Clustering and Solvation in Poly(acrylic acid) Polyelectrolyte Solutions

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Introduction

Clustering affects a wide range of water-soluble macromolecular systems including neutral polymer and polyelectolyte solutions. Clustering often appears as a "slow mode" in light scattering investigations.[1,2] Many polyelectrolyte studies have focused on charge interactions, ionic strength, and the effects of salt addition.[3−5] We are interested here in the clustering and solvation effects. A number of possible causes of clustering have been discussed.[5−7] The investigations reported here show that the almost forgotten chain ends effect can cause clustering. This was demonstrated recently[7] for a water-soluble neutral polymer—poly(ethylene oxide)— and will be shown here for a polyelectrolyte system— poly(acrylic acid)—in semidilute solutions. The chain ends effect does not, however, account for all of the observed clustering in water-soluble polymers.

The small-angle neutron scattering (SANS) experimental technique is used to observe clustering (low-Q signal) and solvation properties (high-Q signal). The scattering wavenumber Q is proportional to the scattering angle. The SANS technique probes inhomogeneities with size ranges from the nanoscale (a few nanometers) to the submicron (fraction of a micrometer) window.[7] This covers the range of interest to investigate solvation effects and clustering phenomena with the same technique.

A recent study[7] was conducted on 4% (mass fraction) solutions of poly(ethylene oxide) (PEO) with varying chain ends in a set of three solvents: d-water, d-benzene, and d-methanol (prefix d- represents deuterated solvents). The three different chain ends correspond to $CH_3O-PEO-OCH_3$, $HO-PEO-OH$, and $CH_3O-PEO-OH$. The first case (hydrophobic chain ends) shows clustering in d-water but no clustering in d-benzene, whereas the second case (hydrophilic chain ends) shows clustering in d-benzene but almost no clustering in d-water. These findings along with other experimental observations point to the chain ends effect as a cause of clustering in 4% PEO solutions. A gel-like or network-like picture of the clusters was proposed.[7] The chain ends effect is one (but not the only) cause of clustering.

Clustering in PAA Solutions

Clustering in a model polyelectrolyte system is discussed here. Poly(acrylic acid) (PAA), $-[CH_2CH-$

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$(COOH)]-$, of molecular weight $M_w = 127\,000$ g/mol (degree of polydispersity $M_w/M_n = 1.09$) was purchased from Polymer Source. Solutions of 5% PAA in d-water (by weight) were measured and found to show the same clustering feature (in the SANS data) as the PEO/d-water case.

The SANS intensity data are fitted to the following functional form:[7]

$$I(Q) = A/Q^n + C/\{1 + (|Q - Q_0|L)^m\} + B \qquad (1)$$

The first term describes scattering from clusters, and the second term characterizes the solvation properties and local interactions around polymer chains. The factors A and C, the incoherent background B, and the two exponents n and m are used as fitting parameters. The parameter L is a correlation length for the local solvation structure, and Q_0 is the polyelectolyte peak position. PAA is a weak acid in d-water solution so that the polyelectrolyte peak is very weak and overwhelmed by solvation (i.e., concentration) fluctuations. It can be clearly observed only when NaOH base is added to the solution. As observed by SANS, PAA/d-water behaves mostly like PEO/d-water (i.e., $Q_0 = 0$) for our semidilute solutions.

The PAA sample purchased from Polymer Source was synthesized by anionic polymerization using secondary butyl $CH_3CH_2CH(CH_3)-$ as the initiator. Most anionic polymerizations use (vinyl) hydrophobic initiators that are more stable than other groups (containing $-CH_2-O-$ bonds, for example). To control precisely the functional group located on the polymer chain end, we have resorted to atom transfer radical polymerization (ATRP).[8] ATRP offers high degrees of conversion, tolerance for a variety of functional groups, including acrylates, and affords facile control of molecular weight while maintaining narrow molecular weight distributions. A series of PAA polymers ($M_w = 21\,700$ g/mol, $M_w/M_n = 1.07$) containing end groups with varying hydrophobicity were synthesized at NIST. Initiator/end groups were $HOOC-$, C_6H_5- (phenyl−), or Br− (the transferred atom). The clustering intensity factor A/Q^n (with $Q = 0.004$ Å^{-1}) is shown in Figure 1 for this series (5% PAA in d-water). The parameters A and n are obtained from fits to the SANS data.

