

Solution characterization of surfactant solubilized polyaniline

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Abstract

Solutions of polyaniline (PANI) doped with camphor sulfonic acid (CSA) in *m*-cresol are studied with dynamic light scattering. Dynamic light scattering measurements performed on dilute solutions ($c \ll c^*$) show that, while some aggregation is present, PANI–CSA exists as single chains in solution at low concentrations (about 10^{-4} – 10^{-6}) in *m*-cresol. The conformation of the polymer chains was studied as a function of polymer and added salt concentration. We find that the polymers extend as the polymer concentration is lowered and that the increase in the hydrodynamic radius can be expressed by a power law of the electrostatic screening length. This behavior is typical of polyelectrolytes in dilute solution, providing a basis for understanding the conformation changes of this metallic polymer in solution.

Keywords: Surfactant; Polyaniline; Light scattering

1. Introduction

Polyaniline (PANI) was first synthesized in 1862 [1] and its properties as a conducting polymer have been extensively studied [2,3]. Fig. 1 summarizes the repeat unit for the various forms: the three insulating forms, leucoemeraldine base, emeraldine base and pernigraniline base, and the metallic emeraldine salt form. Leucoemeraldine has a bandgap of nearly 4 eV and the other two insulators have bandgaps on the order of 2 eV.

Scientific interest in PANI originates from the fact this conjugated polymer can be doped either by charge transfer or by the acid/base (protonation) reaction that converts the semiconducting emeraldine base form to the conducting emeraldine salt. The excellent environmental and thermal stability in the conducting form and the potential for relatively low cost make PANI an attractive material for applications in batteries [4], light-emitting diodes [5], and anti-static packaging and coatings [6].

Historically, PANI has been considered an intractable material; it decomposes before melting and is insoluble in common solvents. In recent years, however, three solvents have been reported to dissolve PANI: *N*-methylpyrrolidinone (NMP) [7], specific amines [8] and concentrated acids [9,10]. In both NMP and amine-based solvents, the polymer

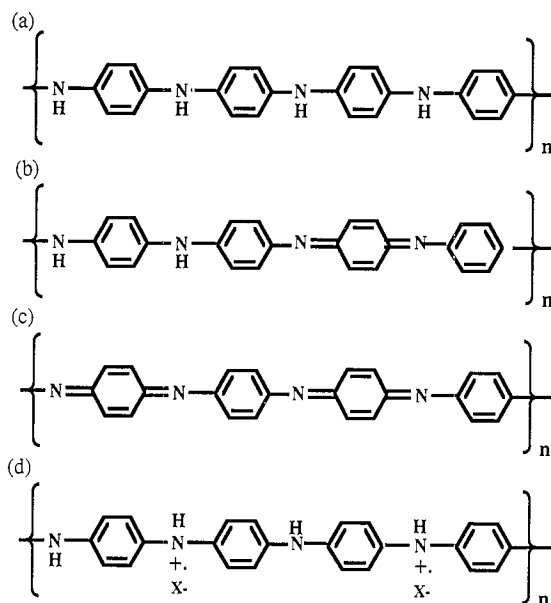


Fig. 1. Four forms of PANI: (a) leucoemeraldine base, (b) emeraldine base, (c) pernigraniline base, and (d) metallic emeraldine salt.

is dissolved and subsequently cast from solution in its blue emeraldine base form. Consequently, films, fibers and blends processed from these solvents must be doped to form the conducting emeraldine salt form. The polymer can be processed directly in the metallic form from acids to make conducting fibers, films and polyblends. Processing from strong

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acids, however, presents obvious difficulties. Moreover, such acids generally cause degradation of commercial bulk polymers and, thus, limits opportunities for blending PANI to improve its material properties.

Recently, Cao et al. [11,12] have shown that PANI can be solubilized in a number of common organic solvents in the metallic emeraldine salt form by the addition of protonic surfactants such as camphor sulfonic acid (CSA) and dodecyl-benzene-sulfonic acid (DBSA). In these systems, the acid from the surfactant dopes the polymer, converting it into a polyelectrolyte. The charged (SO_3^-) head group of the surfactant associates with the positively charged backbone through Coulomb attraction, providing a solubilizing side chain compatible with organic solvents such as *m*-cresol, chloroform, dimethylsulfoxide, toluene and xylene. In addition to the improvement in the processing of PANI films, the counter-ion-induced solubility has also enabled the fabrication of low surface resistance transparent electrodes [12] for flexible devices [5] and for the fabrication of conducting polyblends [13] with a variety of bulk polymers.

