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CONFORMATION OF A CONJUGATED POLYELECTROLYTE IN AQUEOUS SOLUTION: SMALL ANGLE NEUTRON SCATTERING

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

Small angle neutron scattering (SANS) by a conjugated, luminescent polyelectrolyte, poly[5-methoxy-2-(4-sulfobutoxy)-1,4-phenylenevinylene] (MBL-PPV), was investigated at semi-dilute concentrations in aqueous solution at room temperature. The polymer conformation was studied in pure deteurated water and in solutions with added salt, in solutions with added dicationic quencher and in solutions with added surfactant. A single broad peak in the scattered intensity, I(q), was observed for all concentrations in salt free solutions; the peak position and peak intensity per monomer unit scale with the MBL-PPV concentration as $q_m \sim c^{1/2}$ and $I(q_m)/c \sim c^{-1/2}$, respectively. The upturn of I(q) at low q ($q<0.08Å^{-1}$) results from aggregation of the polymer chains; the sizes of the aggregates increase with increasing concentration. The addition of excess salt completely removes the broad peak from the scattering

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pattern as the salt ions screen the repulsive interchain electrostatic interaction. In high salt solutions, $I(q) \sim q^{-1}$, over a wide range of q, indicating a rigid-rod conformation for the conjugated chains with persistence length greater than 800Å. Cationic surfactant, DTA, was found to separate the polyelectrolyte chains from each other. Initial experiments in the presence of dicationic quencher indicate an increase in the aggregate size.

Key Words: Conjugated polymers; Polyelectrolyte; Neutron scattering; Chain conformation; Luminescence

INTRODUCTION

Polyelectrolytes have been of broad scientific interest for decades with applications in biotechnology, materials science and materials processing [1]. Recently, water soluble conjugated polymers (conjugated polyelectrolytes) were demonstrated to offer potential for use as a new class of high sensitivity chemosensors [2, 3] and biosensors [4] with implications for drug development, toxicology and medical diagnostics [5]. The photoluminescence (PL) of conjugated polymers serves as a spectroscopic indicator of the presence of a quencher-bioactive ligand molecule. The PL from the polymer can be quenched (off) by the formation of a quencher/polymer complex weakly bound by the attractive Coulomb interaction. Recovery of the PL ("unquenching") occurs when the quencher (tethered to a biospecific ligand) is pulled away from the conjugated chain by a biomolecule that interacts specifically with the attached ligand [4, 5].

In studies of the water soluble conjugated polymer, poly[5-methoxy-2-(4-sulfobutoxy)-1,4-phenylenevinylene] (MBL-PPV), the PL efficiency and the Stern-Volmer quenching constant were found to be sensitive to the presence of salt ions (in biological buffers), [6] surfactant molecules [7, 8] or biopolymers, such as proteins or DNA [6]. This sensitivity was attributed to changes in the polymer chain conformation.

Light scattering (LS) and small angle neutron scattering (SANS) provide direct and important experimental information on polyelectrolytes in solution. LS and SANS are sensitive to structures with sizes of order $2\pi/q$ where q is the magnitude of the scattering vector, $q=4\pi\sin(\theta/2)/\lambda$, λ is the wavelength and θ is the scattering angle. Our recent LS studies of MBL-PPV indicate that there is significant aggregation of conjugated polyelectrolytes even in dilute solution [6].

SANS is particularly valuable in providing information on size, shape, volume fraction and interaction of particles in the range from ten to a few thousand angstroms. [9] SANS has been broadly employed in the study of polyelectrolytes [10-14]. The effect of the repulsive interaction between macro-ions was analyzed using a scaling approach and in terms of a lattice model [14-17]. In the scaling approach, [16] de Gennes pictured a semi-dilute polyelectrolyte solution as a dense packed assembly of "blobs" of radius, corresponding to the correlation length. The lattice approach assumes the existence of ordered structures, [17] with polyelectrolyte cylinders or rods aligned in parallel, in solution. Both the scaling approach and the lattice model predict a single, broad but distinct maximum in the neutron scattering intensity, I(q), as observed in the SANS studies of polyelectrolytes (PSSNa) [18, 19] and in many other subsequent SANS studies. [10-14, 20-22]. The more general isotropic scaling approach is characterized in reciprocal space by a maximum in the scattering profile at q_m which varies with the inverse of the correlation distance, and therefore scales with the polymer concentration as $q_m \sim c^{1/2}$. Since the lattice model proposed a lattice of rod-like molecules, the peak position is given by the Bragg condition $q_m = 2\pi/d^*$, where d* is the inter-cylinder distance; again $q_m \sim c^{1/2}$. Both theories assume a uniform distribution of macromolecules and predict very weak scattering at small momentum transfer, q, due to the osmotic incompressibility of the polyelectrolyte chains.

$$S(q \to 0) = kBT \frac{\partial c}{\partial \Pi} \tag{1}$$

where k_B is Boltzmann's constant, T is temperature, Π is the osmotic pressure and c is the monomer concentration. This equation also predicts that at high ionic strength, the charges will be screened and the scattering intensity should provide information on the neutral chain behavior [18-20].

