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Synthesis and Solution Properties of Fluorocarbon-Containing Poly(acrylic acid)

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Introduction

The synthesis and properties of water-soluble polymers (HMWSP) having pendant hydrophobic groups has attracted attention in recent years due to their unique rheological properties.1–4 Such macromolecules in aqueous solution form micelle-like microdomains through hydrophobic inter- or intramolecular association. In general, below the critical overlap concentration (C*), intramolecular association dominates, leading to collapsed conformations. At higher polymer concentrations physi-
cally crosslinked reversible networks form through intermolecular association, leading to sharp increases in solution viscosity. Because of this physical association, the viscosity exhibits large dependence on shear force. In most cases, such solutions show a strong shear thinning (pseudo-plastic) behavior. However, upon removal of shear force, physical networks reform leading to a recovery of viscosity. In some cases, shear thickening may occur in a certain range of shear rate. Other external factors such as ionic strength, pH and surfactants may play an important role in the solution viscosity especially if the polymer is a polyelectrolyte.[11–41]

The covalent attachment of hydrophobic groups onto the polymer backbones such as hydroxyethyl cellulose[15, 16] and poly(acrylic acid)[17] via polymer modification is the one way of synthesizing hydrophobically modified (HM) polyolelectrolytes. Since such reaction is performed in organic solvent, the distribution of the attached hydrophobic groups plausibly are random rather than blocky. An alternative synthesis of HM polyolelectrolytes is the radical copolymerization of ionic monomers (e.g. acrylic acid (AA).[8] 2-acrylamido-2-methylpropanesulfonic acid (AMPS),[9] maleic acid[10, 11] and dimethyldiallylammnonium salts[12, 13]) with hydrophobe-containing comonomer in organic solvent or water. In the former case, such solution polymerizations are either homogeneous or occur with polymer precipitation. Thus random distribution of hydrophobic groups are obtained.

In aqueous media, so-called micellar copolymerization are carried out in the presence of surfactants that serve to disperse the hydrophobic monomer. In this case copolymerizations may form "blocky" distribution due to the copolymerizations occurring in the comonomer rich micelles.[14] In the case where the comonomers have surfactant property (surf-macromonomer) the copolymerizations require no additional surfactant, but still a blocky distribution of hydrophobic groups is formed.[13]

The solution properties of hydrophobically modified polyelectrolytes depend very much on the size and the nature of the hydrophobic groups, and the way they are attached to the backbone. For example, the alternating copolymer poly[(maleic acid)-co-(alkyl vinyl ether)] exhibit quite different behaviors depending on the number of methylene groups in the alkyl vinyl ether.[15–18] Thus, when the number of methylene groups is smaller than two, the polymers resemble normal polyelectrolytes and undergo a progressive conformational expansion upon neutralization. However, when the number is more than four, the transition from a compact globular coil to the normal extended conformation upon neutralization takes place within a fairly narrow range of degrees of neutralization, and the transition drifts to a large range with increasing the number of methylene groups. If increasing the number to more than 10, the copolymers appear to retain a fairly compact conformation in the whole range of degrees of neutralization.

Our previous studies have demonstrated that the copolymers poly[(acrylic acid)-co-(alkyl acrylate)] show stronger thickening capacity with increasing the alkyl chain length.[19] Substitution of hydrocarbon groups with perfluorocarbon groups also leads to a more pronounced viscosifying effect.[20–22] This is consistent with Ravey and Stebe’s proposal that the hydrophobicity of a CF3 group is equivalent to that of 1.7 CH2 groups concerning the critical micelle concentration.[23]

According to Selv[24] and McCormick et al.[25–27], a blocky distribution of hydrophobes is another important factor that favors the intermolecular association, which results in the enhanced thickening properties. However, relatively large amounts of surfactant are required in such polymerization. Given the profound effects of surfactants on the association of HM polymers, the complete elimination of surfactant is essential and this is difficult, time consuming and incomplete even using dialysis.[21]

As one of the most common polyelectrolytes, poly(acrylic acid) and its salt have been widely used as thickening agents. Iliopoulos et al.[7] found that, by grafting a small amount of alkyl groups onto the PAA backbone by polymer reaction in organic solvent, the modified poly-(sodium acrylate) exhibits much higher thickening power than the unmodified polymer. They also reported that fluorocarbon modified poly(sodium acrylate) shows an even more pronounced hydrophobic association.[22] However, these polymers were synthesized by post-polymerization of poly(acrylic acid) (M∞ = 150000) with long chain Rf or RF alkylamines, and a random distribution of alkyl groups was proposed.