Because PANI has only recently been shown to be soluble, very little is known about molecular weights, structure and solution properties of this polymer in its various solvents. One of the problems in studying the solution properties of PANI is its intense absorption in the visible which limits the use of light scattering to obtain molecular weight information and solution quality. What is predominantly known about PANI solutions has been obtained with gel permeation chromatography (GPC). Molecular weights ranging from 9000 to 200 000 g/mol have been reported for the emeraldine base form of PANI in NMP using polystyrene as the standard [14–18]. In addition, these measurements show the existence of large molecular weight structures in these solutions which are reduced when LiCl is added to the solution [19]. This observation indicates that the polymer is aggregated in this solvent and that the aggregation can be reduced when LiCl is added to the solution. Because the conformation of the polymer in these solvents is not known, GPC measurements give only relative and not absolute information about sizes and molecular weights in the same solvent.

Intrinsic viscosity measurements of PANI in H_2SO_4 have also been employed to make molecular weight estimates [9,20]. In these experiments, Mark–Houwink coefficients for Kevlar/ H_2SO_4 (rigid rod) and Nylon-6/ H_2SO_4 (flexible coil) are applied to inherent viscosity values of PANI samples to give molecular weights in the limit of the two extreme polymer conformations. While this technique provides an adequate means of characterizing PANI samples with respect to one another, the lack of knowledge of the conformation of PANI in solution limits its use as a method of determining absolute molecular weights.

Because of its charged backbone and the surfactant character of its side chains, we expect surfactant solubilized PANI in the emeraldine salt form to behave very differently in solution compared to the emeraldine base and other soluble conjugated polymers. The properties of solutions of poly-

electrolytes are considerably different from those of neutral polymers since segmental correlations are governed by electrostatic interactions. As a polyelectrolyte, the properties of PANI can be expected to depend critically on the concentration of counter-ions in solution, the dielectric constant of the solvent and the presence of any added electrolytes in the solution.

Scattering studies on dilute solutions of polyelectrolytes without added salt have demonstrated that the polymer chains expand with decreasing polymer concentration. This expansion of the polymer chain is due to decreased screening of the charge along the backbone when the concentration of counter-ions in solution is reduced. The expansion of the polymer chain with decreasing ionic strength has been addressed in a theoretical model by Odijk [21] and by Skolnick and Fixman [22]. In this theory, the persistence length of the polymer l_p is the sum of two contributions: an intrinsic persistence length l_0 and an electrostatic persistence length l_e . The Odijk theory predicts the total persistence length to scale with the square of the electrostatic screening length λ_c^2 and, therefore, inversely proportional to the concentration of ions in solution, I . Experimental results on a variety of polyelectrolytes show that the Odijk model describes the expansion of rigid polymers like DNA, but not that of flexible polymers such as polystyrene sulfonate. Experimentally, these flexible polymers have been shown to scale as $I^{-1/2}$ [23,24]. Recently, a new model has been developed by Barrat and Joanny [25] which predicts the scaling of l_p in the limit of intrinsically flexible and/or weakly charged polymers as $I^{-1/2}$. Clearly, one could measure the scaling of the polymer size with decreasing ionic strength and, depending on which power law is observed, obtain information on the intrinsic rigidity of the polymer backbone.

Solutions of polyelectrolytes and oppositely charged surfactants have also been extensively studied [26–32]. Fluorescence probe, light scattering and electrochemical binding measurements of these systems in water show complicated phase diagrams with inter- and intra-polymer associations and phase separation. The overall picture that has emerged from these efforts is that the surfactant molecules absorb to the polymer in micelle-like structures in what is known as a ‘pearl-necklace’ structure. The binding of the surfactant molecules to the polymer backbone occurs at a well-defined surfactant concentration and this concentration is well below the critical micelle concentration (CMC) measured in the absence of polymer. Phase separation is observed to take place at a surfactant molar concentration approximately equal to the number of charges on the polymer and this phase separation can be reversed if salt or more surfactant is added. Factors which have been shown to determine the solution properties of these systems are linear charge density of the polymer, micelle surface charge density and ionic strength of the solution.

