

Hydrophobically modified polyelectrolytes

I. Dilute solution properties of fluorocarbon-containing poly(acrylic acid)

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Dilute solution viscosity of fluorocarbon-containing hydrophobically modified poly(acrylic acid) was measured in aqueous solutions of various NaCl concentrations. The intrinsic viscosity ($[\eta]$) and Huggins coefficient (k_H) were evaluated using Huggins equations. It is found that, at low NaCl concentration, the modified polymers exhibit values of intrinsic viscosity ($[\eta]$) and Huggins coefficient (k_H) similar to those of unmodified polymers. For both of the modified and unmodified polymers, the intrinsic viscosity decreases with increase of NaCl concentration, while the Huggins coefficient increases upon addition of NaCl. But the variation of $[\eta]$ and k_H is more significant for the modified polymers, which reflects the enhanced intra- and intermolecular hydrophobic association at higher NaCl concentration.

Keywords Polyelectrolytes, hydrophobically modified, fluorocarbon-containing, intrinsic viscosity

Introduction

Hydrophobically associating water-soluble polymers have gained extensive studies in the 1980's and 1990's owing to their unique rheological properties.^{1,2} These polymers are usually defined as hydrophilic polymers with a few amounts of hydrophobic groups attached to the macromolecular backbone. Upon dissolving into water, the hydrophobic groups tend to aggregate with each other and form hydrophobic domains, which is defined as the hydrophobic association. It is just this kind of hydropho-

bic association that endows the polymer solution with unique properties such as much higher viscosity in the semi-dilute solution compared with its unmodified precursor, strong pseudoplastic behavior, *etc.* Due to its unique solution property, this kind of polymer is widely used as thickening agents in water-proof paintings, mobility control agents for enhanced oil recovery, controlled release of bioactive materials, *etc.*

As one of the main water-soluble polymers, poly(acrylic acid) has been widely used in paintings, papermaking, oil recovery, foods, pharmaceuticals and cosmetics. In most cases, the usage requires high thickening capacity. Since fluorocarbon units exhibit much stronger hydrophobicity than their hydrocarbon analogues, fluorocarbon-modified poly(acrylic acid) can provide more satisfied properties to meet higher requirements. For example, this polymer exhibits much higher thickening capacity at much lower polymer concentration than the hydrocarbon-modified and the unmodified polymers.

In 1989, Zhang *et al.*³ firstly reported the synthesis and solution properties of fluorocarbon-containing hydrophobically associating polymers. Since then, more and more interests were excited on this kind of polymers.⁴⁻²⁰ Their precursor unmodified polymers include hydroxyethylcellulose,¹² polyacrylamide and its derivatives,^{3-10,19} ethoxylated urethanes,¹⁸ polyethylene glycols,^{13,15,19,20} poly(acrylic acid),^{16,17} poly(choline methacrylate),¹⁴ and polydiallyldimethylammonium chlo-

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ride,¹¹ *etc.* In recent years, extensive studies were concerned on the synthesis and solution properties of fluorocarbon-containing hydrophobically modified poly(acrylic acid) in our group. It was found that the rheological behavior of this kind of polyelectrolyte is governed by the competition between electrostatic repulsion and hydrophobic association. Therefore, the polymers exhibit quite different solution properties from their unmodified polymers. For instance, in semi-dilute solutions, addition of NaCl may cause a rapid increase in viscosity, while it reduces the solution viscosity for the unmodified polyelectrolyte.

Until now most studies have been focused on the solution properties in semi-dilute regime. Nothing has been done on the dilute solution properties of fluorocarbon-modified poly(acrylic acid), although there are several reports on hydrocarbon-modified water-soluble polymers.²¹⁻²⁵ In this paper, we discuss the dilute solution properties of fluorocarbon-containing hydrophobically modified poly(acrylic acid) in the presence of sodium chloride.

