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Conformational Changes of Doped Polyaniline as Characterized by Small-Angle Neutron Scattering (SANS)

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14. ABSTRACT

The use of small-angle neutron scattering (SANS) and solution viscosity were used to study the conformation changes of doped and undoped polyaniline (PANI) in 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (HFIP). In this study, solutions of deuterated polyaniline [doped with deuterated methane sulfonic acid (MSA) were prepared in non-deuterated (HFIP)] solvent, which dissolved both forms of PANI and thus facilitated comparison between the insulating and conducting states of PANI. The use of two different standard models [Zimm and Debye (Gaussian) coil] was needed to treat the SANS data in order to analyze the weight average molecular weight, Mw, radius of gyration, Rg, and the second virial coefficient, A2. The conformation of polyaniline was strongly influenced by the degree of doping as evidenced by the both the increase in intrinsic viscosity and the radius of gyration. Doped PANI adopted an expanded conformation and allowed for an increase in the second virial coefficient.

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1. Introduction

Historically, conductive polymers, like polyanilines, are difficult to process through thermal methods or by solution processing due to the absence of a true melting point and their intractability in common solvents. The development by Cao et al.[1] of readily soluble forms of polyaniline (PANI) through the use of functionalized protonic acids has pointed the way to a multitude of combinations of dopants and solvents and has allowed processing of these once intractable polymers. The role of the dopant in PANI is two fold: to induce electrical conductivity and to aid in solubilizing the PANI by acting as a surfactant between polymer and solvent. The degree of solubility of PANI has been linked to the polymer's final solid-state properties. For instance, Zheng et al.[2] showed a clear relationship between the degree of aggregation of PANI in solution and the degree of crystallinity and, in the end, an increase in electrical conductivity of the as-cast film.

Impeding complete solution processing of this highly conjugated, ionic polymer is its tendency to exhibit self-association interactions such as those induced by hydrogen bonding, and electrostatic and van der Waals forces.[3] Recently, the solvent 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (HFIP) has been found to break apart these secondary interactions and be particularly useful in dissolving both the undoped and doped versions of PANI. It is thought that the highly hydrogen bonded HFIP molecule breaks up the proposed PANI self-association interactions, thereby increasing the number of polymer-solvent contacts and thus allowing the HFIP to be imbibed into the coiled PANI.[4] Given this breakthrough in dissolving and processing PANI, little is known about its chain conformation in a "good solvent" such as HFIP and the role of doping level on the chain conformation.

The geometry of this highly conjugated polymer in solution is of particular interest since the conformation of doped PANI chains in HFIP has a direct impact on the morphology of solution-cast films. Therefore, in order to solution process PANI, it is important to characterize the polymer in solution and determine the extent of self-association or aggregation. One standard method of obtaining information on chain conformation and dimension measurements is light scattering. Using this technique, Liao et al.[5] reported evidence of side-on aggregation in very dilute solutions. However, generally speaking, this method is very limited in characterizing conducting polymers due to the strong absorption of the incident laser beam.[6] Some success in characterizing PANI by dynamic light scattering (DLS) has been reported using solutions of PANI in N-methylpyrrolidone (NMP) and *m*-cresol. Here, Sehgal and Seery[7] reported the presence of aggregates in these solutions based on simple models of scatter with a bimodal size distribution. In any case, most light scattering experiments do not work well with colored solutions (such as PANI) due to the high absorbtivity of conductive polymer. These efforts often result in light scattering data that are convoluted and difficult to interpret.

An alternative technique that can be used to get polymer chain dimensions is small-angle neutron scattering (SANS). In this technique, radiation is elastically scattered by a sample, and the resulting scattering pattern is analyzed to provide information about the size, shape, and orientation of some component of the sample, independent of solution color or absorbtivity of the conjugated polymer. In this technique, the scattered radiation is from the deuterium nuclei on both the PANI backbone and the counter-anion (Figure 1). Neutron radiation can be produced to cover a range of wavelengths from 0.01 to 3 nm and is useful when characterizing polymers in solution, which are on the order of 1–10 nm. Unlike light scattering, highly colored solutions are not of concern in providing the contrast needed. The elastic scattering comes from the deuterium nuclei of the PANI and not from the entire polymer as in light scattering. This scattering contrast between the deuterated PANI and undeuterated solvent gives good signal-to-noise ratios.