Despite these efforts, a clear picture of the pearl-necklace structure in polyelectrolyte–surfactant solutions has not emerged. Three structures have been proposed [30]: a col-

lapsed chain due to the neutralization of the polymer charges by the micelles, an expanded chain due to repulsive forces between the micelles and a multi-polymer complex. Scattering measurements on low polymer concentration/high micelle surface charge density indicate that the chains exist as extended structures [30] until the polymer is saturated with micelles; at higher surfactant concentrations, the chains collapse because of screening from the ions in solution.

It is not clear that the previous work on polyelectrolyte-surfactant solutions will give insights into the solution properties of PANI-CSA. One factor which distinguishes this system from other polyelectrolyte-surfactant solutions is the insolubility of the polymer prior to addition of the surfactant. This characteristic would suggest that polymer-solvent interactions are important in considering the binding of the surfactant to the polymer chain. The use of non-aqueous solvents is another feature that makes the PANI systems different from those previously studied. In organic solvents, surfactants form smaller inverted micelles at significantly lower concentrations [33,34]. The insolubility of the polymer combined with the charged backbone would suggest a picture in which the surfactant molecules are individually bound to ionic sites on the backbone in order to shield more effectively the polymer from the solvent.

We report results of dynamic light scattering studies of PANI-CSA in *m*-cresol. We are specifically interested in this system because PANI films processed from this solvent-surfactant combination show relatively high conductivities (200–400 S/cm) compared to that for doped powders or films processed from other solvents (typically 1 S/cm). Recent absorption and X-ray diffraction measurements on PANI films processed from various solvent-surfactant systems show that highly conductive films have different crystal structures and absorption spectra that are distinctly different from low conductivity films. These observations imply a strong correlation between the solution properties and the final solid state properties. Therefore, it is important to understand the factors which affect the chain conformation in solution and solution quality in order to obtain optimal solid state properties.

Dynamic light scattering results on dilute solutions of PANI-CSA in *m*-cresol show that, while there exists some aggregation, PANI-CSA in this solvent is a true molecular solution with the polymer existing as single chains. Concentration dependence measurements show that the polymer radius increases with decreasing polymer-surfactant complex concentration. This behavior is typical of dilute solutions of polyelectrolytes. As a polyelectrolyte, factors which will affect the chain conformation and solution quality are the dielectric constant of the solvent and overall ionic strength of the solution.

We have also studied the effects of water on the solution properties of this system. We find that adding water to pre-dried PANI-CSA/*m*-cresol solutions causes the polymer to coil, but the effect is weak; the polymer radius is reduced only by a factor of approximately two for a water/aniline

ratio of 1000. This reduction in radius is probably caused by the additional water reducing the solvent quality of *m*-cresol for PANI-CSA. In contrast, solutions made from samples that were not pre-dried were significantly less soluble and exhibited both increased aggregation and gelation. These results demonstrate that, to obtain true molecular solutions, it is crucial to remove all residual water from the PANI prior to dissolving it in *m*-cresol. Moreover, while it is not crucial, it is also important to keep water out of the *m*-cresol.

2. Experimental

2.1. Polymer synthesis and solution preparation

PANI was prepared by polymerization in aqueous HCl media, initiated by ammonium persulfate as described by Cao et al. [10]. The resulting product was converted to the emeraldine base form by washing with 3% ammonium hydroxide for 2 h. The polymer was subsequently washed with water, methanol and acetone, and dried at 50 °C for 24 h. Relative molecular weights of the polymer samples were determined by intrinsic viscosity measurements in H₂SO₄. Our experiments were performed on polymer samples with inherent viscosities of 1.2 and 0.69 dl/g.

All chemicals were purchased from Aldrich Chemical Company. PANI and the surfactant, CSA, were dried in a vacuum oven at 50 °C for at least 24 h and stored under nitrogen prior to use. *m*-Cresol used in the light scattering experiments was distilled under nitrogen in order to remove water and any other contaminants. This step yielded great improvements in the polymer solubility and resulting sample quality.

Stock solutions of polymer in *m*-cresol (0.1%) for light scattering measurements were prepared by mixing PANI and CSA in a nitrogen atmosphere at a 1.0 CSA/aniline mole ratio and sonicating for approximately 5 h. These solutions were filtered through 0.5 and 0.2 μm PTFE (Millipore) filters and the final concentrations of the stock solutions were determined with a combination of thermogravimetric analysis (TGA) and absorption measurements. Individual samples were made by diluting the stock solution with filtered *m*-cresol. The resulting dilute PANI-CSA solutions were stable over time, displaying the same correlation function weeks after initial measurements.