Figure 1 shows clearly that increasing hydrophobicity of the end groups increases the clustering intensity. It is actually difficult to eliminate end group hydrophobicity entirely. Clustering remains even with our least hydrophobic end groups. This may be due to residual hydrophobicity coming from the imperfect capping of the solvation tube at the polymer ends or coming from breaks in the solvation tube leaving hydrophobic groups sticking out of that tube (for example).

PAA Solutions in Mixed Solvents

To further understand the nature of clustering and solvation in water-soluble polyelectrolyte solutions, we have measured a series of 5% PAA ($M_w = 127\,500$ g/mol) in three solvents: d-water, d-dioxane, and d-ethanol. We have also mixed these solutions in equal proportions (by weight) to obtain mixtures of 5% PAA in 50% d-water/ 50% d-dioxane, 5% PAA in 50% d-water/50% d-ethanol, and 5% PAA in 50% d-dioxane/50% d-ethanol. Both the
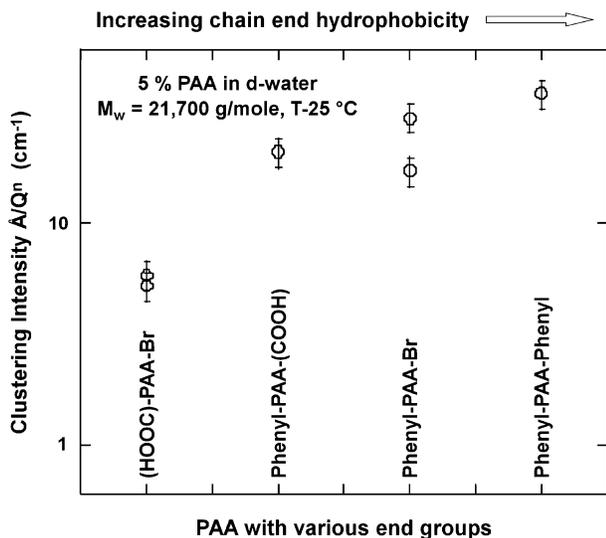
Figure 1. Variation of the SANS clustering intensity A/Q^n for $Q = 0.004$ Å^{-1} with chain end hydrophobicity for 5% PAA/d-water solutions (A and n are fitting parameters). Bromine is the atom transferred in the ATRP synthesis of PAA. The COOH−PAA−Br and the phenyl−PAA−Br cases were remeasured after a second dialysis.

low-Q and the high-Q SANS data show interesting results. The high-Q data show that mixed solvents are more effective at solvating the PAA chains than individual solvents. In the d-water/d-dioxane mixed solvents case, one can conceive that d-water prefers to hydrate the polymer chain around the −COOH groups, whereas d-dioxane prefers to solvate the other −CH$_2$CH− groups. When a pure solvent is used, the solvation tube is "stressed" and fluctuations show up as high values of the solvation intensity (large values of the scale factor C in eq 1). When a mixture of two solvents is used, solvation is more effective, leading to lower values of the scale factor C (i.e., lower than what random mixing would predict). This result has been observed in all three solvent mixture cases (Figure 2a). Moreover, when solvent mixtures are used, the clustering intensity (the first term A/Q^n in eq 1) is systematically higher than what random (or ideal) mixing predicts (Figure 2b). The first observation (better solvation with mixed solvents) is reminiscent of the "cosurfactant" effect in micellar systems. Adding cosurfactant molecules helps better micelle formation by "plugging the holes" on the micellar surface. To our knowledge, this is the first time that such effect is reported for polymer solutions. The solvation tube around the polymer is formed through hydrophilic (i.e., hydrogen-bonding) interactions whereby a few solvent molecules surround each monomer (in cagelike structures), therefore bridging (and shielding) the hydrophobic −CH$_2$− groups along the polymer backbone. Solvation is more effective with mixed solvents because the monomer/solvent hydrophilic interactions are more effective. More effective monomer/solvent hydrophilic interactions implies worse hydrophobic group/solvent interactions which enhances clustering. The hydrophobic groups (−CH$_2$− for example) are more repelled by the solvent and stick more to other hydrophobic sites. This is a possible explanation of the opposite trend observed for clustering and solvation. The hydrophobic groups could either be at chain ends (initiator or terminator groups) or occasionally at break points in the solvation tube. Break points along the solvation tube are probably widely spaced. Our inves-
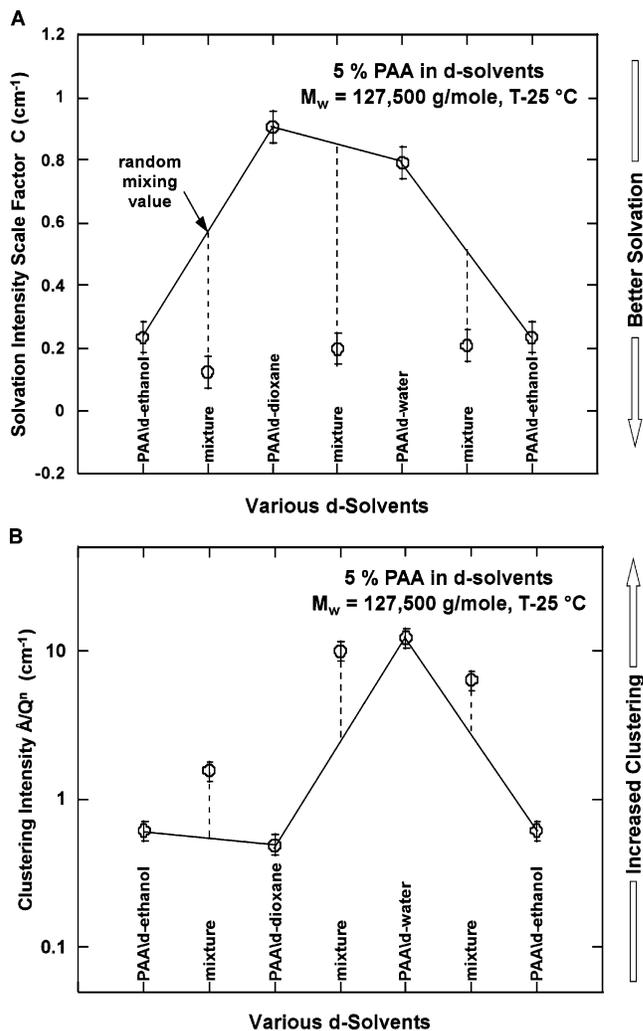