We report here the use of SANS and solution viscosity to study the changes in conformation of doped and undoped PANI. Specifically, we measured the radius of gyration as a function of dopant level. The corresponding changes from compact coil to expanded coil are monitored by the change in molecular conformation as measured by the radius of gyration (R_g). Other properties of PANI, such as molecular weight and the virial coefficient, are also reported.

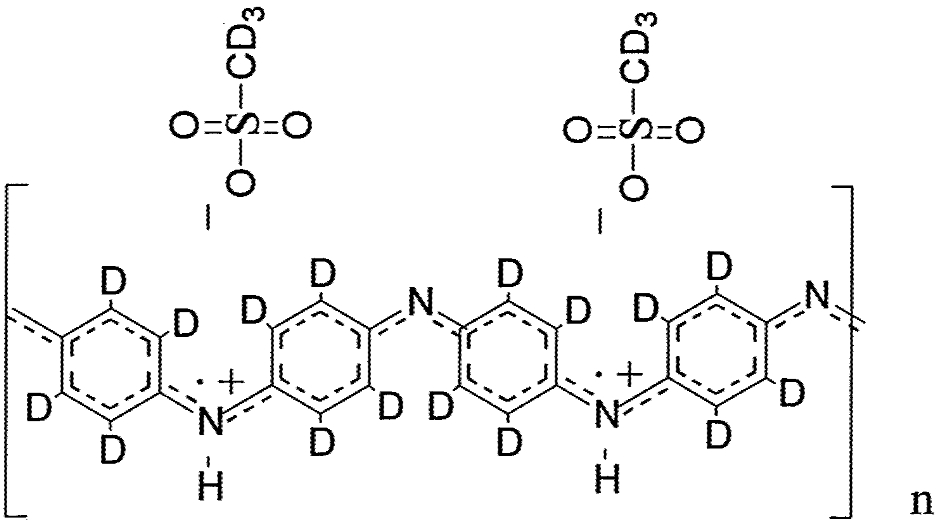

Figure 1. Structure of D-PANI-0.5-D-MSA polymer.

2. Experimental

Partially deuterated polyaniline emeraldine base (D-PANI-EB) was prepared via the $FeCl_3$ method described elsewhere.[8] A solution doping method[8] was used to prepare doped polyaniline in HFIP. Solutions turned from blue/brown color to a forest green characteristic of doped polyaniline. Doping PANI is calculated for polyaniline emeraldine salt from the mole ratio y = (moles of dopant)/(moles of phenyl-NH). Optimally doped polyaniline has the value of $y = 0.5$ or D-PANI-0.5-D-acid. The dopant was deuterated methane sulfonic acid (CD_3-SO_3H), Cambridge Isotopes.

3. Instrumentation

The Small-Angle Neutron Scattering (SANS) data were obtained on the 30-m instrument (in a 16–19 m configuration, approximate range of the measured scattering vector, $Q = 0.06\text{–}0.5\ \mathrm{nm}^{-1}$, thus allowing to probe a range of length scales from 6 to 50 nm) at the W. C. Koehler small-angle scattering facility of Oak Ridge National Laboratory (ORNL). The solvent was 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (HFIP), Aldrich.

Viscosity measurements of unfractionated PANI were done using a No. 75 Ubbelodhe viscometer from Cannon Instrument Co. A typical experiment involves a 0.62% (wt/wt) PANI/ HFIP solution (i.e., 1 g/dL) sample.

4. Results and Discussion

Small-angle neutron scattering (SANS) allows the observation of changes in the scattered radiation, and one can interpret these changes in terms of structural information on the sample. In order to distinguish these changes for polyaniline systems, relatively high solution concentrations (1–2 %) along with deuteration are needed to enhance the neutron scattering of the polymer over the HFIP scattering. In addition, since we cast films from these solutions, the SANS data ideally should approximate the conformation of the polyaniline chains in HFIP.