2.2. Light scattering measurements

2.2.1. Dynamic light scattering

Dynamic light scattering measurements were performed using a Brookhaven goniometer, an ALV-5000 correlator and a Krypton ion laser operating at a wavelength of 530.9 nm. This wavelength was chosen because it is near the minimum of the absorption for the solution. All samples were centrifuged at low speeds to reduce scattering from dust particles.

Dynamic light scattering (DLS) probes molecular and particle motion by measuring the temporal fluctuations of the scattered light intensity [35]. In DLS, these fluctuations are characterized by the temporal autocorrelation function of the scattered intensity:

$$g_2(t) \equiv \langle I(t)I(0) \rangle / \langle I \rangle^2 \quad (1)$$

The intensity autocorrelation function $g_2(t)$ is related to the electric-field autocorrelation function $g_1(t)$ by the Siegert relation:

$$g_2(t) = 1 + \beta |g_1(t)|^2 \quad (2)$$

where β is a constant determined primarily by the collection optics. If fluctuations of the scattered intensity are caused by molecular diffusion, then the correlation functions decays exponentially as $g_1(t) = \exp(-\Gamma t)$, where the relaxation rate is given by $\Gamma = Dq^2$, D is the diffusion coefficient, and q is the scattering vector. In our samples, two relaxation rates were frequently measured. We attributed the faster relaxation rate to single-chain polymer diffusion and the slower relaxation rate to large particles or aggregates convecting through the laser beam. We found that a fit consisting of a sum of a fast exponential decay and a slower Gaussian decay well represented our data. The slower Gaussian decay is consistent with particles convecting through the laser beam and was found to scale with the laser beam diameter, as expected for convection.

2.2.2. Static light scattering

In general, polymer solutions are studied with combination of static and dynamic light scattering measurements. In static light scattering, the excess scattering of the polymer over the solvent as a function of angle is measured. From these data, the radius of gyration R_G can, in principle, be obtained. There are several factors specific to the solutions of PANI-CSA in *m*-cresol used in our experiments which made static light scattering very difficult. In order to ensure that our measurements observed single-chain behavior and to minimize the effects of absorption, experiments must be performed on solutions with very low concentrations of polymer. Because *m*-cresol is a strongly scattering solvent, the excess scattering from PANI is a small fraction of the total static scattering at these low concentrations. Moreover, PANI absorbs light throughout the visible spectrum. In order to determine the excess scattering due to the polymer, one must be able to correct very accurately for this absorption. To minimize the effects of absorption, our scattering measurements were performed using a green laser because this wavelength coincided with the minimum in the absorption spectrum for PANI-CSA. Nevertheless, even at this wavelength, there was significant attenuation of both the incident and scattered light. As a consequence of the weak scattering and strong absorption of the polymer, the excess scattering intensity obtained after correcting for absorption was frequently negative, clearly an unphysical result. These factors made obtaining

quantitative static light scattering data from our samples impossible.

3. Results and discussion

In Fig. 2, we show a typical measurement of $g_1(t)$ for PANI-CSA in *m*-cresol. The data show two distinct relaxation rates in the correlation function; the faster relaxation rate decays exponentially with a decay constant of $\Gamma = Dq^2$ indicative of simple diffusive behavior, whereas the slower component decays more rapidly and is Gaussian ($\exp(-\nu t^2)$). As discussed in the previous section, it is the faster exponential decay which characterizes the single-chain diffusion.

