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Structure and intermicellar interactions in block polyelectrolyte assemblies

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Structure and intermicellar interactions in block polyelectrolyte assemblies

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Amphiphilic diblock polyelectrolytes are becoming popular in industrial applications due to their versatility, ranging from usage in pharmaceuticals to personal care products. Many of these systems also exhibit interesting rheological and morphological behavior. Our system is based on a polystyrene-poly(ethyl acrylate) diblock. The properties can be tuned by utilizing a simple hydrolysis reaction, converting poly(ethyl acrylate) (PEA) to poly(acrylic acid) (PAA). We study the effect of this hydrolysis reaction on the interaction between micelles of polystyrene-poly(acrylic acid) in water using small-angle and ultra-small-angle neutron scattering. We see that as more PEA is converted to PAA, the aggregation number and polystyrene core size decrease. We also studied the effect of cationic (DTAB) and anionic surfactant (SDS) on the PS-PAA diblocks using small-angle neutron scattering. We see that as SDS is added, there are no significant changes in the micellar structure. However, on the addition of DTAB past the CMC, we observe changes in the spectra that may correspond to complexation between the PS-PAA micelles and DTAB aggregates.

Keywords: polyelectrolyte; diblock polymer; SANS; USANS

1. Introduction

Amphiphilic diblock polyelectrolytes, consisting of a hydrophobic block and a charged hydrophilic block, are seeing increasing popularity in industrial applications, ranging from usage in personal care products to biomedical and pharmaceutical applications. Such diblocks also show interesting morphological behavior, as shown by the work of Eisenberg and others (Zhang & Eisenberg, 1995; Cameron et al., 1999).

Our focus has been towards diblock polyelectrolyte gels that have “tunable” rheological properties. Our systems are based on polystyrene-poly(ethyl acrylate) block copolymers, which we hydrolyze to obtain polystyrene-poly(acrylic acid) (Bhatia & Mourchid, 2002). By varying the reaction stoichiometry, we can control the extent of the hydrolysis reaction. Previous work has shown that the elastic modulus and viscosity are strong functions of the extent of the hydrolysis reaction (Bhatia et al., 2001). In addition, the elastic modulus decreases sharply with added anionic surfactant (Bhatia et al., 2001).

In aqueous solution, our copolymers form spherical micelles (Bhatia & Mourchid, 2002). We envision that the unhydrolyzed ethyl acrylate groups, which are hydrophobic, cause an attractive interaction between micelles (Fig. 1). However, the connection between the extent of hydrolysis, micellar structure, and solution rheology is still not well understood. Therefore, small-angle neutron scattering (SANS) and ultra-small-angle neutron scattering (USANS) studies were performed to elucidate the structure of both dilute and concentrated micellar solutions. In addition, the effect of added cationic and anionic surfactant was explored using SANS.

2. Experimental

The diblock polymers was supplied by Rhodia Inc. as polystyrene-poly(ethyl acrylate). Two different molecular weights were examined, 2000/19468 g/mol and 5300/8100 g/mol (listed as MW of PS block/MW of poly(ethyl acrylate) block). The polymer was supplied as an aqueous suspension of latex particles of approximately 40 wt.%. The hydrolysis reaction was run with 10 wt.% polymer in water at 363 K. When the polymer solution reached 363 K, a 2M NaOH aqueous solution was added dropwise. The amount of NaOH added was dependent on the desired degree of hydrolysis. The reaction mixture was then held at 363 K for 24 h. The final degree of hydrolysis was determined using a 200 MHz 1H NMR instrument. After hydrolysis, the polymer was dialyzed using regenerated cellulose membranes with a molecular weight cutoff of 6000-8000 (SpectraPor 1, Spectrum Laboratories) against an aqueous NaOH solution at pH 10 for about one week. This was done to remove impurities and normalize the charge density along the polymer backbone.