More recent studies have shown that there is a sharp upturn in I(q) at small q as a result of aggregate formation [20-22]. By considering long wavelength density fluctuations, a "two-states structure" model was proposed by considering that both ordered clusters and disordered regions exist for polyelectrolytes in solution [21]. The density fluctuation between the two gives rise to the excess scattering at low q.

In this paper, we summarize the results of SANS studies of the conjugated polyelectrolyte, MBL-PPV, in deuterated water. Both salt free and excess salt conditions were studied to examine the polyelectrolyte behavior and to provide information on polymer chain size, structure and conformation with the goal of understanding the behavior of conjugated polyelectrolyte chains under biological buffer conditions. SANS from solutions with added surfactant (7,8) and with added quencher molecules were also studied to provide information on the conformation and the quenching mechanisms [23, 24].

EXPERIMENTAL

The water soluble conjugated polymer, poly[5-methoxy-2-(4-sulfobutoxy)-1,4-phenylenevinylene] (MBL-PPV), [6] was synthesized at UCSB and carefully dialyzed to remove the salts produced during the polymerization [18, 19]. The dicationic quencher, methyl viologen (MV^{2+}), was synthesized at UCSB and the monocationic surfactant, dodecyltrimethylammonium bromide (DTA) was purchased form Fisher Scientific Co. The SANS studies were performed on the Time-of-Flight Small Angle Neutron Diffractometer (TOF-SAD) at the Intense Pulsed Neutron Source Division, Argonne National Lab (ANL), IL [25]. All experiments were carried out at room temperature. To minimize incoherent scattering and to maximize the scattering contrast, D_2O (Aldrich Chemical Co.) from a freshly opened bottle was used as solvent. Because of the weak scattering intensity from MBL-PPV, the signals were collected using 5mm thick quartz cell; the scattered neutron intensity was detected by a 20 cm × 20 cm area detector.

RESULTS AND DISCUSSION

SANS from MBL-PPV at Different Concentrations

Figure 1 shows the SANS profiles from MBL-PPV in D_2O. The double logarithmic plots of scattering intensity per monomer, I(q)/c vs. q at various concentrations are similar with a single broad maximum which is dependent on concentration and an upturn at low q ($q<0.08\text{Å}^{-1}$). These data were fit using a modified Lorentzian equation [26]:

$$I(q) = A + \left(\frac{B}{q^2}\right) + \frac{H}{4\left(\frac{q-q_m}{w}\right)^2 + 1} \tag{2}$$

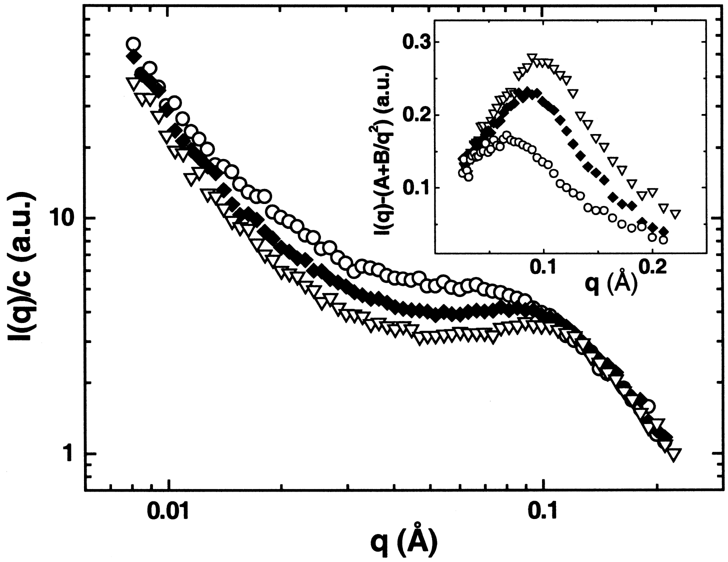

Figure 1. Small angle neutron scattering profiles with different concentrations, I(q)/c vs. q.MBL-PPV 40.4mg/ml (empty circles), MBL-PPV 70.4mg/ml (solid diamonds), MBL-PPV 89.5mg/ml (empty triangles). Inset: I(q)' vs. q where $I(q)' = I(q) - (A+B/q^2)$ and A, B were obtained by fitting the data to Equation 2.