Figure 2. (a) Variation of the SANS solvation intensity scale factor C for the various solvents and (50%/50%) solvent mixtures. Lower values of C imply better monomer solvation. (b) Variation of the SANS clustering intensity A/Q^n for $Q = 0.004$ Å^{-1} for the various solvents and 50%/50% solvent mixtures.

tigations have shown[7] that even one hydrophobic group per polymer chain could produce clustering. One should mention that this picture would apply to solvents other than water provided that a change in terminology from "hydrophobic" to "solvent-phobic" is applied.

Hydrophilic and Hydrophobic Interactions

Solvation is driven by hydrophilic (hydrogen bonding) interactions, and clustering is driven by hydrophobic interactions. This conclusion is reached mostly from the opposite trend for the variation of the low-Q and high-Q intensities. This opposite trend was observed in many other instances. In the 4% PEO/d-water case, it was found[7] that A/Q^n decreases whereas C increases with temperature (from 0 to 90 °C). Moreover, it was also found that A/Q^n increases and C decreases with increased water deuteration (increase in the d-water fraction in a d-water/h-water mixture).[6]

In the case of poly(styrenesulfonate)/water polyelectrolyte systems with added salt, it was pointed out[5] that the correlation length within clusters becomes larger for divalent relative to monovalent counterions whereas polymer chain sizes become smaller. In another investigation,[1] the slow mode and the fast mode amplitudes
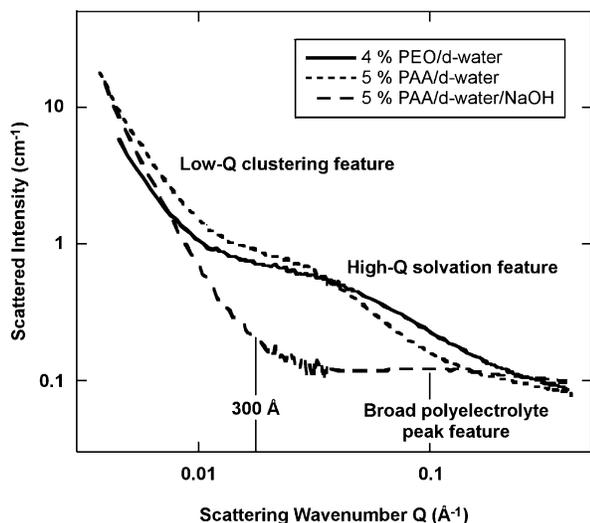
Figure 3. SANS spectra for PEO/d-water, PAA/d-water, and PAA/d-water/NaOH (30% charge neutralization). The first two cases are characterized by typical water-soluble polymer solution features (low-*Q* and high-*Q* variations). The third case shows a broad polyelectrolyte "peak" at high *Q*. Clustering is comparable in these three cases.

were seen to vary in opposite directions when more salt was added to the PAA/water system. The slow mode is associated with cluster dynamics whereas the fast mode is associated with the dynamics of solvated chains. The hydrophobic chain ends effect is expected to be a contributor to the slow mode in polymer solutions. It is not the only one. A number of investigations have looked at the slow mode dynamics.[1,9–13] None, however, has considered the hydrophobic chain ends effect.

