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Fluorescence Studies on Hydrophobic Associations of Fluorocarbon-Modified Poly(acrylic acid) Solutions

Junyan Chen,[†] Ming Jiang,*,[†] Yunxiang Zhang,*,[‡] and Hui Zhou[‡]

Institute of Macromolecular Science and Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China, and Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

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ABSTRACT: Fluorocarbon-containing hydrophobically associating polymers have been synthesized by copolymerization of acrylic acid with a small amount of C_8 fluorocarbon-containing methacrylate. The association behavior of the fluorocarbon-modified poly(acrylic acid) (FA) over a broad pH range has been investigated by a fluorescent probe technique and viscosity measurements. The copolymer has the strongest intermolecular association and maximum viscosity at the acidic condition of pH 5.5. Both pyrene and fluorocarbon-substituted pyrene ($PyCOR_f$) are usable to detect this strong association and its dependences on both the fluorocarbon content and polymer concentration. Less acidic pH causes progressive disruptions of hydrophobic association, leading to a dramatic decrease in viscosity. At pH > 7, the stretched polymer chains reach a viscosity plateau much lower than the maximum viscosity but still higher than the viscosity of the poly(acrylic acid) homopolymer. This indicates that relatively weak associations are present. $PyCOR_f$, due to its high affinity to the fluorocarbon domains, is effective in monitoring the formation of this kind of weak association while pyrene fails to do so.

Introduction

Hydrophobically modified water-soluble polymers have attracted considerable attention in both academic studies and applications over the past two decades for their unusual rheological features.[1−12] Most of the associating polymers are amphiphilic. They are composed of a hydrophilic main chain or backbone and a hydrophobic end or side chains. Hydrocarbon chains containing from 8 to 18 carbon atoms commonly are used as hydrophobes. In recent years, it has been reported that, compared to hydrocarbons, fluorocarbon hydrophobes exhibit much stronger associations in aqueous solutions due to their low cohesive energy density and surface energy.[9,13] In fact, Ravey and Stebe reported that a CF_2 group was equivalent to 1.7 CH_2 units in terms of hydrophobicity.[14] As for the hydrophilic main chain, both electrolytes and nonelectrolytes have been extensively studied. Among these, different types of poly(ethylene oxide), polyacrylamide, and cellulose are the most common nonelectrolytes, while poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) are widely used polyelectrolytes.

Grafting a small number of alkyl chains with 8−18 carbon atoms into a poly(acrylic acid) (PAA) main chain by chemical modification has proved very effective in modifying the rheological properties.[15] The influence of pH on the viscosity of the copolymers was interpreted in terms of conformational changes of the chain caused by the ionization of the carboxyl groups. The pH-induced conformational transition of unmodified PMA and PAA, i.e., from a hypercoil to an extended chain with increasing pH, has been studied extensively.[16,17] For PMA at low pH, a random coil exists, but it greatly expands at pH 4−5, where 30% of the carboxylic groups are neutralized. PAA shows similar pH-dependent behavior, but expansion of the polymer occurs gradually over a span of several pH units. Such conformational transitions may greatly affect the association between hydrophobic groups of hydrophobe-containing polymers and make it more complicated to describe than the corresponding neutral systems. Recently, the study of the pH effect for hydrophobically modified PAA has been extended to hydrogels composed of cross-linked PAA and alkyl chains. Khokhlov et al.[18] reported that generally the aggregates of *n*-alkyl side chains broke up with ionization of the PAA gel. A greater hydrophobicity of the gel requires a higher degree of ionization to destroy these aggregates. They also found that the introduction of hydrophobes only slightly affected the apparent dissociation constant of PAA.

Recently, a series of investigations on poly(sodium maleate-*alt*-ethyl vinyl ether)s modified with high content of *n*-octyl chains (30 mol %) was conducted by McCormick et al.[19−22] The alkyl-substituted copolymers in dilute aqueous solutions collapse into compact aggregates due to the loss of polyelectrolyte character and an increase in hydrogen bonding. As the pH is raised progressively beyond 6.7, disruption of hydrophobic clusters occurs, greatly reducing the aggregation number. This is the so-called “globule-to-extended chain” transition. Selb et al.[23] and Peiffer et al.[24] reported that, for polyacrylamides containing both hydrophobic groups and ionic sites, the competition between hydrophobic attractions and electrostatic repulsion greatly affects its thickening efficiency in aqueous solution. One of the main effects of introducing charges onto the polymer backbone is the lowering of the degree of association.