We have synthesized fluorocarbon modified poly-(acrylic acid) via radical precipitation polymerization in organic solvent and reported the properties of dilute solution of the copolymers.[28] Also hydrogenated PAA copolymers modified with different lengths of alkyl groups (n = 8, 12, 14, 16, 18) were synthesized by same method.[19] According to our recent research on the reactivity ratio of AA and FMA,[28] the fluorocarbon-containing comonomers are randomly distributed in the polymer backbone. Nevertheless, for aqueous solutions a very strong hydrophobic association was observed. This seems to suggest that blocky distributions of hydrophobes are not required for strong association. In the following we report some of our recent findings on the synthesis and solution properties of fluorocarbon-containing poly-(acrylic acid).

**Experimental Part**

**Materials**

Acrylic acid (AA) was vacuum distilled before using. 2-(N-ethy1perfluoroctanesulfamido)ethyl (meth)acrylate (FA or FMA) (Scheme 1), that was kindly supplied by the 3 M Co., was recrystallized from methanol twice and dried under
diethyl ether was added into the flask to wash out the leach filter, white solid polymer powders were obtained. The above except for the absence of comonomer. The final copolymerizations were carried out in the same way as Table 1.

Polymer Characterization

The compositions of copolymers were determined by anionic chromatography on Dionex 2010I and by elemental analysis using copolymers of neutralized form, which were listed in Table 1.

Table 1. Polymer composition of PNaAA and copolymers. Polymerization condition as given in the Experimental Part.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FA/FMA in feed mol-%</th>
<th>Fluorine content in polymer wt-%</th>
<th>FA/FMA content in polymer mol-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNaAA</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>FA-50</td>
<td>0.5</td>
<td>1.11a</td>
<td>0.33</td>
</tr>
<tr>
<td>FA-100</td>
<td>1.0</td>
<td>2.62a</td>
<td>0.80</td>
</tr>
<tr>
<td>FA-150</td>
<td>1.5</td>
<td>4.26b</td>
<td>1.33</td>
</tr>
<tr>
<td>FA-200</td>
<td>2.0</td>
<td>5.18b</td>
<td>1.65</td>
</tr>
<tr>
<td>FMA-50</td>
<td>0.5</td>
<td>1.46a</td>
<td>0.44</td>
</tr>
<tr>
<td>FMA-100</td>
<td>1.0</td>
<td>2.76a</td>
<td>0.84</td>
</tr>
<tr>
<td>FMA-150</td>
<td>1.5</td>
<td>3.81a</td>
<td>1.18</td>
</tr>
<tr>
<td>FMA-200</td>
<td>2.0</td>
<td>5.52b</td>
<td>1.77</td>
</tr>
</tbody>
</table>

a) Measured by anionic chromatography.
b) Measured by elemental analysis.

The Brookfield viscosity (BV) of the polymer solution was measured using a Wells Brookfield viscometer equipped with two different sizes of spindles (18# and 34#) and a temperature-control water bath at 25 °C. All the measurements were conducted at the shear rate of 0.4 s⁻¹.

The effect of additives (such as NaCl, SDS and FC-143) on the solution viscosity was demonstrated by adding the additives directly into the polymer solution and measuring the solution viscosity. The additives were allowed to dissolve completely before the viscosity measurements.

The effect of pH value on the solution viscosity was performed using polymers that were in their acid forms. NaOH solution was added to adjust the pH value of the solutions. The initial pH values of polymer solutions were around 4. The amount of water produced during the neutralization reaction is so small that it had little effect on the solution concentration.

The dilute solution properties of both unmodified and modified polyelectrolytes in different NaCl concentrations were studied using a Ubbelohde viscometer at 25.0 ± 0.1 °C.

Fluorescence measurements were performed on an FZ-1 fluorescence spectrophotometer with a slit of 7.5 nm for excitation and 2.5 nm for emission. Pyrene was used as a free probe. The excitation wavelength was 333 nm. Detailed description of the solution preparation was published elsewhere.[28] The polyelectrolytes used for fluorescence measurements were synthesized in 1,4-dioxane instead of benzene.