In this study, the deuterated polyaniline was used in non-deuterated HFIP solvent. The SANS data are treated with two different models: (a) Zimm analysis, originally developed for light scattering gives information about the weight average molecular weight, M_w, radius of gyration, R_g,, and the second virial coefficient, A_2; and (b) Debye (Gaussian) coil analysis, which also permits the calculation of M_w R_g, A_2. The standard method of obtaining molecular weights and radii of gyration from scattering experiments on dilute solutions was developed by Zimm and makes use of the relation for the scattered intensity

$$I(Q)^{-1} = I(0)^{-1}(1 + R_g^2Q^2/3), \qquad (1)$$

where I(0) is the intensity of scattering at Q = 0, and R_g is the radius of gyration. Changes in the direction of traveling of the neutrons before and after scattering are defined by the scattering or wave vector, $Q = (4\pi/\lambda)\bullet\sin(\theta/2)$, where the wavelength of the neutron, $\lambda = 0.475$ nm. It should be noted that at small angles, Q is proportional to the scattering angle θ. To calculate R_g, the data are extrapolated to zero scattering angle, θ, or zero Q in plots of $I(Q)^{-1}$ as a function of Q^2. I(0) is given by

$$I(0) = Kc / (M_w^{-1} + 2A_2c), \qquad (2)$$

where c is the concentration of solution in g/cm^3, M_w is the weight average molecular weight in g/mol, and A_2 is the second virial coefficient (i.e., "goodness" of interaction between polymer and solvent where $A_2 \approx 0$ for theta solvents). K is defined by

$$K = [(\Sigma b/V)_p - (\Sigma b/V)_s]^2/(\rho^2 N_a), \qquad (3)$$

with $(\Sigma b / V)_{s,p}$ the scattering length densities of the polymer (p) and solvent (s), respectively. The density of the polymer is ρ (taken from the solid) and N_a, Avogadro's number = $6.022\bullet10^{23}$ entities/mol.

The concentrations were converted from (wt/wt) concentrations (here defined as x) by

$$c = \rho_p/(1 + [((1 - x) / x) \bullet (\rho_p/\rho_s)], \tag{4}$$

where the density of deuterated polyaniline (D-PANI) optimally doped with deuterated methane sulfonic acid (D-MSA) or D-PANI-0.5-D-MSA = 1.425 g/cm^3. Values of 1.596 and 1.526 g/cm^3 were used. Here it was assumed that the volume of the solution is given by the sum of the volume of the polymer and solvent components (i.e., no volume change).

The values of extrapolated I(0) and R_g were obtained from the plots of $I(Q)^{-1}$ vs Q^2 for the Zimm model analysis and I(Q) vs Q for the Debye coil analysis of the SANS data. The values of I(0) for both treatments were then plugged into Eq. (2), which may be rewritten in the form of y = mx + b:

$$Kc/I(0) = 2A_2c + 1/M_w, \tag{5}$$

where Kc / I(0) is the y-axis and c is the x-axis. The slope and y-intercept of this plot will yield the values of A_2 and M_w, respectively.

The results of the SANS experiment on D-PANI-y-D-HMSA/HFIP solutions are seen in Table 1. From this table, comparable results are obtained using both the Zimm and Debye Coil model treatments of the SANS data. The doped and undoped forms of polyaniline show qualitative differences in molecular weight and size of polyaniline. The PANI-EB shows molecular weights between ≈ 95,000 and 102,000 g/mol. As the polymer is doped with deuterated methane sulfonic acid, these molecular weights decrease dramatically to approximately 18,000 g/mol. Accompanying this molecular weight decrease is a decrease in the size of the polyaniline. R_g decreases from approximately 20 nm for the undoped form to 2 nm for the doped polymer. In addition, Table 1 shows that the second virial coefficient, A_2, changes from $-0.18 \bullet 10^{-3}$ to $3.2 \bullet 10^{-3}$ as the polymer is doped to the optimal level.

