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Mobility of Fluorescent Polyacrylamide Derivatives in Water–Acetone Mixtures

Jaroslav Rička,* Hermann Gysel, Johannes Schneider, René Nyffenegger, and Thomas Binkert

Institute of Applied Physics, University of Bern, 3000 Bern, Switzerland.
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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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molecular weight of the polymer (which we approximate by the weight-average M_w) and N_A the Avogadro number. V_v is equivalent to the volume of a rigid sphere having the same intrinsic viscosity as the polymer. Viscosimetry measures the energy dissipation due to polymer molecules in a shear flow and is complementary to the fluctuation method of dynamic light scattering.

Time-Resolved Fluorescence Depolarization.[6] Here the equivalent volume is calculated with the Stokes–Einstein relation for the rotational diffusion of spheres

$$V_F = \frac{kT}{6D_R\eta_0} \tag{4}$$

where D_R is the measured rotational diffusion coefficient of the label attached to the polymer backbone. Because of this attachment D_R reflects also the local mobility of the polymer backbone. V_F represents the volume that a free fluorescent sphere with the rotational diffusion constant D_R would have.

To measure D_R, the fluorescent labels are first excited by a narrow pulse of polarized light. The subsequent decay of the fluorescence intensity is resolved into its polarized ($I_\parallel(t)$) and depolarized ($I_\perp(t)$) components and recorded. From the difference $I_\parallel(t) - I_\perp(t)$ one can then recover (taking into account the finite width of the excitation light pulse) the polarization anisotropy function $r(t)$, which is related to a second-order reorientational correlation function of the transition moment of the label dye. In the simplest case of isotropic reorientation $r(t)$ assumes a simple exponential form

$$r(t) = r_0 \exp(-t/\tau) \tag{5a}$$

$$\tau = 1/6D_R \tag{5b}$$

In general, however, the decay of $r(t)$ may be more complicated and a careful analysis is necessary prior to the interpretation of the measurement.

Certain aspects of polymer–solvent systems that are similar to ours have been investigated by these methods in the past. Measurements of the diffusivity and gyration radius of poly(acrylamide) in water–acetone mixtures[1] have been already mentioned. Further examples are also the investigations of light scattering and viscosity of poly(acrylamide) in water by Patterson et al.[7] and the measurements of average fluorescence depolarization of FITC-labeled (at the chain end) poly(acrylamide) by Chryssomallis et al.[8]

Experimental Section

Preparation and Purification of Fluorescent Poly(acrylamide) Derivatives. As a first step of preparation a commercially available poly(acrylamide) ($M_w = 5.5 \times 10^6$ (Aldrich) used without further purification) was partially converted into poly(vinylamine) by means of Hofmann amide degradation. We have followed closely the procedure described in Ref 9 during which the polymer is allowed to react in a NaHBr solution for 1 h at 50 °C.[10]

To perform the labeling, we dissolved the converted polymer (1 g/L) in a 0.1 M $NaHCO_3$ solution to which the desired amount (7×10^{-3}–7×10^{-2} g/L) of fluorescein isothiocyanate (FITC, Fluka puriss) was added. After the mixture was allowed to react for 12 h, the polymer was precipitated by titrating 5 M HCl into the solution (precipitation occurred at pH 3). The labeled polymers were then ultrafiltered in watery solutions (membrane pore diameter of 100 nm) to remove possible cross-linked reaction products and then diafiltered (pore diameter of 5 nm) against 0.1 M KI solution and against pure water to remove the unreacted FITC and low molecular weight fragments of the polymer.

Dynamic Light Scattering. The experiments were performed with an apparatus described elsewhere.[11] The light source was an argon ion laser (Lexel) at 488 nm. The scattered light was observed at 90°. The correlator (Malvern K7023) was controlled by a microcomputer and operated in "intensity-controlled storage mode". This mode of operation is particularly useful when dealing with aggregating samples. Where the scattered intensity increases during the measurement upon the buildup of aggregates, early measurements that are still free of aggregates can be separated. In the same way, submeasurements distorted by dust particles in the scattering volume are eliminated. This is achieved by dividing the measurement into submeasurements of approximately 1-s duration. The averaged intensity during one submeasurement is then used not only to normalize the corresponding contribution to the correlation function but also to select one of four memory groups for its (additive) storage.