Results and Discussion

A random distribution of fluorocarbon units was confirmed by the reactivity ratio FMA/AA determined in our group ($r_1 = 1.11$, $r_2 = 0.56$).[28] Although FMA seems to be more reactive than AA, the possibility of even short FMA blocks is remote considering, the low mole fractions of FMA in feed ($\leq 2$ mol-%). For example, the probability of M₁ – M₂ dyads is $1.6 \times 10^{-2}$, for a feed ratio $F_1 / F_2 = 0.151/0.849$ which was reported in previous paper.[28]

Polymer Synthesis

Acrylic acid and a certain amount of hydrophobic comonomer (FA or FMA) were put into a 50 ml round-bottom flask, 30 ml benzene added to solve the monomers, then capped the flask with a rubber stopper. 1.2 ml AIBN solution (125 mg in 25 ml benzene) was injected into the flask. The solution was purged in the bath of ice water with dry pure nitrogen for 30 min and then moved into a 50 ± 0.5 °C oil-bath with magnetic stirring to initiate the reaction. The reaction was left to proceed for 24 h. As the polymers were insoluble in benzene, they precipitated from the solution during the polymerization. When the polymerization was over, they remained monomers and initiator. After filtering by 3# sand filter, white solid polymer powders were obtained. Sodium chloride (NaCl, A.R.), sodium dodecyl sulfate (SDS) and ammonium perfluoroctanoate (FC-143) were also used as received.

Preparation of Sodium Acrylate (Co)polymers

The polymers obtained above were dissolved into deionized water while at the same time adjusting the pH value with 1 M sodium hydroxide (NaOH) solution to be around 11. The polymer solutions were poured slowly into a large vacuum to give white powder. 2,2-Azobisobutyronitrile (AIBN) was recrystallized from methanol. Benzene (A.R.), and dioxane (A.R.) were distilled before using. Acetone, diethyl ether and ethanol (A.R.) were used as received.

Sodium chloride (NaCl, A.R.) was used as received.

Benzene (A.R.) was recrystallized from methanol. 2,2-Azobisobutyronitrile (125 mg in 25 ml benzene) was injected into the flask. The reaction is so small that it had little effect on the solution viscosity. The additives were allowed to dissolve completely before the viscosity measurements.

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Scheme 1. Molecular structure of perfluorocarbon comonomer.

Table 1. Polymer composition of PNaAA and copolymers. Polymerization condition as given in the Experimental Part.
Semi-Dilute Solution Properties

The Brookfield viscosity (BV)-polymer concentration profiles of PAA-FA or PAA-FMA copolymers containing between 0 to 2 mole percent comonomer and PAA homopolymer are shown in Figure 1 and 2. For polymers containing 0.50 mol-% comonomer or less, such as FA-50 and FMA-50, the BV increase is small with increasing the polymer concentration, which is similar to that of unmodified PNaAA. However at greater comonomer contents typical HMWSP behavior occurs. When the concentration exceeds a critical value, which is defined as the critical overlap concentration ($C^*$, around 1 wt.-%), the BV increases sharply eventually giving gel-like solution. This behavior is ascribed to the formation of hydrophobic microdomains that act as physical crosslinks giving network-like structures, which results in the sharp increase in BV. For copolymers with higher content of FA or FMA, the network-like gel can be formed at lower concentration. Thus, the higher the comonomer content, the lower the $C^*$, for example, the $C^*$ decreases to 2 wt.-% for the FA-200 copolymer with a comonomer content of about 1.6 mol-% for FA series and to 1 wt.-% for FMA-200 copolymers with similar mole percent of comonomer for FMA series.

