corresponds to our nearest-neighbor model for the linear chains would be to allow a $\Delta\epsilon$ for each 90° bend and zero energy for each pair of contiguous bonds that lie collinearly. One wonders whether this problem has an analytic solution for the simple cubic lattice or even for the square lattice.[12]

(4) Because of (2) and (3) above, the use of a Gaussian correction term to account for the reduction in the number of configurations when rings are formed may be too simplistic. Computer modeling may be necessary to decide to what extent the Gaussian approximation is valid for small ring sizes.

(5) Even if we solved the one-chain problem exactly, there would be a difference in the predicted bulk properties depending on whether we had concatenated or nonconcatenated systems. Our results correspond to rings that are ghosts to each other as far as linking is concerned. The purely concatenated or purely nonconcatenated systems would be expected to have different configurational entropies.

(6) The relation between T_g and T_2 may need examination. We have simply assumed that $(T_2 - T_g)$ is a constant, but this may not be valid over wide temperature ranges. Perhaps considerations along the lines of the suggestions of Havlicek and Nicolais[13] are more appropriate. Another aspect that needs reexamination is whether the configurational entropy, S_c, equals zero at the second-order transition temperature, T_2, or, as has been suggested previously, T_2 occurs at some critical small value of S_c. Recent Monte Carlo calculations[14,15] show that there is local trapped motion of polymer beads and molecules at low volume fractions of holes (low temperatures). The various regions of local mobility are isolated from each other at low temperatures and do not allow transport of a bead or of a polymer chain throughout the medium. As the number of holes is increased, the regions of local mobility expand until they overlap, thereby allowing percolation of beads throughout the medium at the higher temperatures corresponding to the larger number of holes. This view is in complete accord with the idea that there is a residual configurational entropy corresponding to localized bead motion within the chain even below the second-order transition temperature. An interesting question is whether this residual entropy is a function of the number of flexed bonds as well as the number of holes. The Monte Carlo treatments can be used to answer this question, but so far only the effects of holes have been considered. A Monte Carlo treatment which included both flexes and holes but concluded that the percolation occurred at a fixed fraction of holes would validate the free volume theory. On the other hand, if percolation occurred at a small value of the configurational entropy, the GD theory would be validated.

This paper is, we believe, the first to give a theoretical explanation of why the glass temperature of rings can increase as we lower the molecular weight. It is a configurational entropy explanation. A simple version of the free volume theory would predict that the glass temperature of rings would remain constant or perhaps decrease slightly.

Acknowledgment. We thank G. B. McKenna for several helpful discussions.

Registry No. Polystyrene, 9003-53-6.

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Mobility of Fluorescent Polyacrylamide Derivatives in Water–Acetone Mixtures

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Received September 30, 1986

ABSTRACT: The global and local mobility of a poly(acrylamide) derivative in dilute solution in marginal and poor solvents is investigated by quasi-elastic light scattering, viscosimetry, and time-resolved fluorescence depolarization. A transition from the coil state to a compact globular state is observed by both light scattering and viscosimetry, while the local mobility as probed with the fluorescent label fluorescein isothiocyanate slightly decreases.

Introduction

The configuration of a polymer molecule is strongly influenced by the quality of the solvent. In good solvents a linear polymer assumes the configuration of an expanded random coil. As the solvent quality decreases, the formation of contacts between segments becomes increasingly probable and the molecule collapses eventually into a compact globule state. This collapse is usually accompanied by aggregation. The behavior of isolated polymer molecules in the collapsed state can be studied only in the limit of very low concentration. The first such observation has been reported by Nishio et al.[1] According to their results the diffusional mobility of high molecular weight poly(acrylamide) increases drastically upon increasing the acetone content in watery solutions of the polymer, thus reflecting the transition into a compact configuration.

Such changes in the global translational mobility are expected to be also accompanied by changes in the local mobility of the polymer backbone. To investigate this point, we have chosen a system similar to that of Nishio et al.,[1] i.e., a poly(acrylamide) derivative in water–acetone mixtures. For the investigation of the local mobility, we have modified the polymer to contain a small amount of fluorescent groups randomly attached to the polymer backbone. The aims of our study can be summarized as follows: (a) to investigate the changes of the translational mobility of isolated polymer molecules (in dilute solutions) by means of dynamic light scattering; (b) to measure the change of intrinsic viscosity with change of solvent quality (since intrinsic viscosity is a function of polymer configuration, its measurement shall provide a valuable independent confirmation of the light scattering data); (c) to investigate the changes in the local mobility of the polymer backbone by means of time-resolved fluorescence depolarization and to set the findings in relation to the measurements of the global translational mobility.

In order to be able to compare the data of three independent and rather different experiments, the results must be reduced into a suitable form. We suggest the concept of "equivalent hydrodynamic volumes" be employed, which will now be introduced together with a brief description of the basic principles of the methods.

Dynamic Light Scattering.[2] Dynamic light scattering measures the diffusion coefficient D of the polymer, which is related to an equivalent hydrodynamic volume V_L through the Stokes–Einstein relation.

$$R_L = \frac{kT}{6\pi\eta_0 D} \tag{1a}$$

$$V_L = \tfrac{4}{3}\pi R_L^3 \tag{1b}$$

where η_0 is the solvent viscosity, T the temperature, k the Boltzmann constant, and R_L the hydrodynamic radius. V_L thus is equivalent to the volume of a rigid sphere having the same diffusion coefficient as the polymer molecule.

The diffusion coefficient D is obtained from the decay of the autocorrelation function of the scattered light intensity (this intensity fluctuates because of the Brownian motion of the scatterers, i.e., of the polymer molecules). In the simplest case of a monodisperse solution of rigid spherical particles the normalized autocorrelation function $g(t)$ decays exponentially

$$g(t) = 1 + k\exp(-2Dq^2t) \tag{2}$$

Here q is the absolute value of the scattering vector and k a constant depending on the experimental configuration and the solvent contribution to the light scattering. Both the polydispersity and the flexibility of the polymer will cause deviations from the exponential form (2). Prior to the interpretation of the data, a careful analysis is necessary to distinguish between the two effects. According to Berne and Pecora[3] the flexibility effect becomes more important with increasing radius of gyration of the polymer coil. Providing the flexibility influence can be ruled out, it is appropriate to analyze the deviations from the exponentiality in terms of cumulants:[4] The first cumulant Γ of the autocorrelation function is proportional to the z average of the diffusion coefficient (for the monodisperse case $\Gamma = 2Dq^2$). The second cumulant yields the normalized variance μ_2/Γ^2 and is thus a measure of the polydispersity.

Viscosimetry.[5] The equivalent hydrodynamic volume V_v for the viscosimetry is obtained from a suitable form of the Einstein–Simha viscosimetric relation

$$V_v = \frac{2}{5}\frac{[\eta]M_v}{N_A} \tag{3}$$

where $[\eta]$ is the intrinsic viscosity, M_v the viscosity-average

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