Table I

sample no.	1	2	3
deg of labeling[a]	0	1:100 000	1:5 000
cloud point[b] (% acetone)	32.2	33.3	33.8

[a] The ratio of the molar concentration of FITC labels to the molar concentration of monomer in the sample. [b] The acetone content at which the high molecular weight fraction of the polymer precipitated (see Characterization).

Viscosimetry. The viscosity was measured in a Schott AVS-300 apparatus equipped with an KPG Ubbelohde microviscosimeter (diameter of 0.32 mm). Since the viscosity of water–acetone mixtures depends strongly on their composition, precautions were taken to prevent acetone evaporation. For an appropriate acetone vapor pressure to be maintained the openings of the viscosimeter were connected by tubings to a vessel containing a water–acetone mixture corresponding to the measured one. With this setup the reproducibility of the viscosity measurements was better than 0.05%.

Time-Resolved Fluorescence Depolarization. Our monophoton fluorometry apparatus is described elsewhere.[12,13] It is equipped with a reference channel to normalize the two measured time profiles, $I_\parallel$ and $I_\perp$, with a precision better than 0.4%. A pneumatic polarizer changer for quasi-simultaneous measurements of $I_\parallel$ and $I_\perp$ minimizes the effects of fluctuation of the shape of the excitation light pulse. The excitation light source is a thyratron-triggered spark gap (Edinburgh Instruments) operated in N_2 at 4 bars. At this pressure the spectrum of the flash lamp exhibits a broad continuum. The excitation wavelength of 490 nm was chosen with a Jarrel-Ash monochromator, and a Schott OG 515 filter was used to block off the scattered light. The data were evaluated by the standard least-squares reconvolution method.[6] For the elimination of errors due to the wavelength dependence of the response of the detector, the method of relative deconvolution was subsequently used for final evaluation of the measurements.[14]

Preparation of Samples. Stock solutions containing 500 mg/L of the polymer, 0.1 M KI (in order to screen the Coulomb interaction of charged groups, KI was used, despite approximately 20% quenching of fluorescence, because of its good solubility in water–acetone mixtures), 0.01 M Tris buffer at pH 8.5 (to enhance the FITC fluorescence), and 0.1% NaN_3 (to prevent bacterial growth) were prepared as follows:

The polymer was first dissolved in a watery solution of the salts. Then acetone was added until a slight turbidity was observed (around 33% acetone, see Table I), indicating the precipitation of the high molecular weight fraction of the broad molecular weight distribution of the polymer (see section Characterization). The solution was then clarified by filtration through a Millex SR Filter. Samples with polymer concentrations of 50–400 mg/L and acetone contents between 25 and 42% by weight were then prepared by adding an appropriate amount of water or a water–acetone mixture containing 60% acetone (both of course also containing the salts and buffer). Prior to the measurements, all samples were once more filtered through the SR filter (with the exception of viscosity and fluorescence measurements at acetone contents above 38%) and checked for dust and aggregates by visual inspection of small-angle light scattering.

Characterization of the Labeled Polymer

The chemical composition of the samples has been assessed by ^{13}C NMR. Comparison of our data with the