Figure 3 compares SANS data for a PEO/d-water neutral polymer solution, for a PAA/d-water polyelectrolyte solution, and for the same PAA/d-water solution after addition of enough NaOH base to titrate 30% of the acidic protons to COO^- ions. The addition of a base (or salt as done in ref 3) changes mostly the high-*Q* SANS signal. It affects clustering also because it changes the hydrophobic nature of the solvent (i.e., the hydrophobic groups/solvent interactions). Adding small amounts of NaOH base damps solvation fluctuations at high *Q*, therefore allowing the weak PAA/d-water polyelectrolyte peak to become prominent (see Figure 3). Without the addition of NaOH, SANS data from PAA/d-water have the same features as in the case of PEO/d-water (i.e., $Q_0 = 0$ in eq 1). Figure 3 shows clearly that the low-*Q* feature is similar in the three cases. It also shows that clusters are observed for interdistances larger than 300 Å (i.e., for *Q* values lower than 0.02 Å^{-1}) only, so that clustering cannot be produced by monomer/monomer hydrophilic (hydrogen bonding) interchain interactions. Clustering is due to chain ends effect (demonstrated here) and to breaks in the solvation tube, leaving hydrophobic groups sticking out. These breaks are spaced by interdistances larger than 300 Å.

Conclusions

The hydrophobic chain ends effect is found to contribute to clustering in a water-soluble PEO/d-water solution and in a PAA/d-water polyelectrolyte solution. However, this effect is not the sole cause of clustering. Other possible causes include breaks in the solvation tube around the polymer (or polyelectrolyte) chain, therefore exposing hydrophobic groups. A few breaks per chain would be enough to produce clustering. In the polyelectrolyte case, another mechanism forming macrodomains mediated through counterion clouds has been proposed.[5]

Moreover, we have found that mixed solvents give a more effective solvation of the polymer than individual solvents. This is manifested as reduced concentration fluctuations. Mixing solvents helps improve the hydrophilic (or solvent-philic) monomer/solvent interactions. Mixing solvents, however, yields an enhanced clustering effect because better solvation for the water-soluble monomers implies worse solvation for the hydrophobic (water-insoluble) groups. These conclusions were reached for 50%/50% solvent mixtures.

Supporting Information Available: Details of atom transfer radical polymerization synthesis of poly(acrylic acid). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Sedlak, M. *J. Chem. Phys.* **1996**, *105*, 10123; *J. Chem. Phys.* **2002**, *116*, 5236; *J. Chem. Phys.* **2002**, *116*, 5246.
(2) Reith, D.; Muller, B.; Muller-Plathe, F.; Wiegand, S. *J. Chem. Phys.* **2002**, *116*, 9100.
(3) Schmitz, K. S. *Macroions in Solution and Colloidal Suspension*; VCH Publishers: New York, 1993.
(4) Prabhu, V. M.; Muthukumar, M. *J. Chem. Phys.* **2003**, *119*, 4085.
(5) Zhang, Y.; Douglas, J. F.; Ermi, B. D.; Amis, E. J. *J. Chem. Phys.* **2001**, *114*, 3299.
(6) Hammouda, B.; Ho, D.; Kline, S. *Macromolecules* **2002**, *35*, 8578.
(7) Hammouda, B.; Ho, D.; Kline, S. *Macromolecules* **2004**, *37*, 6932.
(8) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2004**, *101*, 2921.
(9) Tanahatoe, J. J.; Kuil, M. E. *J. Phys. Chem. B* **1997**, *101*, 9233.
(10) Seghal, A.; Seery, T. A. P. *Macromolecules* **1998**, *31*, 7340; *Macromolecules* **2003**, *36*, 10056.
(11) Petekidis, G.; Vlassopoulos, D.; Fytas, G. *Macromolecules* **1998**, *31*, 6129.
(12) Tsianou, M.; Kjoniksen, A. L.; Thuresson, K.; Nystrom, B. *Macromolecules* **1999**, *32*, 2974.
(13) Kanao, M.; Matsuda, Y.; Sato, T. *Macromolecules* **2003**, *36*, 2093.

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