where A is an incoherent baseline parameter, B is an arbitrary intensity scaling factor, H is the intensity peak height, w is the FWHM and q_m is the peak position. Note that log(I) was fitted (rather than I) so that all the data points have the same weight (Figure 2). The inset to Figure 1 shows a double log plot of I(q)' = I(q) – ($A+B/q^2$) vs q. The maximum of I(q)' moves to larger q with increasing concentration, corresponding to a smaller correlation length ($l_c=2\pi/q_m$) (16) or "Bragg distance" ($d^*=2\pi/q_m$) (15) with increasing concentration. The fitting parameters are summarized in Table 1.

Figure 3 shows the concentration dependence of peak position and peak intensity, q_m vs. c and $I(q_m)/c$ vs. c. The data indicate that $q_m \sim C^{0.52}$ in good agreement with predictions of $q_m \sim c^{1/2}$ by both the scaling and lattice models [16] and the theoretical studies of "rigid" polyelectrolytes in the semi-dilute polyelectrolyte regime [27, 28]. The data also show that the peak scattering intensity per monomer unit scales with polyelectrolyte concentration as $I(q_m)/c \sim c^{-0.48}$, again in good agreement with the theoretical prediction [29] and consistent with earlier experimental results obtained from polyelectrolytes [14, 15].

Figure 1 also showed an upturn of I(q) at small q for all concentrations (the B/q^2 term in Equation 2). This increase at low q originates from aggregation of the polyelectrolyte chains into relatively large clusters [20-22]. Independent evidence of aggregation was obtained from light scattering (the size and molecular weight increase with increasing concentration) and from measurements of the photoluminescence efficiency (the PL efficiency decreases with increasing MBL-PPV con-

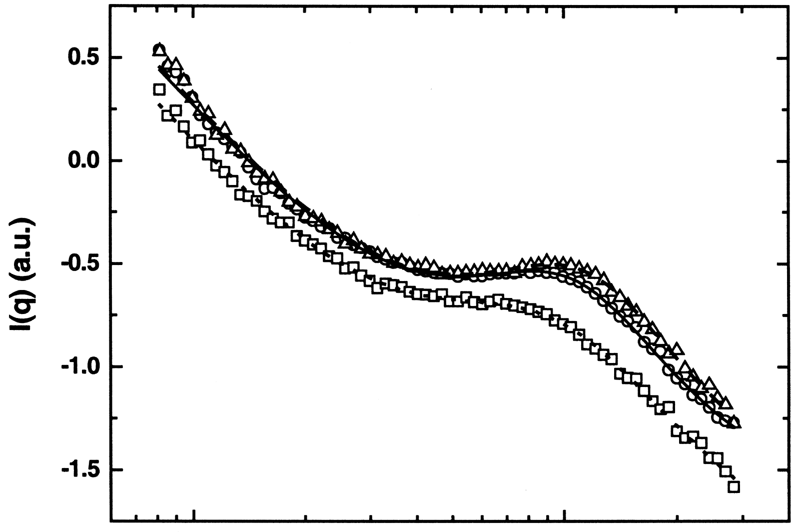

Figure 2. SANS data (concentration dependence) obtained by fitting the data using Equation 2. Raw data: 40.4mg/ml (empty squares, fitted curve: dotted line), 70.4mg/ml (empty circles, fitted curve: solid line), 89.5mg/ml (empty triangles, fitted curve: dash line).

Table 1. SANS Data of MBL-PPV–Concentration Dependence

C (mg/ml)	q_m (Å^{-1})	I(q_m)	ξ or d* (Å)	$\langle R_g \rangle_A$ (Å)
40.4	0.067430	0.16639	93.181	285.53
70.4	0.092150	0.24695	68.184	299.39
89.5	0.10147	0.27630	61.922	305.63

centration) [6]. Note that when compared to similar data obtained from sodium poly(styrenesulfonate) ($q < 0.03$ Å^{-1}) [21] or poly(N-methyl-2-vinylpyridinium chloride) ($q < 0.04$ Å^{-1}), [20] the upturn in I(q) for conjugated MBL-PPV is evident at relatively large q values. This might result from the rigid backbone of conjugated polymer chain (see below).