Similar trends were found by Iliopoulos et al.[22] for both the hydrocarbon and fluorocarbon modified poly(sodium acrylate). As mentioned above, they used the polymer reaction to synthesize the modified PAA using PAA (MW $\approx 10^5$) reacts with alkyl $R_H$ or $R_F$ amine and confirmed that the molecular weight of modified PAA was not degraded after the reaction by GPC and the alkyl $R_F$ group was $C_8F$ as similar length as we used in comonomers of FA or FMA ($C_8F$ was $-CH_2C_7F_{15}$ and ours is $-C_8F_{17}$). Also the MW of FA-PAAs or FMA-PAAs copolymers were in between $10^4$ to $10^5$ which was reported in our previous work.[28] Thus, it seems that the results of hydrophobic association are compatible from both. Comparing the viscosity-polymer concentration profiles with those of Iliopoulos,[22] it is obvious that the present copolymers exhibit much stronger thickening efficiency that are reflected by the low value of $C^*$. For instance, the sample FA-200 (with a modification degree of 1.65 mol-%) has a $C^*$ of 2 wt.-%, while the chemically modified polymers require about 7 mol-% of the similar ($C_F_{17}$) fluorocarbon group, such as Iliopoulos’s sample (7C8F). At 3.0 wt.-% concentration solution of FA-200 copolymers, the viscosity is 26 400 cP at the while the viscosity of 3C8F (2.1 mol-% of CH2C7F15, assuming modification yield of 70%) is only around 5 000 cP at a much higher concentration (7.5 wt.-%) and a shear rate (0.06 s$^{-1}$) that is lower than used here (0.4 s$^{-1}$).

The copolymers of FMA series have much higher viscosity than the FA series at the same polymer concentration. This might lie in the existence of methyl group on FMA comonomer, but the real reason is unclear. The effect of NaCl addition on polymer viscosity provides additional evidence for hydrophobic association. When a polyelectrolyte is dissolved in deionized water, the electrostatic repulsion tends to extend the macromolecules. As NaCl is added, the electrostatic repulsion is screened, leading the macromolecules to a more collapsed conformation. So the solution viscosity decreases gradually with the addition of NaCl. For hydrophobically modified polyelectrolytes, however, things were quite different. For the case of FMA-150 at low polymer concentration (0.50 wt.-%), addition of only 0.50 wt.-% NaCl reduces the solution viscosity about five-fold (Figure 3). However, at a FMA-150 concentration of 1.0 wt.-% and at same salt concentration the viscosity increases about 100 fold and then gradually decreases at higher NaCl concentration (Figure 3). Similar results have also been reported by Iliopoulos et al.[22]

In the absence of salt the expanded polyelectrolytes chains appear to discourage inter- and presumably intramolecular hydrophobic association possibly due to chain-
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chain repulsion.\cite{3, 4} In the presence of salt, and the charge screening, the chains become more flexible, thus allowing increased hydrophobic association. This leads to an intermolecular association-mediated increase in viscosity at high polymer concentration and a decrease in viscosity at low polymer concentration where intramolecular association prevails. At higher NaCl concentrations very strong association leads to coil collapse even at high polymer concentration.

**Effects of Added Surfactant**

The addition of FC-143 (Rf surfactant) the solution viscosity of 1.0 wt.-\% solution of FA-200 first sharply increases to give a maximum and then decreases as shown in Figure 4. A 0.50 wt.-\% solution of this copolymer shows little or no effect. Furthermore addition of SDS to a 1.0 wt.-\% solution likewise shows no effect. The strong copolymer concentration dependence is consistent with competitive inter- and intramolecular association mediated by micellar bridging.\cite{32, 33} Thus a critical polymer concentration is needed for the formation of sufficient intermolecular association, which is the source of viscosity enhancement.

Interactions of HMWSP with surfactants have been studied extensively.\cite{22, 29–31} The lack of effect observed above of hydrocarbon surfactants on the viscosity of water soluble polymers with pendant perfluorocarbon groups is consistent with the known incompatibility of hydrocarbons and fluorocarbons.\cite{14} This was also reported by Xie and Hogen-Esch\cite{36} for perfluoroctyl acrylate copolymer of poly(N,N-dimethylacrylamide) and by Petit et al.\cite{22} for above PAA copolymers.

**Effects of Temperature**

As shown in Figure 5 the viscosity of the FA and FMA copolymers decreases with temperature. This differs from what solution viscosity is observed for the FA and FMA copolymers of polyacrylamide\cite{20, 21, 35} and poly(N,N-dimethylacrylamide).\cite{36} In these two cases the viscosity decreases first, then rises to a maximum (between 60 and 80°C. for PAM and around 40°C for PDAM copolymers). At present it is not clear whether these differences are due to the polyelectrolyte nature of FA-PAA or FMA-PAA copolymers.