A simple and useful way to characterize the light scattering data is to extract a hydrodynamic radius R_H from the measured diffusion coefficient D using the Einstein–Stokes relation:

$$R_H = k_B T / 6\pi\eta_0 D \quad (3)$$

where k_B is Boltzmann's constant, T is the absolute temperature and η_0 is the solvent viscosity. Obtaining a radius in this manner implicitly assumes that the polymer conformation is that of a random coil. Nevertheless, Eq. (3) can still provide a useful measure of polymer dimensions in solution even if the polymer takes on radically different configurations. For example, rigid rods obey a similar Einstein–Stokes [36] law but with a logarithmic correction involving the aspect ratio of the rod. In this case, the hydrodynamic radius obtained from Eq. (3) is related to the length L and diameter d of the rod through

$$R_H \sim \frac{L}{2 \ln(L/d)} \quad (4)$$

3.1. Effect of water

One of the major difficulties in our experiments has been obtaining good sample quality and long-term stability. We

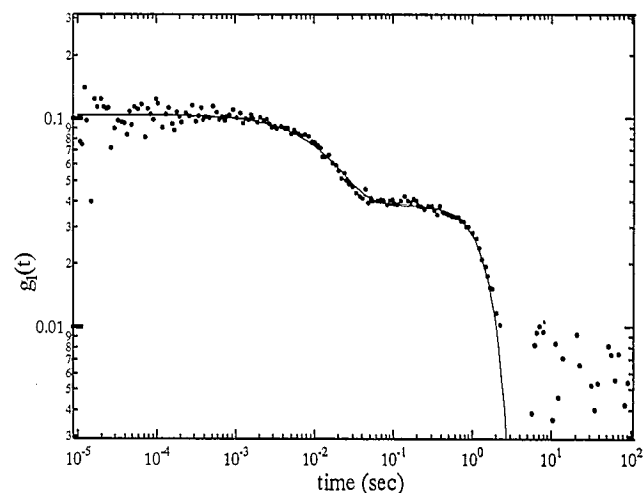


Fig. 2. Typical correlation function $g_1(t)$ obtained for PANI-CSA in *m*-cresol.

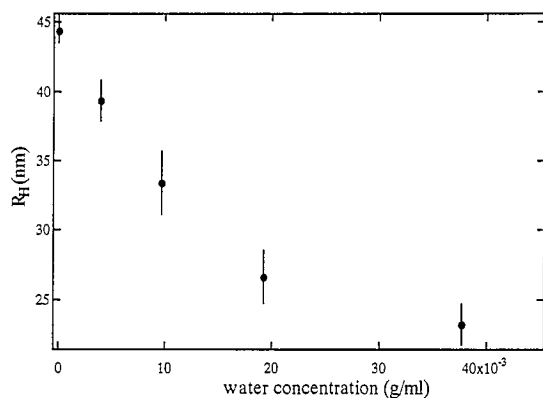


Fig. 3. R_H of PANI-CSA in *m*-cresol as a function of water concentration with PANI concentration 1.96×10^{-5} g/ml.

have prepared samples under a variety of conditions including different concentrations of original stock solution, polymer/surfactant ratio, solvents and atmospheres (air or nitrogen). The most determining factor in preparing true molecular solutions of PANI-CSA has been absence of water in the solution constituents when making the original solutions. Both PANI and CSA are very hygroscopic, and the presence of water in the compounds or solvent prior to making solutions reduces the solubility of the complex and increases the amount of aggregation in the solutions. Cao [37] has measured a reduction in the solubility of PANI-DBSA in xylene from 12 to 0% with the addition of 2.5 wt.% water. Our light scattering measurements on samples which were not completely dried or which had different degrees of water content prior to making the complex show many different sizes upon dilution and had an increased number of large aggregates in solution. In addition, these samples were not stable over time; the aggregation increased and, in some cases, gelation occurred.

Fig. 3 shows a plot of R_H versus water concentration for a 1.96×10^{-5} g/ml PANI sample that has been doped in a 1:1 mole ratio of CSA/aniline in *m*-cresol for water concentrations of $0-4 \times 10^{-3}$ g/ml. In these experiments, PANI was thoroughly dried before being dissolved in *m*-cresol to which known amounts of water had been added. With the addition of water, we observe a steady decrease in the hydrodynamic radius of the polymer, indicating that the chains are coiling up on themselves. This behavior is typical of polymers in a solvent whose thermodynamic quality is reduced by adding increasing amounts of a poor solvent.

TGA measurements on PANI show that the polymer absorbs approximately 7–10 wt.% water upon prolonged exposure to air. This corresponds to roughly 0.4–0.6 water per aniline repeat unit. In our experiments, we did not observe any measurable effect on the size of the polymer radius until considerably higher water/aniline fractions (about 1000); even at these concentrations the size of the radius was reduced only by a factor of two. This observation indicates that the overall effect of water is diluted by the solvent. Because we observed such varying degrees of sample quality from polymers which contained water prior to being dissolved in solution and did not in solutions to which water was added, we

have concluded that the most significant procedure in preparing true molecular solutions is the removal of water from the polymer and surfactant before they are dissolved.