Experimental

Materials

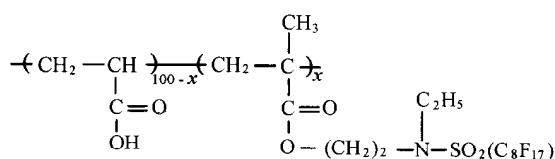
Acrylic acid (AA) was vacuum distilled before using. 2-(*N*-ethylperfluorooctanesulfoamido) ethyl methacrylate (FMA) kindly supplied by the 3M Co. was recrystallized from methanol twice and dried under vacuum to give white powder. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Benzene (A. R.) was distilled before using. Acetone, diethyl ether, ethanol (A. R.) and sodium chloride (A. R.) were used as received.

Polymer synthesis

The fluorocarbon-containing hydrophobically modified poly(acrylic acid) was synthesized by precipitation copolymerization of acrylic acid with hydrophobic comonomer (FMA) in benzene. Details of the synthesis are described as follows: Acrylic acid and a certain amount of FMA were put into a 50 mL of round-bottom flask, 30 mL of benzene was added to dissolve the monomers, then the flask was capped with a rubber stopper. 1.2 mL of AIBN solution (125 mg in 25 mL of

benzene) was injected into the flask. The solution was purged in a bath of ice water with dry pure nitrogen for 30 min and then moved into a $(50.0 \pm 0.5)^\circ\text{C}$ 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, diethyl ether was added into the flask to wash out the remained monomers and initiator. After filtering by 3 # sand-leach filter, white solid polymer powders were obtained. The polymers were vacuum dried at 50°C for at least 5 h. Unmodified poly(acrylic acid) was also synthesized in the same way as above without the comonomer. The final conversion was approximately 91%. The structure of the copolymer is shown in Scheme 1.

Scheme 1 Molecular structure of FMA copolymer



Viscometric measurements

The dilute solution properties of the copolymers were studied in their sodium salt form. The copolymer obtained above was dissolved in water and the pH value of the solution was adjusted to around 10 with NaOH. The polymer solution was then poured slowly into acetone to precipitate the copolymer. After vacuum dried at 50°C , the final polymer was in its sodium salt form, namely its neutralized form. The polymer sample is represented as follows: PNaAA is the unmodified polymer, FMA-50 is the copolymer of AA and FMA, which contains 0.5% FMA in molar fraction.

Viscometric measurements were carried out with an Ubbelohde viscometer at $(25.0 \pm 0.1)^\circ\text{C}$. The flow time of 0.02 mol/L, 0.04 mol/L, 0.08 mol/L, 0.16 mol/L, 0.32 mol/L NaCl solution are 120.77, 120.16, 120.49, 121.23, 121.77 sec, respectively. The polymer samples were dissolved in the NaCl solution and diluted with the same solution.

Viscosity data were calculated using Huggins equa-

tion shown as below:²⁶

$$\eta_{sp}/c = (t - t_0)/t_0c = [\eta] + k_H[\eta]^2c \quad (1)$$

where η_{sp} is the specific viscosity, η_{sp}/c is the reduced viscosity, c is the polymer concentration, t is the flow time of polymer solution, t_0 is the flow time of solvent, $[\eta]$ is the intrinsic viscosity and k_H is the Huggins coefficient.

Results and discussion

It is well known that, for polyelectrolyte, the relationship between reduced viscosity and polymer concentration depends very much upon the degree of ionization of the polyelectrolyte and on the ionic strength of the solution. In the solution of very low ionic strength, the plots of reduced viscosity versus polymer concentration ($\eta_{sp}/c \sim c$) show two extremes: a minimum at a high concentration region and a maximum at a low concentration region.²⁷ Thus it is difficult to determine the intrinsic viscosity of the polyelectrolyte. Fortunately, this difficulty can be overcome by using a method of "isoionic dilution".²⁸ According to this method, the total counterion concentration remains unchanged during the dilution of the solution. Therefore, the plot of η_{sp}/c versus c is in accordance with the Huggins equation.