**Effects of pH**

As shown in Figure 6 the solution viscosity of PAA reaches a maximum at a pH between 8–9, where almost all of the carboxyl groups are neutralized. The decrease in viscosity at pH value above 9 is caused by the salt effect of polyelectrolytes. In the case of our polymers, the effects are quite different. Thus, when increasing the pH above 4.0 dramatic viscosity increases are observed giving a viscosity maximum at the pH range of 5–6 that is at least an order of magnitude larger than observed for PAA. A further increase in pH leads to sharp viscosity decreases followed by renewed viscosity increases above a pH of 11.

This complex behavior indicates disruption of the hydrophobic association between pH values of 7 and 11.
Below a pH value of seven the polyelectrolyte character of the PAA copolymers is not fully developed and this still allows association. At higher pH the polyelectrolyte chains are fully expanded as illustrated by viscosity profile of PAA and the ensuing lack of mobility appears to impede hydrophobic association.

The increase in viscosity at the pH values higher than 11 is consistent with the salt effect and may be similar to the influence of NaCl (Figure 3). In this range there is charge screening and thus, presumably, a great chain flexibility allowing increased hydrophobic association. In this NaOH concentration range a “salt” effect also operates thus increasing hydrophobic association.

Dilute Solution Properties

Typical plots of the reduced viscosity against the concentration of several FMA copolymers are given in Table 2 and Figure 7. The reduced viscosity at all salt concentrations decreases linearly with polymer concentration according to the Huggins Equation (1).

\[
\eta_{red} = \frac{\eta}{C} = \eta_0 + k_H \eta^2 C
\]

As shown in Table 2 for both the unmodified and modified polymers, the intrinsic viscosity decreases monotonically with increasing NaCl concentration. However the FMA-200 copolymer gives great intrinsic viscosity decreases. Furthermore the intrinsic viscosity decreases are greater for the copolymers with higher comonomer content. In the case of PNaAA, the decrease of intrinsic viscosity is due only to the screening of electrostatic repulsion. The FMA copolymers seem to follow this mechanism at low NaCl concentration, but at high NaCl concentration, the enhance intramolecular hydrophobic association appears to contribute to the additional chain contraction (see below).

The occurrence of intermolecular hydrophobic association especially at the higher salt concentrations is reflected by the Huggins coefficient \(k_H\). At low salt concentration, the \(k_H\) of the modified polymer is close to that of the unmodified polymer, indicating little intermolecular hydrophobic association. At high salt concentration, however, the \(k_H\) of the modified polymer is much higher than that of the homopolymer. Furthermore the \(k_H\) values increase with increasing the comonomer content. This is also reflected in very low values of the intrinsic viscosities of high salt concentration (see below).

Fluorescence Measurements

Fluorescence spectroscopy has been widely used to detect the hydrophobic microdomains formed by hydrocarbon hydrophobes and pyrene was usually applied as the free probe. In this paper, we also use pyrene to detect the hydrophobic microdomains formed by fluorocarbon hydrophobes. Figure 8 and 9 display the variation of fluorescence intensity ratio \(I_1/I_3\) as a function of polymer

![Figure 6. Effect of pH on the solution viscosity of poly(acrylic acid) and their modified polymers.](image)

![Figure 7. Reduced viscosity as a function of polymer concentration of FMA-200 at different NaCl concentration.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>0.02 m NaCl</th>
<th>0.04 m NaCl</th>
<th>0.08 m NaCl</th>
<th>0.16 m NaCl</th>
<th>0.32 m NaCl</th>
</tr>
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<tr>
<td>(\eta)</td>
<td>(k_H)</td>
<td>(\eta)</td>
<td>(k_H)</td>
<td>(\eta)</td>
<td>(k_H)</td>
</tr>
<tr>
<td>PNaAA</td>
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<td>7.76</td>
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<td>5.47</td>
</tr>
<tr>
<td>FMA-50</td>
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<td>9.76</td>
<td>0.71</td>
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</tr>
<tr>
<td>FMA-100</td>
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<td>0.57</td>
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<td>0.55</td>
<td>5.94</td>
</tr>
<tr>
<td>FMA-150</td>
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<td>6.82</td>
<td>0.74</td>
<td>4.31</td>
</tr>
<tr>
<td>FMA-200</td>
<td>12.87</td>
<td>0.56</td>
<td>9.31</td>
<td>0.65</td>
<td>6.10</td>
</tr>
</tbody>
</table>
concentration at the pH of 5 and 11, respectively. At pH 5, the value of $I_1/I_3$ for unmodified PAA solution is around 1.8, which is typical value in water, and only decreases slightly to 1.76 at the polymer concentration of 10 g/L. This result proves that there are no hydrophobic microdomains in PAA solutions in the range of concentration studied. For modified polymers, the value of $I_1/I_3$ is about 1.8 at low concentrations and decreases with increasing polymer concentration. This decrease reflects the formation of hydrophobic microdomains in which pyrene preferentially locates. The decrease is more pronounced at higher modification degree. For instance, at the concentration of 10 g/L, the values of $I_1/I_3$ drop to 1.24, 1.52, and 1.64 for FMA-200, FMA-100, and FMA-50, respectively. This indicates that higher fluorocarbon modification degree increases the extent of hydrophobic associations.