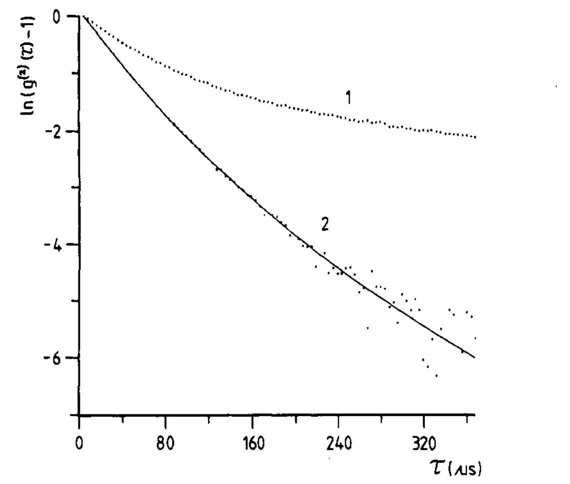

Figure 1. Autocorrelation function of the scattered light intensity at 30% acetone: curve 1, prior to the fractional precipitation; curve 2, a small fraction of high molecular weight particles has been removed by fractional precipitation (see Preparation of Samples). The best fit using three cumulants is also shown.

published spectra[15,16] identifies acrylamide and acrylic acid as major components. The content of vinylamine has been estimated by fluorescamine assay[17] to be approximately 5%. This low degree of conversion is sufficient because the labeling has to be kept low to avoid the influence of intramolecular energy transfer on the fluorescence depolarization. The degree of labeling was determined by comparison of the fluorescence intensity of the samples with the fluorescence intensity of a reference compound, FITC–ethylamine, at known concentration. The results of three samples investigated in this study are shown in Table I. According to HPLC results, the samples did not contain any free unattached dye.

The molecular weights of these samples were estimated from viscosimetry data measured at zero acetone content. The reduced viscosity $(\eta - \eta_0)/(\eta_0 c)$ was found to be constant over the polymer concentration range 50–500 mg/L (this indicates an efficient screening of the Coulomb interaction at the given ionic strength of the solvent). The resulting intrinsic viscosity of 70 cm^3/g does not depend on the degree of labeling.

Because we lack a Mark–Houwink relation for the given copolymer, the molecular weight can only be estimated. The known Mark–Houwink relations for homopolymers of the components at high ionic strength, taken from the comprehensive survey of Molyneux,[18] would yield the following results: poly(acrylamide) $M_w = 1 \times 10^5$–1.5×10^5, poly(acrylic acid) (alkaline solutions, high ionic strength) $M_w = 0.75 \times 10^5$, poly(vinylamine) $M_n = 0.4 \times 10^5$. Apparently, the procedure used for the amide degradation is accompanied by multiple scission of the polymer backbone. The viscosimetric equivalent volumes V_v in following sections were calculated with the lower estimate for poly(acrylamide) $M_w = 1 \times 10^5$.

For all samples quasi-elastic light scattering revealed a highly nonexponential correlation function (see Figure 1, curve 1). It has been satisfactorily fitted by assuming 90% by weight of the polymer sample consists of molecules having a hydrodynamic radius R_L of approximately 6 nm and 10% by weight are particles of $R_L \approx 65$ nm. The high molecular weight fraction has been successfully removed by fractional precipitation described in the previous section (see Figure 1, curve 2). The acetone content at which the precipitation of the large particles occurs depends on the degree of labeling (see Table I). Although the dye content is rather small, it appears to influence significantly the solubility of the polymer in water–acetone mixtures. From the hydrodynamic radius of 6.5 nm (at 33% acetone) the radius of gyration R_g can be estimated (assuming nondraining conditions in the Kirkwood–Riseman model[19]) to be approximately 10 nm. Such a small R_g implies a negligible contribution of the internal motions to the correlation function, and the application of the method of cumulants for the evaluation of the measurements is therefore justified. After the fractional precipitation, the normalized variance μ_2/Γ^2 amounts to 0.2 (three cumulants were necessary to fit the data). The molecular weight distribution is still rather broad, but this fact does not interfere with the objectives of the present study.