In Figure 1, at low q, the SANS profile turns up more sharply with increasing concentration, which suggests the presence of larger structures with increasing concentrations. Ise [21] and Percora [22] argued that the Guinier law could be used to analyze the data at small angles for information on the radius of gyration,

$$I(q) = I(0)e^{(-\frac{1}{3}\langle R_g \rangle_A^2 q^2)} \tag{3}$$

where $\langle R_g \rangle_A$ is the apparent radius of gyration. Although the Guinier method is a convenient and powerful technique, it can be used quantitatively only for homogeneous dilute solutions. Nevertheless, $\langle R_g \rangle_A$ can be interpreted in terms of a dilute concentration of aggregates or it can simply be regarded as a correlation length giving the scale of local inhomogeneity [22]. As illustrated in Figure 4, ln I(q) is

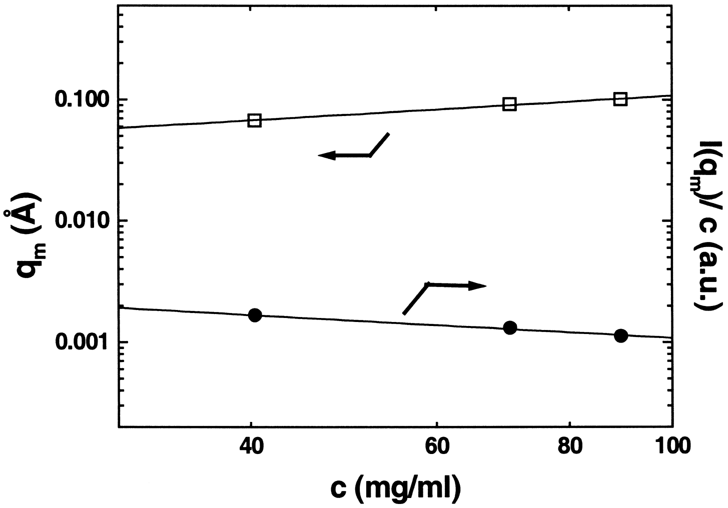

Figure 3. Concentration dependence of SANS maximum position and intensity. q_m vs. c (empty squares; $q_m \sim c^{0.51}$) and I(q_m)/c vs. c (solid dots; I(q_m)/c ~ $c^{-0.48}$).

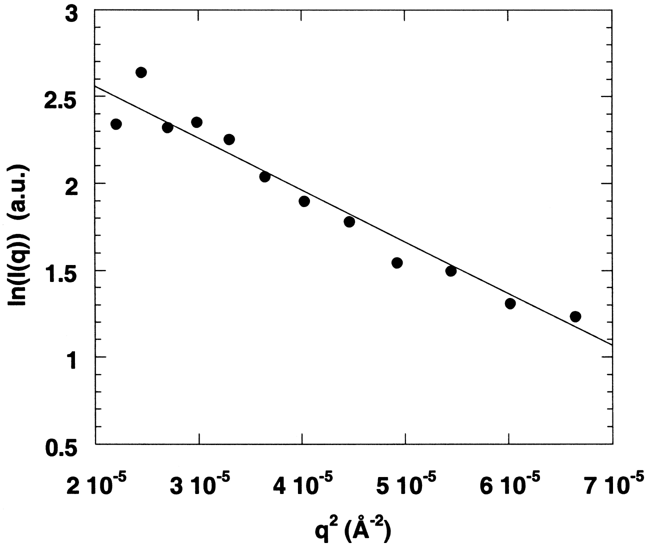

Figure 4. Guinier analysis to estimate the apparent radius of gyration at low q for MBL-PPV(70.4 mg/ml) (see Equation 3).

proportional to q^{-2} at low q, consistent with Equation 3. The corresponding values of $\langle R_g \rangle_A$ are listed in Table 1; $\langle R_g \rangle_A$, increases as the concentration increases (the results obtained from sodium poly(styrenesulfonate are similar) [21]. From this rough estimate, we see that the size of the aggregates increases with increasing concentration. The formation of MBL-PPV aggregates may contribute to the large Stern-Volmer constants when quenched by bipyridinium derivatives, [4, 23, 24] due to the combination of efficient energy transfer and exciton migration [30, 31].

Effect of Salt

To further explore the polyelectrolyte behavior, excess salt was added to the MBL-PPV solutions. As shown in Figure 5, the addition of excess salt causes the disappearance of the broad peak in I(q), consistent with screening of the electrostatic repulsive interaction between the charged chains by the salt ions[23]. For example, in the 32.6 mg/ml MBL-PPV solution with 73.4 mg/ml LiCl salt, the Debye screening length is estimated (23) to be 2.3 Å, which is much smaller than the correlation distance of MBL-PPV chains in pure solution (as in Table 1, the correlation distance between the polyelectrolyte "blobs" is 93 Å for 40.4 mg/ml MBL-PPV solution).