Most of the efforts to understand the mechanisms of associations have focused on the rheological properties and their dependence on the structures of associates. In recent years, a combination of techniques including laser light scattering (LLS),[7] nuclear magnetic resonance (NMR) spectroscopy,[25] and fluorescence spectroscopy[8] have been widely used in exploring the hydropho-

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[†] Fudan University.

[‡] Chinese Academy of Sciences.

* To whom correspondence should be addressed.

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Chart 1. Structure of Copolymers

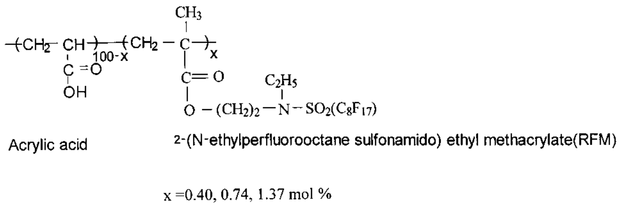

Table 1. Characterization Data of PAA and Copolymers

polymer[a]	$M_\eta \times 10^{-5}$	comonomer in feed (mol %)	fluorine in polymer (wt %)	comonomer in polymer (mol %)	conversion of comonomer (%)
PAA	3.2	0			
FA-50	1.7	0.50	1.75[b]	0.40	80.0
FA-100	2.5	1.00	3.21[c]	0.74	74.0
FA-200	3.6	2.00	5.80[c]	1.37	68.5

[a] The nomenclature used for hydrophobically modified copolymers is FA-*x*, where *x* is proportional to molar content of fluorocarbon substituent in feed. [b] Measured by ionic chromatography. [c] Measured by elemental analysis.

bic microstructure of the solutions. Among these, the fluorescence probe technique has proved most common and useful.

In our previous work,[8] the fluorescent probe technique was used on the copolymers of poly(*N*-isopropylacrylamide) (PNIPAM) bearing a small amount (0.06−0.88 mol %) of C_8 fluorocarbon chains. Free probe pyrene provided some indication of the hydrophobic association of the polymers but no compelling evidence due to its poor solubility in the fluorocarbon microdomains. However, the fluorocarbon-modified probe, i.e., 1-(perfluorooctanoyl)pyrene (PyCOR$_f$), which contains the same fluorocarbon chain as that in the copolymers, possessed a much higher solubility in the fluorocarbon region. Thus, the modified probe was preferentially located in the hydrophobic domains. The increase in the intensity of the monomer emission of PyCOR$_f$ with a concomitant decrease in its emission peak at 550 nm clearly indicated the occurrence of hydrophobic domains and provided more reliable information than obtainable by pyrene.

In this paper, we extend our research to a hydrophobically associating polyelectrolyte, poly(acrylic acid) bearing fluorocarbon chains by using fluorescent probe techniques. Our principal interests focus on two features: (1) the pH-dependent configurational transition effects on the association of hydrophobic groups and (2) a comparison of two kinds of free probes, i.e., pyrene and the chemically modified pyrene.

Experimental Section

Materials. Acrylic acid was purified by vacuum distillation of the commercial product. The fluorine-containing comonomer, 2-(*N*-ethylperfluorooctane sulfonamido) ethyl methacrylate (RFM, Chart 1), was obtained from 3M Co. and recrystallized twice from methanol. Fluorocarbon surfactant, pentadecafluorooctanioc acid potassium salt, was also provided by 3M Co. Pyrene (Aldrich, 99%) was used as received. PyCOR$_f$ was prepared by Friedel−Crafts acetylation of pyrene with perfluorooctanoyl chloride in 1,2-dichloroethane as described previously.[8] 1,1′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. All of the solvents were of analytical grade and redistilled before use.