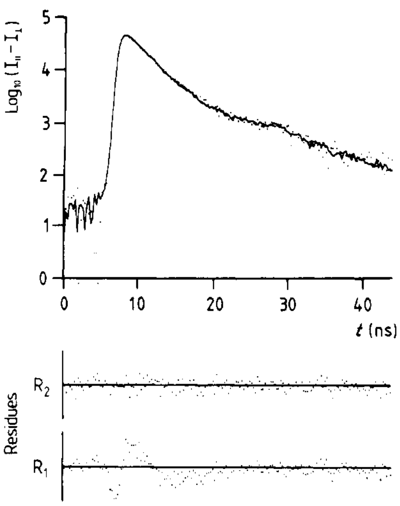

Figure 2. Typical time course of the difference of polarized components $I_\parallel$ and $I_\perp$ of the sample fluorescence. The solid line is the best fit using a double-exponential model of the decay of anisotropy $r(t)$; R_2 are the corresponding residues. For comparison the residues R_1 obtained under the assumption of a single-exponential decay of $r(t)$ are also shown.

Results and Discussion

General Remarks. In the light scattering experiments the polymer concentration was varied between 50 and 400 mg/L. At the lower end of this range the polymer contribution to the light scattering by the solution was only 50% of the solvent background. No concentration dependence of the light scattering data was found (except for an increased tendency toward aggregation during the measurements at higher polymer concentration). The light scattering is particularly sensitive to aggregates. Their formation during the course of a measurement was observed in all samples at acetone concentrations above 36%. The increasing rate of this process limited the highest measurable acetone concentration to 38%. The unlabeled sample 1 and the slightly labeled sample 2 did not exhibit any difference in light scattering data (see Figure 3). The light scattering of the relatively strongly labeled sample 3 could not be measured because the absorption of the laser radiation by the dye molecules caused local heating and thus undesirable convection in the scattering volume.

The viscosity was measured in the polymer concentration range 100–400 mg/L at acetone contents below 30%. In this polymer concentration range the reduced viscosity was found to be constant. The specific viscosity of a 100 mg/L polymer solution at 30% acetone was only 0.0016, a value approaching the reproducibility of the measurements. Therefore, at higher acetone contents, the viscosity was measured only at the polymer concentration 400 mg/L. Viscosimetry is rather insensitive to aggregates, allowing measurements up to an acetone content of 40% (to prevent the loss of polymer material, the samples above

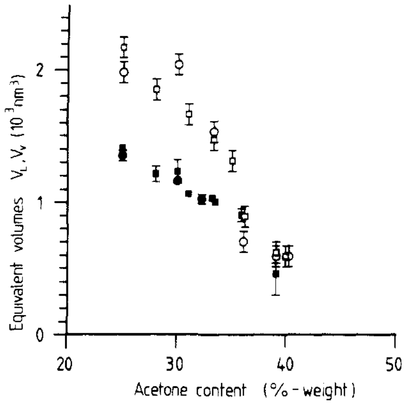

Figure 3. Dependence of the equivalent volumes V_L (from light scattering, solid symbols) and V_v (from viscosimetry, open symbols) on the acetone content. Both equivalent volumes decrease sharply with increasing acetone content, indicating the collapse of the polymer molecules in poor solvent (circles, sample 1; squares, sample 2).

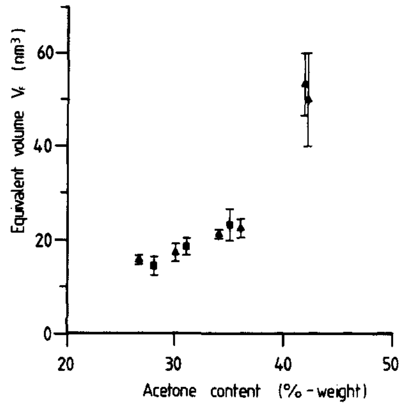

Figure 4. Dependence of the equivalent volume V_F (from the time-resolved fluorescence depolarization) on the acetone content showing the variation of the local mobility (squares, sample 2; triangles, sample 3).

36% acetone were used without filtering). As in the case of light scattering, the results were found not to depend on the degree of labeling (see Figure 3).