Samples for SANS and USANS were prepared by dissolving freeze-dried polymer in D2O (Cambridge Isotope Laboratories) and stirring for several days at 353 K. Calculated scattering length densities, ρ, for all relevant molecules are listed in Table 1. Small angle neutron scattering (SANS) measurements were performed on the 30-meter SANS line (NG3) at the NIST Center for Neutron Research (NCNR) in Gaithersburg, MD. Spectra were obtained at 25°C for a polymer concentration of 4.0 wt.%. Quartz sample cells with a path length of 1 mm were used. The detector distances used in these experiments were 1.33 m, 4 m, and 13.1 m, depending on the sample concentration and contrast. Deuterated water was used to quantify the solvent scattering, which was subsequently subtracted from the spectra. Incoherent scattering was estimated from the signal at high q and was also subtracted from the data. The q-range covered in these experiments was 0.005 Å⁻¹ < q < 0.7 Å⁻¹ (where q = 4π sinθ/λ with θ = half the scattering angle and λ = wavelength of the incident neutrons). USANS experiments were performed on NCNR’s perfect crystal SANS instrument (BfS). Sample preparation was identical to the SANS samples. Quartz sample cells with a thickness of 1 mm were used.

For the surfactant studies, either dodecyltrimethylammonium bromide (DTAB) from Sigma or sodium dodecyl sulfate (SDS) from Fluka was added to 4 wt.% solutions of the smaller molecular weight diblock (5300/8100) in D2O. The concentrations of DTAB used were 0.2, 0.4, 0.5, 0.6, and 0.8 wt.%, and for SDS the concentrations used were 0.2, 0.3, 0.4, 0.5, 0.6 wt.%.
Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>( \rho \times 10^6 ) Å(^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(ethyl acrylate)</td>
<td>0.8446</td>
</tr>
<tr>
<td>polystyrene</td>
<td>1.21855</td>
</tr>
<tr>
<td>D(_2)O</td>
<td>6.37225</td>
</tr>
<tr>
<td>poly(sodium acetate)</td>
<td>4.2698</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. SANS on varied extent of hydrolysis

Samples of the larger molecular weight diblock (2000/19468) were hydrolyzed to different degrees as discussed in section three. The extent of hydrolysis is described by the value \( f \), which can vary between zero and one. A \( f \) value of zero is the case where none of the poly(ethyl acrylate) is hydrolyzed, and a \( f \) value of one is the case where the poly(ethyl acrylate) is completely converted to poly(acrylic acid).

The SANS data were modelled by using a polydisperse spherical form factor:

\[
F(q) = \frac{9}{2\pi\sigma} \int_0^{\infty} e^{-(r-R_{core})^2/2\sigma^2} \left( \frac{\sin(qr)-qr\cos(qr)}{(qr)^3} \right) dr
\]

This two-parameter form factor includes \( R_{core} \), the average sphere radius, and \( \sigma \) the standard deviation of the sphere size distribution. We interpret \( R_{core} \) and \( \sigma \) as characteristic of the polystyrene core size distribution.

For the structure factor, we utilized the adhesive hard sphere model as defined by Baxter (1968), which includes the hard-sphere radius \( R_{interaction} \), a dimensionless temperature \( \tau \) which describes the micellar attractions, and the volume fraction of spheres, \( \phi \), as fitting parameters. To incorporate polydispersity effects into the structure factor, we use the method of Kotlyarchuk and co-workers (1984), who define a polydispersity correction factor \( \zeta \) as:

\[
\zeta(q) = \left[ \frac{3}{2\pi\sigma} \int_0^{\infty} e^{-(r-R_{core})^2/2\sigma^2} \left( \frac{\sin(qr)-qr\cos(qr)}{(qr)^3} \right) dr \right]^{1/3}
\]

The scattered intensity is then expressed as:

\[
I(q) = N(N\Delta\rho)^2 F(q)\zeta(q)
\]

To reduce the number of fitted parameters, we must recognize that parameters \( \phi \) and \( R_{interaction} \) are not independent; they are related through the number density of scatterers \( N \):

\[
\phi = \frac{4\pi}{3} R_{interaction}^3 N
\]