Fig. 1 and Fig. 2 show typical plots of reduced viscosity, η_{sp}/c , as a function of polymer concentration in 0.02 mol/L and 0.32 mol/L NaCl solution. As expected, for both the unmodified and modified polyelectrolytes, the reduced viscosity decreases linearly as the polymer concentration decreases. At low NaCl concentration, the slope of the plot of the unmodified and the modified polyelectrolyte is very close to each other, but at high NaCl concentration, it is much lower for the unmodified than for the modified polyelectrolyte. Using

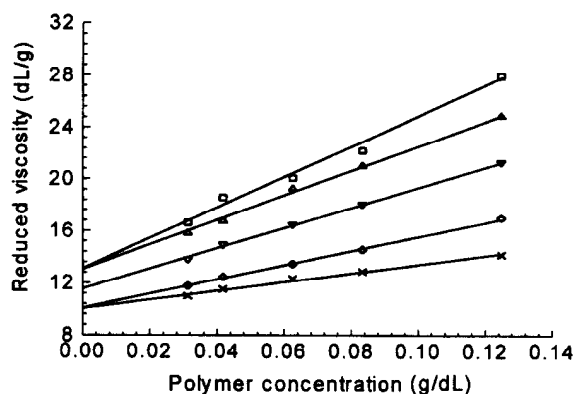


Fig. 1 Reduced viscosity versus polymer concentration of polymers in 0.02 mol/L NaCl solution. \times PNaAA, \square FMA-50, ∇ FMA-100, \diamond FMA-150, \triangle FMA-200.

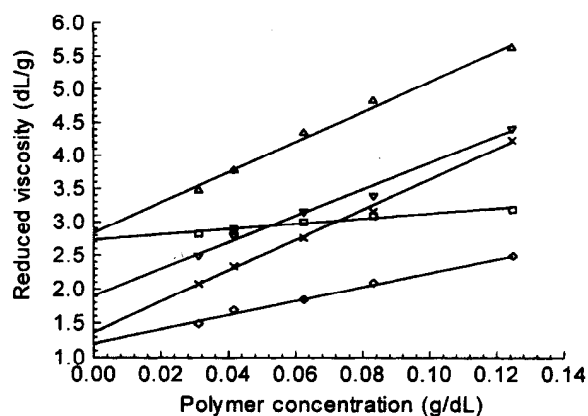


Fig. 2 Reduced viscosity versus polymer concentration of polymers in 0.32 mol/L NaCl solution. \square PNaAA, \triangle FMA-50, ∇ FMA-100, \diamond FMA-150, \times FMA-200.

the Huggins equation, we can get the intrinsic viscosity and the Huggins coefficient of the unmodified and the modified polyelectrolyte at different NaCl concentrations, which are shown in Table 1. The effects of NaCl concentration on the specific viscosity and the Huggins coefficient of the unmodified and modified polyelectrolytes are also depicted in Fig. 3 and Fig. 4, respectively.

Table 1 Intrinsic viscosity $[\eta]$ (dL/g) and Huggins coefficient k_H of the polyelectrolytes

Sample	0.02 mol/L NaCl		0.04 mol/L NaCl		0.08 mol/L NaCl		0.16 mol/L NaCl		0.32 mol/L NaCl	
	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H
PNaAA	10.00	0.36	7.76	0.49	5.47	0.59	3.52	0.72	2.73	0.52
FMA-50	13.11	0.62	9.76	0.71	7.57	0.68	4.68	1.32	2.83	2.62
FMA-100	11.51	0.57	8.68	0.55	5.94	0.86	4.26	1.30	1.90	4.84
FMA-150	10.16	0.53	6.82	0.74	4.31	1.33	2.21	3.82	1.21	6.66
FMA-200	12.87	0.56	9.31	0.65	6.10	1.03	3.05	2.95	1.35	10.37

It can be seen in Fig. 3 and Table 1 that, at low NaCl concentration, both the unmodified and the modified polymers exhibit similar values of $[\eta]$ and k_H . But as the NaCl concentration gets higher, the modified polymers show more pronounced decrease in $[\eta]$ and increase in k_H . For instance, when the NaCl concentration goes from 0.02 mol/L to 0.32 mol/L, the $[\eta]$ of PNaAA decreases from 10.00 to 2.73 dL/g, and the k_H increases from 0.36 to 0.52. For FMA-200, however, the $[\eta]$ decreases from 12.87 to 1.35 dL/g, while the k_H increases from 0.56 to 10.37.