3.2. Concentration dependence of PANI-CSA in *m*-cresol

In Fig. 4 plots of R_H versus PANI concentration obtained from dynamic light scattering measurements are shown for PANI samples with two different average molecular weights, one having an intrinsic viscosity of 1.2 and the other of 0.69 dl/g in H_2SO_4 . As expected, the sample with the lower intrinsic viscosity exhibits smaller hydrodynamic radii at comparable concentrations, consistent with the lower molecular weight. In the concentration range of about 10^{-4} to 10^{-6} g/ml of polymer, the hydrodynamic radii of both samples increase with decreasing polymer concentration. This extension of the polymer chain with decreasing polymer concentration is a classic signature of a polyelectrolyte in dilute solution and occurs because of the reduction in the concentration of ions in solution (ionic strength) as the overall concentration of polymer is decreased. This reduction in ionic strength reduces screening of the charges along the backbone of the polymer. As the screening decreases, the charges along the backbone repel each other more strongly, and the polymer extends.

We can use the results from our light scattering measurements to obtain estimates of the weight average molecular weight of these polymers. The polymer radius R scales with the degree of polymerization N as

$$R \sim (\lambda a) (N/\lambda)^\nu \quad (5)$$

where a is the distance between monomers, λa is the persistence length l_p of the polymer, N/λ is the number of persistence lengths in a polymer chain and ν is either 0.5 or 0.6 depending on whether the solvent is a theta solvent or good solvent. If we assume that PANI at these concentrations in *m*-cresol is a random coil, an estimate of the molecular weight can be obtained. To this end, we assume the polymer at the highest concentration measured to be the most coiled, and we assume that in this case $\lambda = 1$; at lower concentrations the

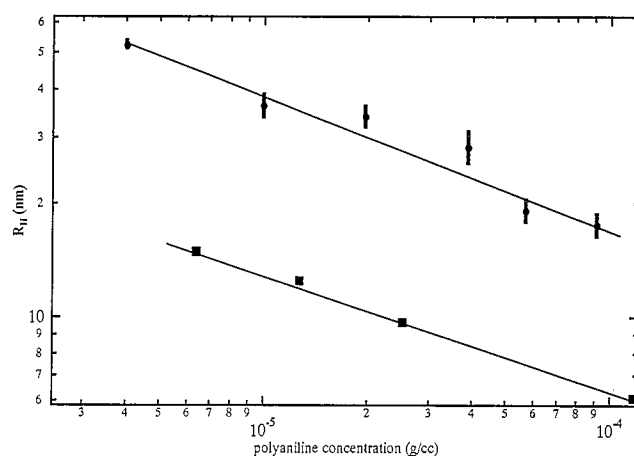


Fig. 4. R_H vs. PANI concentration for PANI-CSA in *m*-cresol with $[\eta] = 1.2$ (●) and $[\eta] = 0.69$ dl/g (■).

polymer is stiffer and, in general, λ will be greater than unity. Thus, taking $a = 0.507$ nm, $\lambda = 1$ ($l_p = 0.507$ nm), assuming good solvent conditions, and taking the smallest radius we measured for our $[\eta] = 1.2$ dl/g sample (17 nm), the number of monomers is given by the scaling relation $N = (R_H/a)^{5/3} = 365$ or a weight average molecular weight of $M_w = 33\,000$ g/mol. With the assumption that $\lambda = 1$ for our highest concentration, a self-consistent application of the scaling relation Eq. (5) requires that $\lambda = 18$ or $l_p = 9.1$ nm for our lowest concentration.

To get a sense of the range of molecular weight possibilities permitted by these data, we repeat the above estimate but now assume that $\lambda = 3$ ($l_p = 1.5$ nm) for the smallest radius of the $[\eta] = 1.2$ dl/g sample. The scaling relation now gives $N = 168$ or $M_w = 15\,000$ g/mol. Once again, a self-consistent application of the scaling relation gives $\lambda = 54$ or $l_p = 27$ nm for our lowest concentration of $[\eta] = 1.2$ dl/g sample. Note that a value $l_p = 27$ nm for the lowest concentration sample corresponds to a persistence length that is half of the measured hydrodynamic radius. Thus, the polymer is already quite stiff at this concentration and is beginning to approach a rather rod-like configuration.