In the solution with an excess of salt, I(q) is proportional to q^{-1}, in agreement with the value expected for rigid rods. The q^{-1} dependence is observed over a remarkably wide range of q = 0.008–0.25 $Å^{-1}$ (see Figure 5), indicating that the

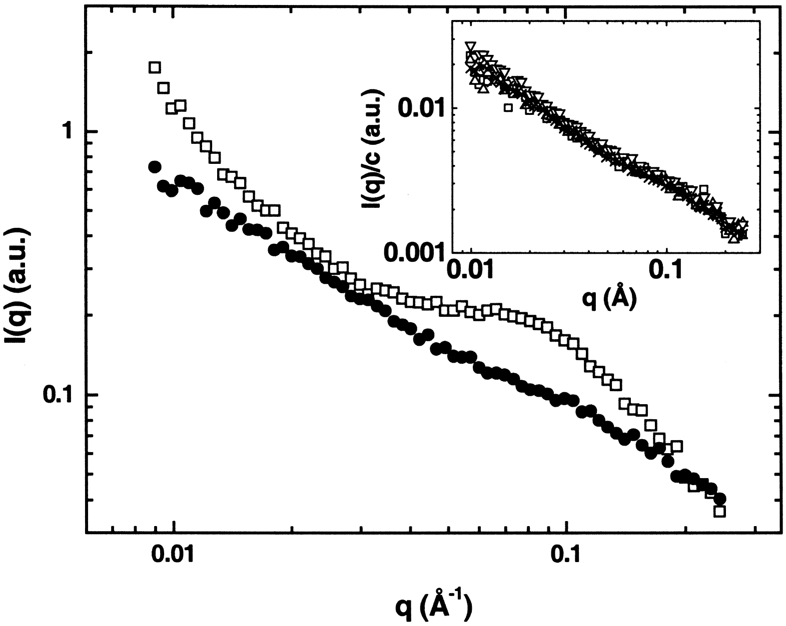

Figure 5. SANS profiles with added salt, I(q) vs. q. Pure MBL-PPV 40.4mg/ml (empty squares), MBL-PPV 32.6mg/ml with 73.4mg/ml LiCl (solid dots). Inset: I(q)/c vs. q for different MBL-PPV concentrations with fixed polymer/salt ratio. MBL-PPV 11.8mg/ml with salt 26.4mg/ml (empty squares), MBL-PPV 17.3mg/ml with salt 39.0mg/ml (empty up triangles), MBL-PPV 24.4mg/ml with salt 54.8mg/ml (empty down triangles), and MBL-PPV 32.6mg/ml with salt 73.4mg/ml (crosses).

polymer chains are rigid rods with a persistence length of at least 800 Å, [26] much larger than the 60 Å for conjugated polymer, MEH-PPV, in organic solvent measured by light scattering, [32] the 30 Å for flexible polyelectrolyte, sodium sulfonated polystyrene in 1M sodium bromide (NaBr) salt solution measured by SANS, [33] the 90 Å for semi-rigid polyelectrolyte, (hydroxyethyl)cellulose, [34] in water or the 250 Å for cellulose in N,N-dimethylacetamide (DMAc) solution with 0.2M lithium chloride (LiCl) [34, 35]. The larger persistence length and the larger radius of gyration of MBL-PPV in aqueous solution, compared to MEH-PPV in organic solvents, contribute to the larger Stern-Volmer constant for MBL-PPV when quenched by bipyridinium [23, 24] compared to that for MEH-PPV when quenched by C_{60} derivatives in organic solvents [36].

The inset shows I(q)/c vs. q for MBL-PPV at different concentrations with the polyelectrolyte/salt ratio fixed. The SANS data superpose onto a single universal curve with slope equal to –1, indicating the rod-like conformation independent of the concentration in solutions with excess salt.

In salt-free conditions, I(q) appears to be a superposition of the overall q^{-1} dependence (suggesting rod-like conformation even in the absence of salt), the peak at q_m from the “ordered” rods that result from the electrostatic repulsion and