Polymerization and Characterization. The copolymers of poly(acrylic acid) and varying amounts of fluorine-containing comonomer (RFM) were synthesized by free-radical polymerization initiated by AIBN in dioxane. After purging the reaction mixture with nitrogen at 0 °C for 30 min, polymerization was carried out for 24 h at 55 ± 1.0 °C. The final white products were obtained by precipitating the reaction mixture into absolute ethyl ether and drying under vacuum at 50 °C for 48 h. The homopolymer was prepared by a similar procedure except that no comonomer was present during polymerization. The contents of the fluorocarbon chains determined by anionic chromatography and elemental analysis are listed in Table 1. The intrinsic viscosities of PAA and modified PAAs were measured in 1,4-dioxane solutions at 30 °C. The molecular weights were calculated using the equation[26] $[\eta] = 7.6 \times 10^{-2}\ M^{0.50}$ and are also listed in Table 1.

Solution Preparation. Concentrated aqueous stock solutions (1 wt %) of polymers were prepared by mixing the polymer with deionized water by continuous magnetic stirring. Final solutions of the desired polymer concentrations were prepared by proper dilution of the stock solution. The pH was adjusted by successive additions of microliter quantities of 0.5 M NaOH to the polymer solutions, during which the change in the concentrations of the polymer can be neglected. A known amount of probe was added into the sample solutions to give final concentrations of 6×10^{-7} M for pyrene and 2×10^{-6} M for PyCOR$_f$. Samples containing pyrene as a probe were ultrasonicated for 20 min and stood for 24 h at room temperature. Others containing PyCOR$_f$ as a probe were heated at 70 °C for 2 days before measurements. Fluorocarbon surfactant solutions were treated via the same procedure. Such treatment was used to overcome the energy barrier caused by the anionic outer layer. Similar fluorescence spectra were obtained, but less distinct, for the untreated samples.

Fluorescence Measurements. All fluorescence measurements were recorded on a FZ-1 fluorescence spectrophotometer with a slit of 7.5 nm for excitation and 2.5 nm for emission. The excitation wavelength was 333 nm for pyrene and 340 nm for PyCOR$_f$. All solutions studied were air-saturated and examined at right angle optical geometry.

Viscosity Measurements. Viscometric measurements were performed with Brookfield LVT viscometer at a shear rate of 0.4 s^{-1}. To ensure the accuracy of the measurements, a higher concentration of 4 wt % for homopolymer solutions and 2 wt % for the modified copolymer solutions were used.

Results and Discussion

Hydrophobic Association Probed by Free Pyrene. Among the various fluorescent probes used for monitoring the formation of microdomains, pyrene is most popular and effective because it exhibits a medium-sensitive change in the vibrational fine structure of its emission spectrum. The ratio of the first to third emission band I_1/I_3 changes from ~1.8 in water to ~0.6 in nonpolar solvents such as hexane. It is well-known that in systems containing both hydrophobic and hydrophilic phases, pyrene is preferentially solubilized into the former. Analysis of pyrene partitioning between the aqueous medium and the hydrophobic domains in the polymer solutions provides important information about the clusters arising through association.[27−31]

Figure 1 displays the variation of the fluorescence intensity ratio I_1/I_3 of pyrene as a function of polymer concentration for PAA and the fluorocarbon-modified copolymers. All the sample solutions were adjusted to slight acidity i.e., pH = 5. In the unmodified poly(acrylic acid) solutions, I_1/I_3 of pyrene is high, around 1.8, typical of its value in water, and only a slight decrease to about 1.75 was found when the concentration was higher than 1 g/L. The high I_1/I_3 value over the whole concentration range proves that there are no hydrophobic microdomains in PAA homopolymer solutions. For the fluorocarbon-containing copolymers, I_1/I_3 is about 1.8 at low concentrations and shows a fluorocarbon-content-de-

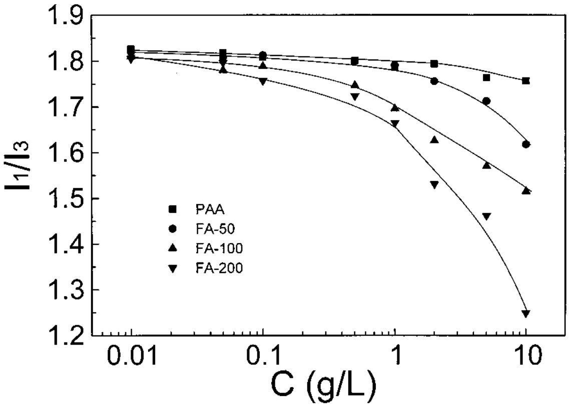

Figure 1. Intensity ratio I_1/I_3 of pyrene at pH = 5 as a function of polymer concentration.