For our system, \( N \) represents the number density of micelles, which can be calculated as:

\[
N = \frac{cN_{AV}}{MW_{PS-PAA/EA} N_{agg}}
\]

where \( c \) is the concentration of the polymer in solution, \( MW_{PS-PAA/EA} \) is the molecular weight of the polymer, \( N_{AV} \) is Avogadro’s number, and \( N_{agg} \) is the aggregation number, defined as:

\[
N_{agg} = \frac{4\pi}{3} \frac{R_{core}^3}{\rho_{PS} MW_{PS-PAA/EA} \rho_{PS}}
\]

Here, \( V_{PS} \) is the volume of the polystyrene block (3666 Å\(^3\)). Combining equations (5), (6), and (7) leads to the following expression for \( \phi \):

\[
\phi = \left( \frac{R_{interaction}}{R_{core}} \right)^3 \frac{cMW_{PS}}{\rho_{PS} MW_{PS-PAA/EA}}
\]

where \( \rho_{PS} \) is the mass density of polystyrene, and \( MW_{PS} \) is the molecular weight of the polystyrene block. Fitting the data using the adhesive hard sphere structure factor and polydisperse form factor thus requires four parameters: \( \sigma, R_{core}, R_{interaction} \), and \( \tau \).

All of the 4.0 wt.% polymer solutions formed strong gels. Fig. 2 shows the experimental data from the 30-meter instrument (NG3) at the NIST Center for Neutron Research. A strong peak is observed at \( \approx 0.01 \) Å\(^{-1}\) for all the samples, which we believe corresponds to the intermicellar distance in these gels. The observed peak gets sharper and more intense as \( f \) decreases. By contrast, the peak position remains fairly constant with \( f \), varying from 0.0102 Å\(^{-1}\) to 0.0113 Å\(^{-1}\) for this series of data. The results from our fits to the data are given in Table 2. The aggregation number was calculated using equation (6).

Figure 2

30-meter SANS results from 4 wt.% PS-PAA gels in D\(_2\)O.

We found that micelle core radius, and hence the aggregation number, decrease as \( f \) increases (Table 2). There are two possible explanations for this trend. First, the effective size of the corona chains could increase as \( f \) increases due to the increasing charge density. Thus, a smaller number of chains would be able to be packed into each micelle, resulting in a decrease in \( N_{agg} \). The other
The desmeared data was fit with a power law, \( I(q) \sim q^d \), and Table 3 summarizes the USANS data fits. We observe a change of the exponent \( d \) from -2.82 to -3.69 as \( f \) increases. Oftentimes, the value of this exponent in the low \( q \) regime is interpreted as a fractal dimension, particularly for attractive colloidal spheres that form fractal flocs, where values of -1.7 to -2.2 have been reported. However, if this were the case, we would expect a value of \( d \) between -1 and -3. Values in the range of -3 to -4, as we observe, may indicate surface scattering from large objects or aggregates. In this case, the exponent would characterize the aggregate interface. The trend in \( d \) is consistent with our physical picture of ethyl acrylate “stickers” and intermicellar attraction. For lower values of \( f \), there is a significant number of ethyl acrylate “stickers” present. We envision that this leads to an attractive force and formation of large micellar aggregates, which may have a loose, open structure and ill-defined interface. Thus, we believe that the exponents that we extract from this data are characteristic of the interface between micellar aggregates and the surroundings.

### Table 3

Values of the slope from a power law fit of the USANS data.