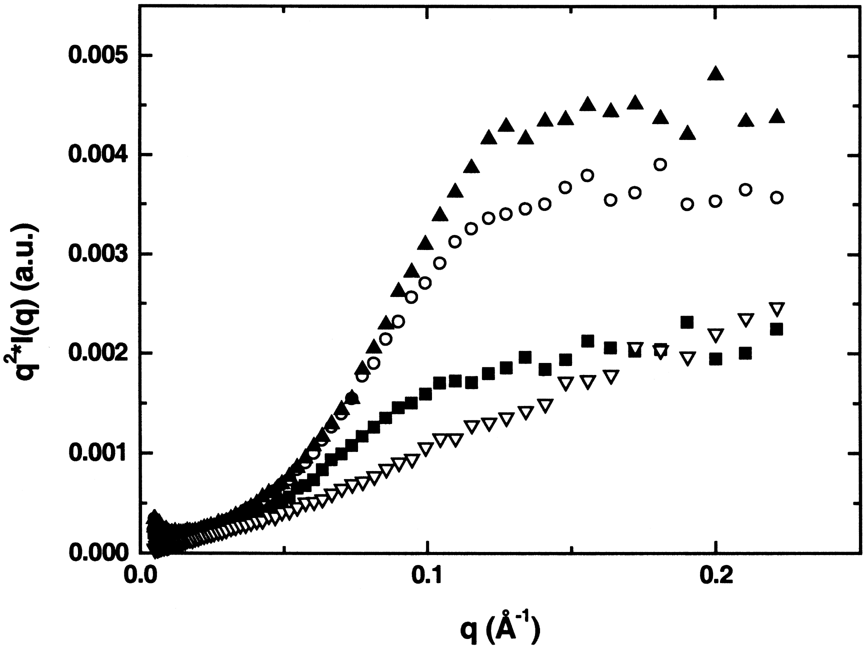

Figure 6. Kratky plots, $q^2I(q)$ vs. q, of SANS. MBL-PPV with excess salt, MBL-PPV 32.6 mg/ml with 73.4 mg/ml LiCl (empty triangles) and pure MBL-PPV at different concentrations: 40.4mg/ml (solid squares), 70.4mg/ml (empty circles), and 89.5mg/ml (solid triangles).

the up-turn at low q due to aggregation. The Kratky plots, $q^2*I(q)$ vs. q in Figure 6, shows the superposition of the peaks and the q^{-1} dependence more clearly [26, 37, 38].

The addition of salt reduces the excess scattering at low q (i.e., above the q^{-1} line), implying reduced aggregation. Analysis of a Guinier plot at very low q gives a smaller $\langle R_g\rangle_A$ after adding salt; 215 Å for 32.6 mg/ml MBL-PPV with salt vs. 283 Å for pure MBL-PPV (Table 2). The apparent radius of gyration of pure 32.6 mg/ml MBL-PPV was linearly extrapolated from the data in Table 1, as shown in

Table 2. SANS of MBL-PPV in Water with Salt, Quencher, and Surfactant

MBL-PPV Sample	C (mg/ml)	q_m (Å^{-1})	$I(q_m)$	ξ or d* (Å)	$\langle R_g\rangle_A$ (Å)
Pure (calculated)	32.6	–	–	–	282.71
With salt (73.4mg/ml)	32.6	–	–	–	215.26
Pure (calculated)	34.7	–	–	–	283.58
With quencher (MV2+)(17:1)	34.7	0.05967	0.23236	105.30	303.49
Pure	40.4	0.06743	0.16639	93.181	285.53
With surfactant (DTA)(40:1)	40.4	0.05759	0.17685	109.10	278.77
With surfactant (DTA)(5:1)	40.4	0.03799	0.62292	165.39	255.62

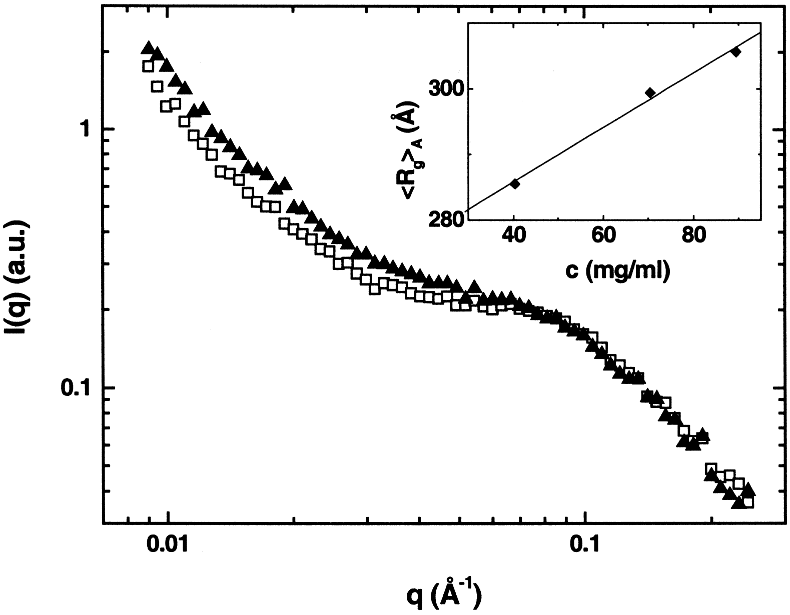

Figure 7. SANS profiles with added quencher, I(q) vs. q. MBL-PPV 40.4mg/ml (empty squares), MBL-PPV 34.7 mg/ml with 17:1 Methyl viologen (solid triangles). Inset: Concentration dependence of apparent radius of gyration. Linear fitting: $<R_g>_A=269.2+0.414*c$.

the inset to Figure 7. The result is similar to observed from poly(N-methyl-2-vinylpyridinium chloride) [19].