The measurements of fluorescence depolarization were carried out at a polymer concentration of 400 mg/L throughout. With the slightly labeled sample 2, this polymer concentration corresponds to only 10^{-7} M concentration of the dye. The unlabeled sample 1 was found to contain traces of fluorescent impurities (despite the thorough purification). Therefore the corresponding (properly normalized) blanks were subtracted prior to the evaluation of the slightly labeled sample 2. The fluorescence depolarization measures the local mobility and is thus insensitive to aggregation (except for the loss of signal due to the precipitation of polymer). The measurements were therefore possible up to an acetone content of 42% (without filtering).

A common feature of all measurements was a non-single-exponential decay of the anisotropy $r(t)$, whereas the fluorescence decays as a single exponential ($\tau_f = 3.6$ ns). As shown in Figure 2, an attempt to apply a single-exponential model for $r(t)$ to fit the measured difference $I_{\parallel}(t) - I_{\perp}(t)$ results in a nonrandom distribution of the residues (residues R_1 in Figure 2). Good-quality fits were obtained with a double-exponential model including a fast relaxation time τ_{rf} ($\approx$0.53 ns) and a slow relaxation time τ_{rs} ($\approx$7.5 ns) (residues R_1 in Figure 2). The corresponding preexponential factors were found to be in a ratio of 1:1 over the whole measured concentration range. The initial anisotropy $r(0)$ amounted to 0.31 ± 0.02, a value that is smaller than the theoretical maximum of 0.4. With the relative deconvolution such a two-exponential model for $r(t)$ implies a simultaneous estimation of five parameters. To improve the accuracy of the parameter estimation, in a second pass of the evaluation the number of free parameter was reduced to three based on the following observations: Both the fluorescence lifetime τ_f and the fast anisotropy relaxation time τ_{rf} do not show any trend with the acetone content. In the second evaluation pass, they were therefore fixed at their average values.

The interpretation of the fast relaxation time τ_{rf} is somewhat intriguing: Its value corresponds roughly to the rotational relaxation of the free label. The presence of the free dye, however, has been ruled out (see Characterization). The nonradiative energy transfer between two labels on the same polymer molecule has been estimated to be negligible at the given degree of labeling. Moreover, τ_{rf} does not depend on the viscosity of the solutions. It is therefore unlikely that it reflects the mobility of the polymer backbone, and we confine the following discussions to the slow relaxation time τ_{rs}. The equivalent volume V_f can in principle be calculated from the time average of $r(t)$. Because of the presence of the fast relaxation component τ_{rf}, such a V_f would be much lower than those shown in Figure 4, approaching the values obtained from ref 8.

Polymer Configuration and Mobility as a Function of Solvent Quality. The dependence of the light scattering equivalent volume V_l and of the viscosimetric equivalent volume V_v on the acetone content is shown in Figure 3. Both V_L and V_v decrease sharply with the increasing acetone content, reflecting clearly the transition from the extended coil state in a good solvent to a compact state in a poor solvent at high acetone content. The viscosimetric volume V_v is larger than V_L, in accordance with the prediction of Kirkwood–Riseman.[19] In the course of collapse, the density of a polymer molecule changes from 0.08 g/cm^3 at 25% acetone to 0.3 g/cm^3 at 40% acetone (these values are obtained when interpreting $^5/_2[\eta]^{-1}$ as a viscosimetric effective density of the polymer). It is interesting to note the density in the collapsed state is equal to the density of (neutral) macroscopic poly(acrylamide) gels at the same acetone concentration.[20]

The equivalent volume V_F (from fluorescence depolarization), being a measure of the local mobility of the backbone, is 2 orders of magnitude smaller than V_L or V_v (Figure 4) but considerably larger than the rotational equivalent volume of the free label (V_F(free) = 1.3 nm^3). In contrast to V_L and V_v, the equivalent volume V_F increases with the acetone content in the range between 25% and 36% acetone, indicating decrease in the local mobility. In qualitative terms this behavior is understandable. Even if the bending modulus of the chain remains unchanged, one expects a slow down of the reorientational motions of the (rather bulky) label due to internal friction in the increasingly denser polymer. The extent of the change, however, is somewhat small. Between 25% and 36% acetone the density of a polymer molecule increases by a factor of 2.6 whereas the local mobility decreases only by a factor of 1.5. Surprisingly, these numbers are in agreement with the results of Viovy and Monnerie[21] obtained on a rather different system, a labeled polystyrene in polystyrene solutions of an overall concentration comparable to our local density of the polymer.