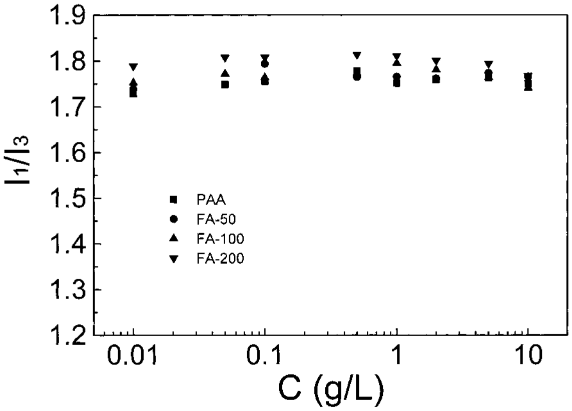

Figure 2. Intensity ratio I_1/I_3 of pyrene at pH = 11 as a function of polymer concentration.

pendent decrease with increasing concentration. This pronounced decrease of I_1/I_3 of pyrene in the copolymer solutions reflects the formation of hydrophobic microdomains in which pyrene preferentially locates. For FA-50 with the lowest fluorocarbon chain content, the I_1/I_3 decrease becomes detectable at a concentration about 1 g/L. However, for FA-200, a continuous decrease of I_1/I_3 starts at a much lower concentration range of 0.01–0.1 g/L. This difference can be attributed to the intramolecular association which may occur at low concentration only in the copolymers with a high fluorocarbon content. The evidence of the intramolecular association was also obtained in our studies of the rheological properties of the modified PAA and will be reported in our forthcoming paper. At the highest concentration of 10 g/L, the I_1/I_3 values drop to 1.24, 1.52, and 1.64 for FA-200, FA-100, and FA-50, respectively. This indicates that higher fluorocarbon content increases the extent of intermolecular associations.

We have reported[8] that homopolymer PNIPAM gave a significant I_1/I_3 decrease as its concentration increased. This was attributed to the hydrophobicity of the PNIPAM chain itself which contains isopropyl groups. However, no such interference was detected in the PAA homopolymer. Therefore, the I_1/I_3 decrease observed for the copolymers at high concentrations can be simply attributed to the preferential location of pyrene in the hydrophobic microdomains.

Figure 2 displays the results of similar experiments carried out at pH = 11 which showed completely different behavior from those at pH = 5. Over the whole concentration range studied, I_1/I_3 values of both homopolymer and the copolymers vary little, within a range from 1.7 to 1.8, reflecting that pyrene is in the vicinity of the hydrophilic backbone or is in the water phase. In other words, the hydrophobic association, if it still exists, and its dependence on polymer concentration at such higher pH value cannot be monitored by pyrene.

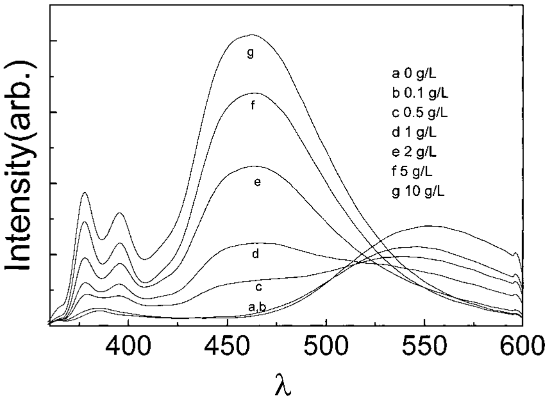

Figure 3. Fluorescence emission spectra of PyCOR$_f$ in FA-200 solution at pH = 5 at various concentrations. λ_{em} = 340 nm.