Effect of Dicationic Quencher

Figure 7 shows the SANS profile of 34.7 mg/ml MBL-PPV when a dicationic quencher, methyl viologen (MV^{2+}), was added with a polyelectrolyte repeat unit/quencher ratio of 17:1 (SANS of 40.4 mg/ml pure MBL-PPV was plotted for comparison). The SANS profile for the solution with quenchers, at the polyelectrolyte/quencher ratio of 17:1, is not much different at high q; the peak is similar to that for the pure MBL-PPV (40.4mg/ml). The peak position and peak height were obtained by fitting the data using Equation 2. The correlation distance obtained from the fit was calculated using $\xi=2\pi/q_m$, as listed in Table 2.

In Figure 7, the scattering intensity, at low q, for a solution of 34.7mg/ml MBL-PPV with quencher, is higher than that for 40.4mg/ml MBL-PPV in a pure solution, suggesting increased aggregation. The apparent radius of gyration of pure 34.7 mg/ml MBL-PPV was linearly extrapolated from the concentration data in Table 1, as shown in the inset to Figure 7. It is clear that the apparent radius of gyration for 34.7 mg/ml MBL-PPV with quencher is larger than that for pure

MBL-PPV (see Table 2) suggesting that the dicationic quencher increases the size of the aggregates.

Effect of Surfactant

In order to clarify the effect of addition of surfactant, SANS of MBL-PPV solutions with a single polyelectrolyte concentration (MBL-PPV 40.4 mg/ml), but different polyelectrolyte/surfactant (dodecyltrimethylammonium bromide, DTA) ratios were studied. The scattering intensity increased with increasing surfactant concentration (decreasing polymer repeat unit/surfactant ratio), and the slope of I(q) ~ q changes at both high q and low q (Figure 8). The inset to Figure 8 shows the very weak SANS from 4.94e-3M pure DTA solution, indicating that there are no detectable large structures and that at the concentration of 4.94e-3M, the DTA concentration in the mixture of MBL-PPV and DTA with 5:1 ratio is below the critical micelle concentration (CMC). The SANS from 40.4 mg/ml MBL-PPV was also plotted in the inset to Figure 8 for comparison.

The increased SANS intensity from MBL-PPV with surfactant (5:1 polymer to DTA ratio) in Figure 8 is much stronger than the sum of SANS intensity from pure MBL-PPV and from pure DTA shown in the set to Figure 8, implying a coop-

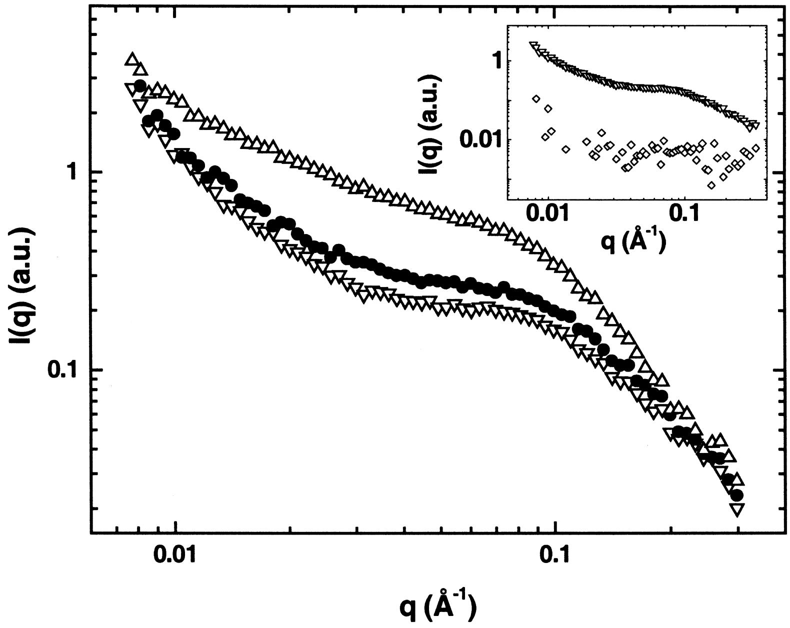

Figure 8. SANS profiles with added surfactant, I(q) vs. q. MBL-PPV 40.4mg/ml, pure MBL-PPV (empty down triangles), with 40:1 DTA (solid dots) and with 5:1 DTA (empty up triangles). Inset: MBL-PPV 40.4 mg/ml (empty down triangles) and DTA (4.94e-3M, relevant to the concentration of DTA in 40.4 mg/ml MBL-PPV with 5:1 DTA) (empty diamonds).