From the solution viscosity data in Figure 2, the hydrodynamic volume is seen to increase from the undoped to the optimally doped polyaniline, indicating that the doped polymer adopts a more expanded conformation. This behavior is in contrast to the SANS data, which indicate that the molecular weight and the size of the polymer chains decrease as a function of doping level. To account for this difference, it should be noted that the two experiments were performed in very different concentration regions. We suggest that since the SANS experiments were done in concentrated solutions (to enhance scattering intensity differences between polymer and solvent) and since

Table 1. Parameters Determined From SANS in HFIP Solution of Undoped ($y = 0$) Deuterated Polyaniline and Deuterated Polyaniline Optimally Doped ($y = 0.5$) with Deuterated Methane Sulfonic Acid.

Doping level	$y = 0$	$y = 0$	$y = 0.50$	$y = 0.50$
Model to treat SANS data	Zimm	Debye	Zimm	Debye
$M_w \bullet 10^3$ (g/mol)	95	102	18	18
$A_2 \bullet 10^{-3}$ (cm^3•mole/g^2)	-0.18	-0.18	3.2	3.2
R_g (nm)	19.5	20	2.4	2.2

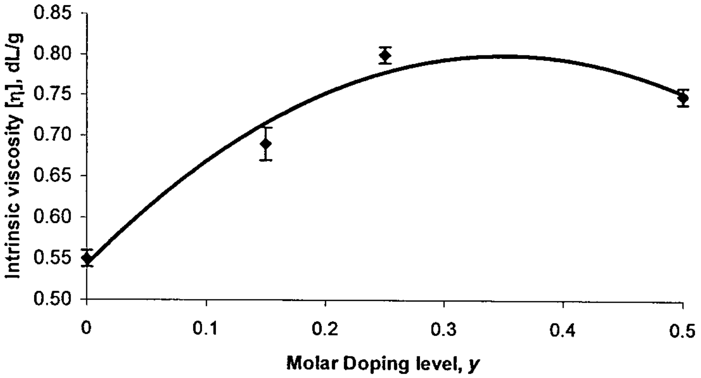

Figure 2. Instrinsic viscosity [η] of PANI-y-MSA (in HFIP solvent at room temperature) as a function of molar doping ratio, *y*.

PANI-EB is known to hydrogen bond strongly between imine and amine groups, both the high values of molecular weight and radius of gyration are due to aggregation of undoped polyaniline chains. GPC measurements of the PANI-EB in HFIP confirm the presence of ultra-high molecular weight or aggregated chains by the presence of a small shoulder in the chromatograph. Strong interactions such as hydrogen bonding between segments of the non-charged polyaniline polymer chains will cause aggregation and decrease the amount of solvent interaction. The negative second virial coefficient from the SANS data in Table 1 corroborates chain aggregation behavior in PANI-EB / HFIP solutions. Doping causes the coiled polymer to expand and increase solvent-polymer contacts as evidenced by the lower magnitude A_2 in optimally doped PANI.

Since the SANS data of PANI-EB suggests aggregation of chains, the molecular weight values of the salt cannot be compared on an absolute basis with the undoped form. The molecular weight of PANI-0.5-HMSA is in approximate agreement with molecular weights determined by solution viscosity measurements (35,000 g/mol) in Table 1 and by previous dynamic light scattering method reported by Gettinger et. al. 9 using *m*-cresol solvent. In addition, while the salt's A_2 value is in the range of other polymer solutions (indicating a good solvent/polymer interaction), the R_g is low for an ionic polymer with a weight average of 18,000 g/mol.

5. Conclusions

The SANS technique is an ideal method for characterizing polymer coil dimensions in solution. The conformation of polyaniline is strongly influenced by the degree of doping as evidenced by both the increase in intrinsic viscosity and the radius of gyration. Doped PANI adopts an expanded conformation and allows for an increase in the second virial coefficient.

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