Hydrophobic Association at Low pH Probed by PyCOR$_f$. Both pyrene and fluorocarbon-substituted pyrene (PyCOR$_f$) were used as probes in our previous studies of fluorocarbon-modified PNIPAM in aqueous solutions. PyCOR$_f$ was more efficient due to its affinity for the microdomains formed by fluorocarbon chains.[8] The presence of the $CF_3(CF_2)_6CO$ group results in the loss of the fine structure of the monomer emission of PyCOR$_f$, so the intensity ratio I_1/I_3 cannot be used. Instead, attention has been focused on the spectrum characteristics and the excimer emissions.

In the experiments with PyCOR$_f$, a relatively high concentration of 2×10^{-6} M was used. Neat PyCOR$_f$ in water presents a single monomer peak at 385 nm, similar to that of pyrene, and a broad band with a maximum at around 550 nm (curve a, Figure 3), which is much longer than that for excimer emission of pyrene in organic media (~480 nm). This unique spectroscopy characteristic of PyCOR$_f$ may be associated with the aggregation of fluorocarbon substituent in water.[32,33]

For PyCOR$_f$ in PAA solutions at pH = 5, similar spectra to that in water were obtained, and no obvious changes were found when the concentrations changed. However, a significant variation of the emission spectra with concentration was found for the fluorocarbon-modified PAA at an acidic condition of pH = 5 as shown in Figure 3. At low concentrations, there is only a weak monomer peak and a strong band at 550 nm. As the polymer concentration is increased, the monomer intensity rises, accompanied by the resolution of its fine structure. At the same time, the broad emission peak diminishes. More noticeably, a new peak at 465 nm, i.e., the excimer emission, appears, and its intensity increases significantly with increasing concentration. The appearance of the excimer emission at 465 nm indicates that abundant probes are located at the hydrophobic domains formed by the aggregates of fluorocarbon side chains. A similar but less pronounced change in the spectra was observed for FA-100 and FA-50 as well.

We use the concentration dependence of the intensity at 465 nm as an indication for the association process. The data are summarized in Figure 4. I_{465} does not

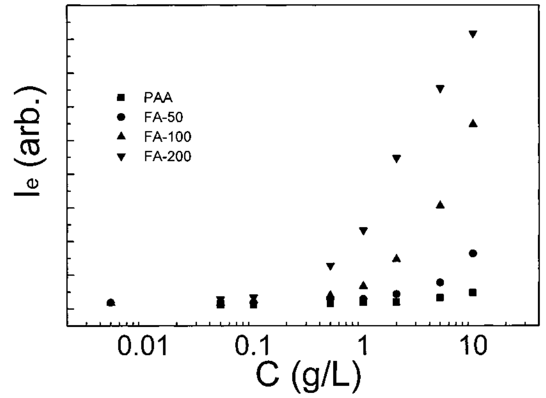

Figure 4. Excimer intensity at 465 nm of PyCOR$_f$ at pH = 5 as a function of polymer concentration.

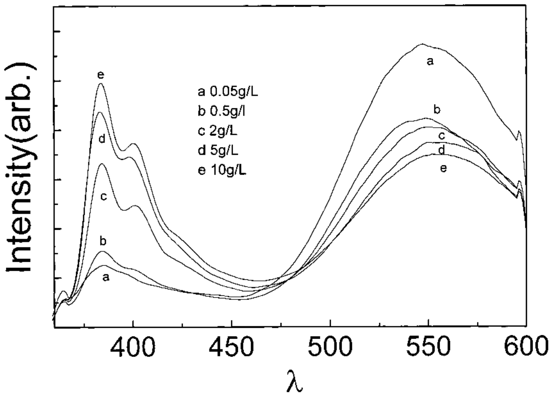

Figure 5. Fluorescence emission spectra of PyCOR$_f$ in FA-200 solution at pH = 11 at various concentrations. λ_{em} = 340 nm.