Another alternative is to assume that the polymers are rigid rods in the lowest concentration solutions. The light scattering data, however, put some important constraints on this type of model. For sufficiently long rigid-rod polymers ($qL \approx 4\text{--}5$ [38]), the exponential part of the decay of the measured temporal autocorrelation function will exhibit the effects of the rotational diffusion of the polymer. In this case, the exponential decay rate cited previously becomes

$$\Gamma = Dq^2 + 6D_r \quad (6)$$

where D and D_r are the translational and rotational diffusion coefficients, respectively. Rotational diffusion is observed as an additional q -independent part to the decay of the correlation function. For our measurements, we always found $\Gamma \propto q^2$ with no detectable offset corresponding to rotational diffusion. Because we do not measure a rotational diffusion contribution to the decay functions, we can place an upper limit on the length of the polymer if it were to have a rigid conformation. If we make a conservative assumption that rotation diffusion coefficients can be detected for $qL \geq 5$, we conclude that the $L < 170$ nm for the samples exhibiting the largest value of R_H , i.e., at the lowest concentrations. By substituting this value of L into Eq. (4), we obtain a value of $R_H \approx 14$ nm. However, we have measured a value $R_H = 54$ nm at our lowest concentrations. Because of the discrepancy between these two values and the conservative nature of our estimates, we conclude that, even at the lowest concentrations measured, PANI is far from being fully extended.

Since the scaling equation for the polymer radius is known to work quite well for polymers of only a few persistence lengths, we conclude that Eq. (5) provides an adequate model for PANI-CSA in *m*-cresol and that the molecular weights of the two samples lie between 15 000 and 33 000 for the

higher molecular weight sample and between 3000 and 7000 for the lower molecular weight sample.

Recently, there has been a great deal of interest in the ionic strength dependence of the conformation of polyelectrolytes in dilute solution. As previously discussed, two classes of models have had some success in describing experiments, the models for intrinsically rigid polymers of Odijk, Fixman and Skolnick, and the models for intrinsically flexible polymers of Barrat, Joanny and others. To compare our results to these models and make an estimate with regard to the intrinsic rigidity of PANI in its emeraldine salt form, we examine how the size of the polymer radius depends on polymer concentration.

The Odijk theory predicts that the electrostatic contribution to the persistence length of a polyelectrolyte chain should scale as the square of the Debye screening length as κ^{-2} where κ is defined as

$$\kappa = (4\pi l_B I)^{1/2} \quad (7)$$

In the above expression, l_B is the Bjerrum length and is equal to 4.9 nm in *m*-cresol. Since $\kappa \sim I^{1/2}$, the polymer radius should scale as $I^{-1/2}$ in a theta solvent. In contrast, the Barrat and Joanny model predicts that the electrostatic contribution to the persistence length should scale linearly with the Debye screening length as κ^{-1} . Thus, the polymer radius should scale as $I^{-1/4}$.

In order to calculate the ionic strengths of our solutions, we have taken into account the fact that *m*-cresol has only a moderate dielectric constant ($\epsilon = 11.8$). A result of dissolving a polyelectrolyte into a moderately polar solvent is that not all of the charges on the polymer backbone are ionized in solution but exist as ion pairs with their counter-ions. Because of this, the number of free screening ions in solution is reduced. A quantitative method used to account for the reduction of counter-ions in solution is Manning condensation theory [39]. In this theory, the smallest distance between charges on the backbone of the polymer is the Bjerrum length l_B . At this charge separation, the electrostatic energy is equal to $k_B T$. In systems in which the distance between charges on the chain is less than l_B , counter-ions 'condense' on the chain and neutralize enough charges so that the average distance between charges becomes l_B . The fraction of free charges remaining on the polymer chain after condensation is just the ratio of the distance between the charges A and l_B . For our system, A is approximately 1 nm (two monomer units) so that the average fraction of ionized charges on each PANI chain is approximately 20%. With this condensation, the number of free screening ions in solution is reduced by $0.80N$ where N is the number of PANI monomers. While the occurrence of Manning condensation will not change the scaling of the polymer expansion with ionic strength, this calculation does indicate that with only 20% of its charge ionized, PANI is fairly weakly charged.