In a previous study on poly(ethylene glycol) labeled with FITC[13] we have been able to interpret quantitatively the results of time-dependent fluorescence depolarization in terms of a "hinged dumbbell" model. Within this model the label is represented as the smaller sphere of the dumbbell and the polymer coil as the larger one. The length of the dumbbell arm adjacent to the label is the sum of two contributions, d_0, describing the structure of the label, and a reorientational persistence length, p, which describes the section of the backbone participating in the reorientation of the label. The latter can be expected to be closely related to the length of Kuhn's equivalent segment of the polymer (p_K).

We now apply this model to demonstrate the consistency of the measurement of the local mobility (fluorescence depolarization) with the measurement of the polymer configuration (light scattering): In the present case the polymer is much larger than the label and its overall rotational mobility can be neglected. The rotational friction constant f of the attached label can be calculated (lever rule) to be

$$6\eta V_F \equiv f = 6\eta[\pi a(p + d_0)^2 + (4\pi/3)a^3] \qquad (6)$$

where $(4\pi/3)\cdot a^3 = V_F$(free) is the equivalent rotational volume of the free label. The equivalent volumes V_F and V_F(free) are measured by time-resolved fluorescence depolarization and the parameter d_0 of FITC is known.[13] The persistence length p can thus be estimated by eq 6 to be 2 nm. An independent estimate of the length of the equivalent segment p_K can be obtained from light scattering data. It can be calculated from the radius of gyration R_G of the polymer in a θ solvent. Assuming this condition is fulfilled somewhere between 25% and 35% acetone (R_L = 7.3–6 nm) and estimating thus R_G to 11–9 nm (using $R_L = 0.67R_G$[19]), we obtain p_K = 2–1.4 nm. This value is in good agreement with the estimate from the fluorescence depolarization.

Combining the information from three independent methods, we have obtained a consistent picture of the polymer collapse in a poor solvent. The global mobility measured by dynamic light scattering and viscosimetry increase during the course of the transition into the compact state, while the local mobility of the backbone, as probed by the time-resolved fluorescence depolarization, decreases due to an increase of the internal friction.

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Notes

Lattice Parameters and Packing Energies for Helical Polyacetylene

MARK L. ELERT*

Chemistry Department, U. S. Naval Academy, Annapolis, Maryland 21402

C. T. WHITE

Code 6129, Naval Research Laboratory, Washington, D.C. 20375. *Received August 15, 1986*

In 1983 Bates and Baker reported[1] the preparation of single crystals of polyacetylene (PA) from a solution of a polyacetylene–polystyrene block copolymer. Electron diffraction and X-ray analysis of the resulting PA crystals showed a hexagonal unit cell markedly different from the orthorhombic crystal structure of PA prepared by the usual Shirakawa technique.[2] To account for their data, Bates and Baker proposed that the PA chains prepared by their technique had crystallized in a helical conformation.

The existence of a helical isomer of polyacetylene is surprising, since conjugation of the π system is expected to favor a planar structure. Furthermore, the IR spectrum reported by Bates and Baker[1] appears to be a superposition of the spectra of polystyrene and planar *cis*-polyacetylene, whereas a recent calculation by Božovič, Rakovič, and Gribov[3] shows that the IR spectra of helical and planar PA are expected to differ significantly. Because of the uncertainty in the experimental evidence in favor of the existence of helical PA, a number of theoretical investigations have been carried out during the past few years to elucidate the structure and stability of the proposed helical conformation.

We have previously reported[4,5] semiempirical MNDO calculations that indicate that planar *cis*-PA may indeed be unstable toward helix formation, with a unit cell length in the helix axis direction close to that reported by Bates