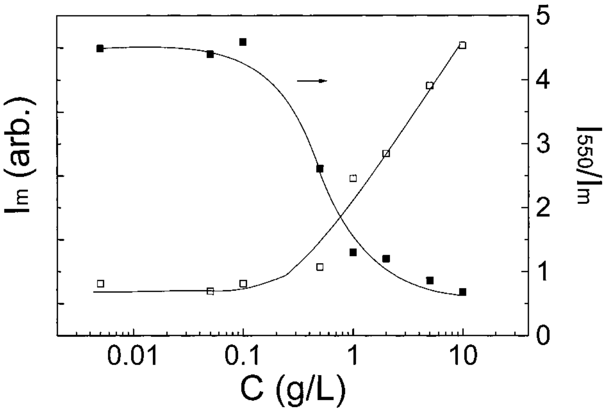

Figure 6. Monomer intensity at 385 nm and intensity ratio I_{550}/I_{385} of PyCOR$_f$ at pH =11 as a function of polymer concentration of FA-200.

significantly change with concentration for the homopolymer, indicating no hydrophobic domains exist for unmodified PAA. For the modified copolymers, all curves display the same trend; i.e., at very low concentrations, I_{465} remains fairly constant until the concentration reaches a critical level which depends on the hydrophobe content. For FA-200, FA-100, and FA-50, the critical concentrations are around 0.1, 0.5, and 2 g/L, respectively. Clearly, higher fluorocarbon content results in lower critical concentration. Generally, this result is in good agreement with those obtained when pyrene was used as the probe. Furthermore, the breaks in the curves in Figure 4 are more distinct than those shown in Figure 1 for pyrene. For FA-200, a sharp increase of the emission is observed. At a high concentration of 10 g/L, the excimer intensity is about 20 times higher than it is at a concentration lower than the critical value. This clearly indicates the formation of hydrophobic microdomains and the preferential partitioning of the probe into the microdomains.

Hydrophobic Association at High pH Probed by PyCOR$_f$. As mentioned previously, pyrene failed to monitor the association of the fluorocarbon chain modified PAA at high pH conditions. Now, we discuss the results of using fluorocarbon-substituted pyrene, i.e., PyCOR$_f$. Figure 5 shows the spectra of PyCOR$_f$ in solutions of FA-200 at different concentrations at pH = 11. Each spectrum exhibits a monomer emission at around 385 nm and a broad emission around 550 nm. With increasing polymer concentration, the monomer emission increases with concomitant appearance of its fine structure. The emission at 550 nm, following a common pattern, gradually decreases as concentration increases. Figure 6 shows both the monomer intensity I_m and the intensity ratio I_{550}/I_m as functions of concentration. At very low concentrations, both monomer intensity and the ratio I_{550}/I_m remain constant. A considerable increase in the monomer intensity and decrease in the intensity ratio are observed as the concentration passes through the range 0.1−10 g/L. It is interesting to note that the two curves have breaks at the same concentration of about 0.2 g/L. As the emission at 550 nm of PyCOR$_f$ only exists in water, it is obviously associated with the self-aggregation of the fluorocarbon substituents in water.[32,33] Although clear assignment of the emission needs further work, the results above show that the ratio of I_{550}/I_m can be empirically used as an indication of the association for the fluorocarbon-substituted PAA at alkaline conditions such as pH = 11. The superiority of PyCOR$_f$ in characterizing the hydrophobic association of fluorocarbon chains over unmodified pyrene is attributed to its better affinity with fluorocarbon microdomains. Differing from the spectra obtained at pH = 5, the curves shown in Figure 5 for the solutions at pH = 11 do not exhibit emission peaks around 465 nm. This significant difference indicates the variation in both the number and microstructure of the hydrophobic domains caused by the pH increase. It is widely accepted that an increase in pH usually results in a rearrangement of the associate structure of hydrophobic group-containing polyelectrolyte. Namely, at high pH, the carboxyl groups are highly ionized and PAA chains are sufficiently extended to cause disruption of hydrophobic clusters and reduction of the number of the aggregation.

Comparison of Viscosity and Fluorescence Studies. I_1/I_3 of pyrene as a function of pH is shown in Figure 7 in both homopolymer and copolymer solutions at a relatively high concentration of 5 g/L. Although the PAA homopolymer dissolves and gives a solution of pH ~ 3, the modified copolymers can only be dissolved at pH range from 4 to 5 caused by the increased insolubility due to the fluorocarbon chains. I_1/I_3 of PAA hardly changes over the whole pH range. The fluorocarbon-modified copolymers show a common feature: at the lowest pH where the copolymer dissolves, I_1/I_3 gives the corresponding lowest value and then increases with pH until it reaches the maximum at pH around 8. Further increase of pH simply intensifies the ionic strength of the media which causes a slight decrease of I_1/I_3.