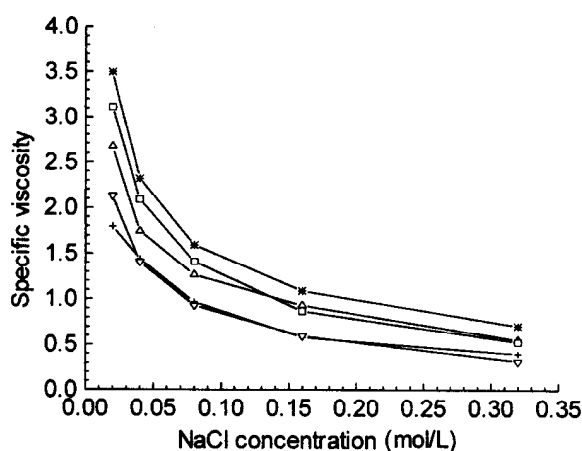


Fig. 3 Effect of NaCl concentration on the specific viscosity of polymers at the concentration of 0.125 g/dL. + PNaAA, * FMA-50, Δ FMA-100, ∇ FMA-150, \square FMA-200.

The concept of $[\eta]$ is used to represent the "effective hydrodynamic specific volume" of the polymer in solution. It may be regarded as the sum of effective hydrodynamic volumes of the separate, non-interacting molecules that make up a gram of polymer.²⁷ It depends on the molar mass, structure and conformation of the macromolecules, *etc.* It is well established that the conformation of polyelectrolyte is largely affected by the existence of low molecular weight electrolytes in the solution. The introduction of counter-ion by adding low molecular weight electrolyte such as NaCl screens the electrostatic repulsion between charged groups along the macromolecules. Thus the macromolecules assume more collapsed configuration, which results in the reduction of $[\eta]$. In dilute solution of hydrophobically modified polyelectrolyte, however, there exists a balance between electrostatic repulsion and intramolecular hydrophobic

association, the former leads to an extended configuration and the latter leads to a collapsed configuration. In dilute solutions of low NaCl concentration, the electrostatic repulsion is so strong that the intramolecular association is depressed. So the molecules of modified polymers show similar values of $[\eta]$ compared with the unmodified polymer. As the NaCl concentration gets higher, the electrostatic repulsion is depressed and the molecules become more flexible. Therefore, the intramolecular association becomes stronger and the molecules prefer a more collapsed configuration, which is reflected by the lower $[\eta]$.

This result is in good agreement with those reported by Iliopoulos *et al.*^{21,22} for dodecyl-modified poly(sodium acrylate). However, it was also observed that, for the sample modified with less hydrophobic octyl groups at high NaCl concentration, the $[\eta]$ was higher than that of unmodified polymer, and the Huggins coefficient took the value typical of nonassociating systems. He ascribed this phenomenon to the heterocontacts effect, which was unable to be screened by the weak hydrophobic aggregation effect. In other report, it was shown that the behavior of $[\eta]$ upon addition of salt was similar for the unmodified and hydrophobically modified chitosan.²⁴ It should be noted that, however, chitosan exhibits much weaker polyelectrolyte character than poly(sodium acrylate).

As is shown in Fig. 4, the Huggins coefficient increases with increase of NaCl concentration, and this increase becomes more significant at the NaCl concentration higher than 0.1 mol/L. Similar result has been reported by Iliopoulos *et al.* for dodecyl-modified poly(sodium acrylate)^{21,22} and Aubry *et al.* for the system of nonionic surfactant-hydrophobically modified (hydroxypropyl)-guar.²⁵ This behavior is in agreement with the general observation that k_H increases when the coil size decreases.²⁷ The value of k_H is universally used to estimate the strength of the interactions between polymer coils at finite polymer concentration. The higher value of k_H , the stronger intermolecular interaction among polymer coils.²⁵ In the case of hydrophobically modified polymer, the interaction between polymer coils is usually termed as the intermolecular hydrophobic association.