At pH 11, however, different behavior is found. In this case there is little variation in the values of $I_1/I_3$ for both the unmodified and modified polymers for the whole polymer concentration range studied. This result shows that, at pH 11, the hydrophobic association can not be monitored by pyrene in the concentration range.

Fluorescence studies were also performed for the polymer solutions at different pH values, which is shown in Figure 10. The value of $I_1/I_3$ of modified polymer increases to a maximum at the pH around 8, then decreases slightly. This indicates that the hydrophobic microdomains formed by inter- or intramolecular association is gradually reduced by the chain ionization. The slight decrease of $I_1/I_3$ at pH higher than 8 may be caused by the re-formation of hydrophobic microdomains due to the enhanced flexibility under excess salt (here NaOH acts as salt). It can be seen that the variation of $I_1/I_3$ can not give us evidence of competition between inter- and intramolecular association. Fortunately, the competition can be proved by viscosity properties (shown in Figure 6). The viscosity of modified poly(acrylic acid) reaches to a maximum at the pH of 5.5, and then decreases dramatically. Combining the results in Figure 6 and 10, it is obvious that intramolecular association dominates at pH lower than 4–5. As the pH gets higher, intramolecular association is gradually broken up, and intermolecular association is enhanced until the pH reaches 5.5. At pH over 5.5, the intermolecular associations are largely destroyed due to the stiffness of the polymer chains, which leads to the sharp decrease in viscosity. It should be noted that the viscosity of FMA-200 is still more than one order of magnitude higher than that of PAA at high pH conditions which indicating the persistence of intermolecular association.

Conclusions

Fluorocarbon-modified hydrophobically associating poly(acrylic acid) was synthesized and its solution properties were studied. The existence of critical overlap concentration ($C^*$) was observed, over which the modified polymers exhibit much higher viscosity than the corresponding homopolymer, and it gives us evidence of the formation of physical networks due to the intermolecular
hydrophobic associations of the fluorocarbon moieties. The addition of NaCl can lead to enhanced intermolecular association over certain polymer concentration, which is reflected by the increase in viscosity. Both the hydrogenated and fluorinated surfactants interact with the modified polyelectrolytes and lead to an enhanced intermolecular association over a certain polymer concentration, but the former interaction is much weaker. Detailed study on comparison is in progress. The modified polymers show very extensive changes in solution viscosity with the increasing of pH. The viscosity reaches a maximum at pH 5–6, which can be ascribed to the enhanced intermolecular association. At pH higher than 11, the viscosity increases again. This increase is caused by the salt effect of excess NaOH.

In dilute NaCl solution, there exists a competition between intramolecular hydrophobic association and electrostatic repulsion. The former tends to lower the intrinsic viscosity, while the latter stretches the polymer chain to a more extended conformation. The high Huggins coefficient at high NaCl concentration reflects the interactions of polymer coils in the polymer solutions of finite concentration.

Fluorescence studies show that pyrene can be used to monitor the hydrophobic microdomains formed through hydrophobic association at low pH value. These microdomains are gradually weakened upon increasing pH value. Comparing with the viscosity studies, it is obvious that there exists the competition between inter- and intramolecular association in polymer solution. The intermolecular association is enhanced to a maximum with increasing pH value to 5.5. At pH higher than 5.5, the intermolecular association is largely destroyed due to the stiffness of the polymer chain.

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