For the two molecular weight samples of PANI-CSA that we have measured, we observe power law exponents intermediate between the two models: 0.34 for the higher molec-

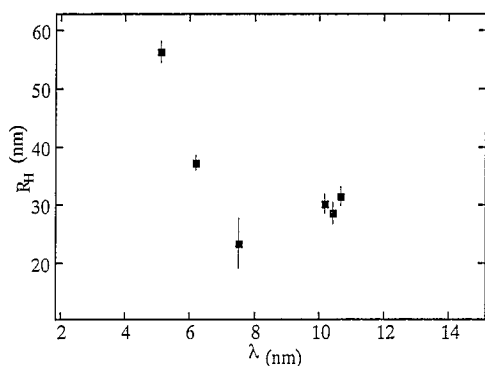


Fig. 5. R_H vs. λ for PANI-CSA with PANI concentration $c = 1.96 \times 10^{-5}$ g/ml in *m*-cresol with added LiCl.

ular weight sample and 0.31 for the lower molecular weight sample. The observation that the radius of PANI scales intermediate between values predicted for intrinsically flexible and rigid polymers is not surprising. Experimental results on polyelectrolytes with varying degrees of intrinsic rigidity show that only DNA and other similar biological molecules with very stiff backbones strictly scale with the Odijk prediction. Moreover, few if any intrinsically flexible polymer systems exist which conform to the various constraints on the length scales in the Barrat–Joanny model (e.g. l_B , electrostatic screening length, and intrinsic persistence length). Thus, the behavior of the vast majority of polyelectrolytes falls in an intermediate regime which cannot be described by any currently available theory.

3.3. Effect of screening salt

We have also investigated the effects of added salt (LiCl) and excess CSA on the conformation of the polymer chain. Fig. 5 shows R_H versus screening length for $[\eta] = 1.2$ dl/g 1:1 mole ratio PANI-CSA sample to which LiCl has been added. The electrostatic screening lengths were calculated under the assumption that the added salt is completely dissociated in the solvent. The data in Fig. 5 show that addition of LiCl causes the polymer to aggregate and eventually precipitate. It is interesting to note that the concentration of salt at which aggregation begins corresponds to the electrostatic screening length being reduced by the addition of salt to approximately the Bjerrum length of *m*-cresol. In contrast, we find no measurable effect on the size of the polymer when excess CSA (above the 1:1 mole ratio) is added. The lack of size dependence with excess surfactant (CSA) indicates that the surfactant may not dissociate into free charges at these concentrations but probably exists as ion pairs or small inverted micelles.

4. Conclusions

Dynamic light scattering measurements taken as a function of polymer–surfactant concentration show an increase in the hydrodynamic radius as the concentration is decreased. From

the measured radii, we have calculated molecular weights of the polymers to be approximately in the range of 15 000–30 000 g/mol for PANI samples with intrinsic viscosities of 1.2 and 3000–7000 g/mol for samples with intrinsic viscosities of 0.69 dl/g in H_2SO_4 .

We have observed an expansion of the polymer radius by approximately a factor of three as the concentration of polymer is decreased from about 10^{-4} to 10^{-6} g/ml. This increase in the radius as a function of decreasing concentration is a characteristic of a polyelectrolyte in dilute solution and occurs because of a reduction in the overall ionic strength of the solution. As a result, charges on the backbone of the polymer are less screened and repel each other, causing the chain to extend. As a polyelectrolyte, both solvent polarity and solution ionic strength are expected to have important effects on the solubility and the chain structure in solution. The strong role of electrostatic interactions in these systems is shown by the coiling up and eventual precipitation of the polymer chains when screening salts are added to the solutions.

Modeling of the polymer expansion with existing polyelectrolyte theories shows that PANI in its emeraldine salt form scales intermediate between power laws predicted for intrinsically flexible and rigid polymers. This result is expected because the majority of charged polymers fall into this category which cannot be described by any current theory.

We have found that the presence of water has significant effects on the solution quality of PANI-CSA in *m*-cresol. We have measured the radius of the pre-dried complex as a function of added water and found the effect to be very moderate. In contrast, solutions made from polymer samples that were not pre-dried had reduced solubility, increased aggregation and less stability over time. From these observations we conclude that one of the most important procedures in the preparation of true molecular solutions of PANI-CSA is the drying of the solution components prior to making up the polymer complex solutions.

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