As discussed above, the $[\eta]$ of polyelectrolyte decreases with increase of NaCl concentration (shown in Fig. 3). The $[\eta]$ of polyelectrolyte is frequently found to be proportional to $C_s^{-1/2}$, which is given

below:^{27, 29-33}

$$[\eta] = [\eta]_e + kC_s^{-1/2} \quad (2)$$

where $[\eta]_e$ is defined as the intrinsic viscosity at infinite salt concentration, k is the constant, C_s is the salt concentration (the NaCl concentration in this article). It is found that both modified and unmodified polymers obey this law in the salt concentration regime studied. Fig. 5 displays the $[\eta] \sim C_s^{-1/2}$ relationship for PNaAA and FMA-200. Using equation (2), we can calculate the $[\eta]_e$ and k of these polymers, which are shown in Table 2.

Table 2 $[\eta]_e$ and k of the polyelectrolytes

Sample	$[\eta]_e$ (dL/g)	k	R
PNaAA	0.266	1.42	0.995
FMA-50	-0.004	1.91	0.991
FMA-100	-0.541	1.76	0.991
FMA-150	-1.873	1.71	0.999
FMA-200	-2.195	2.19	0.995

It can be seen from Table 2 that the values of $[\eta]_e$ of modified polyelectrolytes are much lower than that of unmodified polyelectrolyte and are negative. In the solution of infinite salt concentration, the electrostatic repulsion is fully screened. Therefore, the molecules prefer such a collapsed configuration due to the strong intramolecular hydrophobic association that the extrapolated $[\eta]_e$ values become negative.

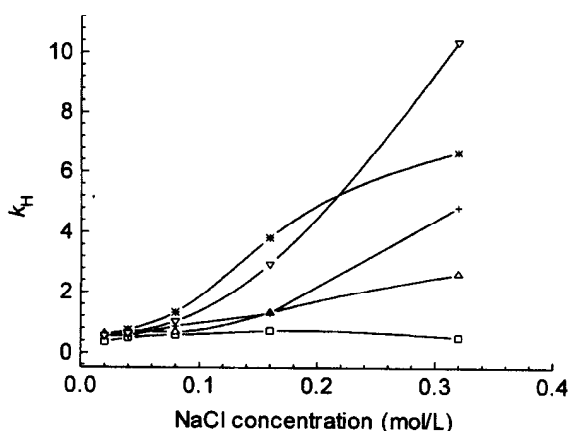


Fig. 4 Effect of NaCl concentration on the Huggins coefficient of polyelectrolytes. \square PNaAA, \triangle FMA-50, $+$ FMA-100, $*$ FMA-150, ∇ FMA-200.

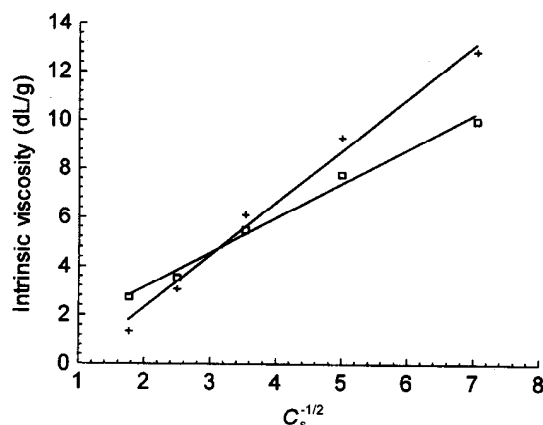


Fig. 5 Intrinsic viscosity as a function of reciprocal square root of NaCl concentration. \square PNaAA, $+$ FMA-200.

Conclusion

The intrinsic viscosity of hydrophobically modified poly(sodium acrylate) in aqueous NaCl solutions is governed by the competition of two kinds of interactions: the electrostatic repulsion between negative carboxyl groups and intramolecular hydrophobic association between fluorocarbon moieties. At low NaCl concentration, the electrostatic repulsion is strong enough to suppress the intramolecular association. Therefore, the modified polyelectrolyte displays similar intrinsic viscosity to the unmodified polyelectrolyte. At high NaCl concentration, however, the electrostatic repulsion is screened and both the intramolecular association and the intermolecular association are enhanced. As a result, the intrinsic viscosity of the modified polyelectrolyte decreases and the Huggins coefficient, which reflects the intermolecular association between polymer coils in solutions of finite concentration, increases with increase of the NaCl concentration.

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