Brookfield viscosity measurements of the polymer solutions are shown in Figure 8. The viscosity of PAA

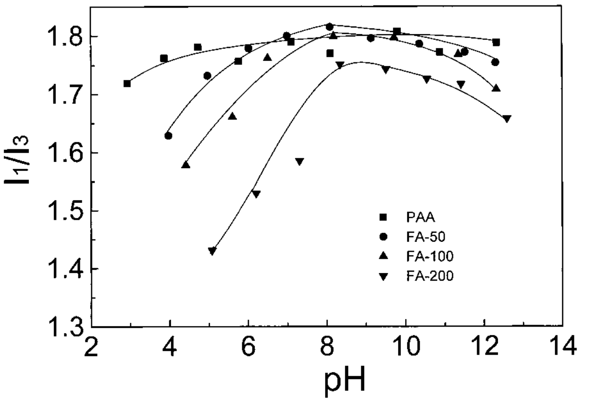

Figure 7. Effect of pH on the intensity ratio I_1/I_3 of pyrene. C_{pol} = 5 g/L.

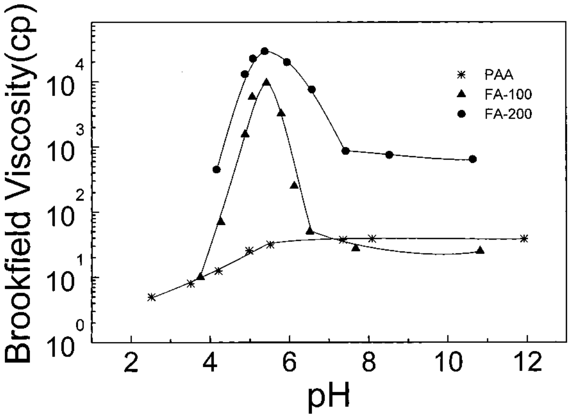

Figure 8. Effect of pH on Brookfield viscosity of homopolymer and copolymers. Concentrations of 4 wt % for homopolymer and 2 wt % for copolymers.

solutions increases when pH increases from 3 as a result of chain extension due to ionization and then approaches a plateau as the pH becomes larger than 5.5. The two hydrophobically modified copolymers show very similar behavior to each other but completely different behavior from that of PAA; i.e., under acidic conditions, the viscosities dramatically increase as pH increases from 4 and then reaches maxima at pH 5.5. This upswing is then followed by a drop as pH increases further and then finally levels off at pH > 7.

In our opinion, increasing negative ionic sites along a polymer backbone by increasing the pH should have three main effects on the viscosity: (1) chain expansion increases viscosity, similar to the behavior of PAA; (2) upon increasing the ionic sites in the copolymer, the repulsive forces lead to chain extension which disrupts the intramolecular associations formed in the coiled configuration and facilitates interchain associations; (3) opposing the aggregation, electrostatic repulsions between highly charged chains hinder intermolecular interpenetration and hence diminish the intermolecular associations of the hydrophobes. Compared to (2) and (3), (1) makes smaller contributions as shown by the relatively small viscosity increase of PAA over the pH range from 3 to 5. Therefore, the dependence of the viscosity of copolymers on pH is thought to be determined by the competition between (2) and (3) mainly. The results in Figure 8 for both FA-200 and FA-100 show that at a low pH range (pH = 3−5), where chains are partially ionized but not sufficiently extended, the favorable effects on intermolecular association prevail over the unfavorable factors. In contrast, the unfavorable effects predominate when the chains are sufficiently extended as pH of the medium increases to near neutral or alkaline conditions.

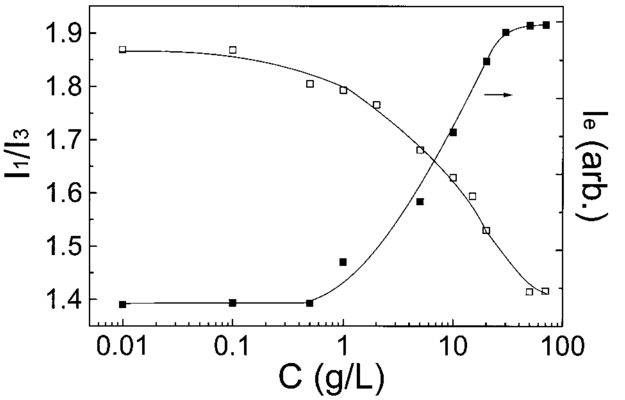

Figure 9. I_1/I_3 of pyrene and I_e of PyCOR$_f$ as a function of surfactant concentration.