erative interaction between the anionic MBL-PPV chains and the cationic surfactant molecules. Apparently, the surfactant modifies the MBL-PPV conformation and, thereby increases the scattering of the MBL-PPV/DTA complex in D_2O. The enhanced scattering is predominantly at q-values in the range from 0.02 to 0.08 $Å^{-1}$, suggesting the formation of structures on the 100-300 Å length scale. This might be indicating the formation of polyelectrolyte/surfactant complex micelles along the polyelectrolyte chains (39,40).

The decrease of I(q) at low q after increasing the surfactant concentration suggests smaller sized aggregates. Moreover, the Guinier estimates show that the typical size of an aggregate decreases with increasing DTA concentration. The SANS data were fitted using Equation 2 which showed that the scattering maximum shifts to smaller q as the surfactant concentration increased (see Table 2). The average distance between the polyelectrolyte chains increases as the DTA/polymer ratio is increased. These results (smaller aggregate size and larger correlation length) suggest that the cationic surfactant molecules separate the polyelectrolyte chains from each other. As a result, the self-quenching of the PL from conjugated polyelectrolyte is substantially decreased, in agreement with the observed increase in the photoluminescence efficiency observed when DTA was added to the conjugated polyelectrolyte, poly[5-methoxy-2-(4-sulfopropoxy)-1,4-phenylenevinylene] sodium (MPS-PPV) [7, 8].

Note that in Figure 8, at high q the slope of I(q) ~ q increases,. This might be due to the stronger peak effect when the scattering intensity of MBL-PPV/DTA complex (5:1 of polymer/surfactant) was increased.

CONCLUSION

We have investigated aqueous solutions of the conjugated, luminescent polyelectrolyte, MBL-PPV, in the semi-dilute range of concentrations at room temperature with and without added salt, with added dicationic quencher and with added surfactant, using small angle neutron scattering. The SANS results in the semi-dilute solutions show the existence of a single, broad peak in the scattered intensity; the maximum position and the maximum intensity scale with the MBL-PPV concentration as $q_m \sim c^{1/2}$ and $I(q_m)/c \sim c^{-1/2}$, respectively, consistent with polyelectrolyte theory. In addition to the peak, there is a distinct upturn of I(q) at low q (typically, $q < 0.08$ $Å^{-1}$) for all samples studied.. The upturn of I(q) at low q indicates the presence of relatively large aggregates. Rough Guinier estimates show that the size of the aggregates increases with increasing concentration. Aggregate formation of MBL-PPV may contribute to the large Stern-Volmer constants when quenched by bipyridinium derivatives, [4, 5, 23, 24] due to the combination of efficient energy transfer and exciton migration [30, 31].

Excess salt screens the electrostatic repulsive interaction between the charged chains and causes the disappearance of the broad peak. The q-dependence, $I(q) \sim q^{-1}$, implies a rod-like chain conformation with a persistence length of approximately 800Å, which is much larger than that of similar conjugated polymers in organic solvents [32], flexible polyelectrolyte in high salt solution [33], and semi-rigid polyelectrolyte and its derivatives in water or salt solution [34, 35]. We attribute this long persistence length to the combination of the intrinsic rigidity of the conjugated backbone and the stiffening from the charges along the polyelectrolyte chain. The larger persistence length and the larger radius of gyration of MBL-PPV chains in aqueous solution may contribute to the larger Stern-Volmer constant for MBL-PPV when quenched by bipyridinium [23, 24], compared to that for MEH-PPV when quenched by C_{60} derivatives in organic solvents [36]. The size of the aggregates decreases with addition of salt.

The cationic surfactant, DTA, was found to strongly interact with the polyelectrolyte chains. At the experimental DTA concentration regime (<5e-3M), surfactant molecules can separate the polyelectrolyte chains from each other, which reduces the self-quenching and, therefore enhance the PL efficiency. It is direct experimental evidence explaining the remarkable enhancement of the photoluminescence [6-8]. Initial experiments show that the addition of dicationic quencher, MV^{2+}, increases the aggregate size.

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