<table>
<thead>
<tr>
<th>( f )</th>
<th>( d ), power-law exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.442</td>
<td>-2.82</td>
</tr>
<tr>
<td>0.610</td>
<td>-3.37</td>
</tr>
<tr>
<td>0.786</td>
<td>-3.72</td>
</tr>
<tr>
<td>0.974</td>
<td>-3.69</td>
</tr>
</tbody>
</table>

### 3.2. Addition of surfactant

Cationic (DTAB) and anionic (SDS) surfactants were added to the symmetric diblock polymers with \( f = 0.85 \). The scattering results for SDS are shown in Fig. 4. As mentioned above, previous work (Bhatia et al., 2001) has shown that the rheology of the system transitions from a gel to a liquid as SDS is added. However, our SANS spectra show almost no change with addition of SDS, other than a decrease at low \( q \). The main peak in the spectra does not disappear or shift as the amount of SDS increases. Thus, the micellar structure is preserved upon addition of SDS, and the intermicellar spacing does not change appreciably. The change at low \( q \) may be indicative of a disruption of the large length scale structure and reduced intermicellar attractions due to the screening of the hydrophobic groups by SDS.

Addition of DTAB is also known to significantly affect the rheology, first causing an increase in the elastic modulus, followed by a decrease (Heitz & Joanicot, 2001; Crichton & Bhatia, 2002). Fig. 5 shows the spectra that result on addition of DTAB to the system. Here, we see a dramatic shift of the main peak to higher values of \( q \); the peak position varies from 0.0126 Å\(^{-1}\) to 0.0158 Å\(^{-1}\) over this data series. As the amount of DTAB increases, the peak shifts to higher \( q \) and slowly broadens. Note that the concentrations of DTAB used are, in some cases, above the CMC of 4.56 g/l, which roughly corresponds to 0.5 wt.% of DTAB. However, the size of a DTAB micelle is roughly 40 Å in diameter, which corresponds to a \( q \) value of about 0.6 Å\(^{-1}\) (Tavernier et al., 1998). There is no formation of a peak in that \( q \) range, so it can be assumed that instead of single DTAB micelles forming, there is some PS-PAA/DTAB complex formation. This could decrease the intermicellar spacing, which is consistent with the peak shift that we observe. This behaviour could also be caused by the DTAB causing the shrinkage of the negatively charged PAA corona.
possible explanations for this trend. First, as the extent of hydrolysis
increases, the corona increases up to about 0.4 wt.% DTAB, then rapidly falls of at 0.6 wt.% DTAB (Crichton & Bhatia, 2002). The peak shift occurs at about 0.4 wt.% DTAB. There are two possible explanations for this peak shift. First, as we approach the CMC of DTAB, there could be the formation of DTAB and PS-PAA complexes, which change the morphology of the micelle and intermicellar distance drastically. Second, with the addition of this cationic surfactant, the negatively charged corona could collapse, leading to a smaller micelle. Finally, a combination of these two effects cannot be ruled out.

4.2. Effect of surfactant

From our SANS studies, it is clear that there is no change in the main peak upon addition of SDS, in spite of the dramatic change in the rheology that has been reported (Bhatia et al., 2001). This suggests that as SDS is added to the system, the structure of the micelles is not changed. However, SDS molecules might be screening the micelle-micelle interactions, which is consistent with the observed rheology. We propose that the hydrophobic tail of SDS is screening the hydrophobic ethyl acrylate groups in the corona. This will weaken the ethyl acrylate interactions between micelles, leading to weaker attractions. After enough SDS is added to the system, the ethyl acrylate attractions can no longer hold the micellar gel together, resulting in a fluid with low elasticity.

On addition of DTAB, a cationic surfactant, something radically different occurs. A shift and broadening of the main peak is seen in the SANS data. From rheology, we observe that $G$ increases up to about 0.4 wt.% DTAB, then rapidly falls of at 0.6 wt.% DTAB (Crichton & Bhatia, 2002). The peak shift occurs at about 0.4 wt.% DTAB. There are two possible explanations for this peak shift. First, as we approach the CMC of DTAB, there could be the formation of DTAB and PS-PAA complexes, which change the morphology of the micelle and intermicellar distance drastically. Second, with the addition of this cationic surfactant, the negatively charged corona could collapse, leading to a smaller micelle. Finally, a combination of these two effects cannot be ruled out.

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References