Comparing the dependence of I_1/I_3 of pyrene on pH (Figure 7) to that of viscosity on pH (Figure 8), it is obvious that I_1/I_3 of pyrene does not reflect the variation of the intermolecular association with the degree of chain ionization. As pH changes from 4 to 5.5, the viscosity dramatically increases while an increase, rather than a decrease, in I_1/I_3 is shown, indicating more pyrene molecules being expelled from hydrophobic microdomains to the water. It may imply that the partitioning of pyrene between the microdomain and water depends not only on the number and size of the microdomains but also on their microenvironment. More ionic groups on the main chains that surround the hydrophobic microdomains certainly hinder the transfer of pyrene from water to the domains and thus lead to an increase in I_1/I_3. At pH = 5.5, the modified copolymers have a maximum viscosity due to the strongest hydrophobic associations. Both pyrene and PyCOR$_f$ are able to detect the onset of this strong association (Figures 1 and 4) when polymer concentration increases.

It is interesting to note that at alkaline conditions (pH > 7) the copolymer FA-200 solutions (2 wt %) still have a viscosity more than 1 order of magnitude higher than PAA solutions (4 wt %). This clearly indicates the presence of hydrophobic associations of FA-200. The results of FA-100 lead to the same conclusion since it has a similar viscosity to PAA when the concentration of the former is only half of the latter. Obviously, the hydrophobic association at pH > 7 is much weaker than at around pH 5. Therefore, pyrene, due to its poor affinity for fluorocarbon associations, is not able to detect the formation of the microdomains. However, PyCOR$_f$ with its fluorocarbon substituent shows much higher sensitivity to the microdomains, as shown in the plots of I_m and I_{550}/I_m as functions of polymer concentrations (Figure 6).

Supplementary Comparison of Pyrene and PyCOR$_f$. The ability difference in monitoring fluorocarbon microdomains between pyrene and PyCOR$_f$ can also be clearly seen in the experiment with fluorocarbon surfactant. The cmc of a small molecular fluorocarbon surfactant, pentadecafluorooctanoic acid potassium salt, was measured using pyrene and PyCOR$_f$ as probes. The intensity ratio I_1/I_3 of pyrene and the excimer intensity of PyCOR$_f$ at 465 nm are both presented in Figure 9. The I_1/I_3 decrease of pyrene becomes detectable at a concentration about 0.4 g/L, i.e., cmc. It levels off at a value of 1.4, even higher than that in normal hydrocarbon surfactant micelles (~1.2), although the fluorocarbon microdomain is more hydrophobic than its hydrocarbon analogues. It is reasonable to attribute this high value to the poor solubility of pyrene in the fluorocarbon regions. Besides, Eisenberg et al.[28] reported that the (0,0) band in the excitation spectra shifts from 333 to 338.5 nm when pyrene molecules transfer from a water environment to the hydrophobic micellar cores. Thus, the ratio $I_{338.5}/I_{333}$ of pyrene reflects the location of the pyrene probe in hydrocarbon surfactant systems such as SDS. However, in the present case, no such shift is found in the excitation spectra and $I_{338.5}/I_{333}$ of pyrene hardly changes when I_1/I_3 varies significantly. This fact may imply that most of the pyrene molecules are still located in the outer layer of the fluorocarbon cores. Emission spectra of PyCOR_f in the surfactant solutions are similar to those shown in Figure 4 for FAs at acidic pH. The excimer intensity is very low and remains constant under a critical concentration. It dramatically increases as the concentration reaches 0.5 g/L. The break in the curve is much more distinct as compared to the curve of I_1/I_3. This result also indicates that PyCOR_f is more effective in monitoring the onset of the aggregates formed by fluorocarbon chains.

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