Interaction of Fluorocarbon Containing Hydrophobically Modified Polyelectrolyte with Nonionic Surfactants

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The interaction of fluorocarbon containing hydrophobically modified polyelectrolyte (FMPAANa) with two kinds of nonionic surfactants (hydrogenated and fluorinated) in a semidilute (0.5 wt%) aqueous solution had been studied by rheological measurements. Association behavior was found in both systems. The hydrophobic interaction of FMPAANa with fluorinated surfactant (FC171) is much stronger than that with hydrogenated surfactant (NP7.5) at low surfactant concentrations. The interaction is strengthened by surfactants being added for the density of active junctions increased. Whereas distinct phenomena for FC171 and NP7.5 start to be found as the surfactants added over their respective certain concentration. The interaction of polyelectrolyte with fluorinated surfactant increases dramatical ly while that with hydrogenated surfactant decreases.

Keywords fluorocarbon-modified polyelectrolyte, nonionic surfactant, fluorinated, rheology

Introduction

Water-soluble polymers have gained considerable attention in the past decades because of their widely industrial applications and friendliness to environment.[1-3] Especially hydrophobically modified water-soluble polymers (HMWSP) which bear a small amount of hydrophobes on the hydrophilic backbone can form associative network through interaction with surfactants added in their aqueous solution.[4,5] The surfactant molecules are usually absorbed onto the microdomains or form micelles by self-aggregation, thus the interaction can be enhanced or reduced upon addition of surfactants, which can be reflected by significant change of rheological properties. Interactions of hydrophobically modified polymers with surfactants depend on the molecular structures and properties of both surfactants and polymers.

As a significant kind of the HMWSP, the interaction of hydrophobically modified polyelectrolytes (HMPE) with surfactants has been studied. As yet, most studies have been focused on the interaction between hydrogenated-modified polyelectrolytes and conventional hydrogenated surfactants, and few works have been done on the interaction of fluorocarbon-modified polyelectrolytes (FMPE) with hydrogenated or fluorinated surfactants.[4-5]

It is well known that fluorocarbon groups are both hydrophobic and lipophobic, which seems to suggest that interaction of FMPE with hydrogenated surfactant is different from that with fluorinated surfactant. Published papers have covered the difference between FMPE and HMPE in the association with hydrogenated surfactant.[4-5] For the very FMPE, however, only a few comparison in its interaction with hydrogenated and fluoronated surfactant has been mentioned.[5b] Recently we extended our previous studies to the interaction of two kinds of nonionic surfactants [hydrogenated (NP7.5) and fluorinated (FC171)] with solution of fluorocarbon modified poly(sodium acrylate) and found some interesting behavior,[6,7] there may exist a different mechanism in the association of NP7.5 and FC171 with FMPE.

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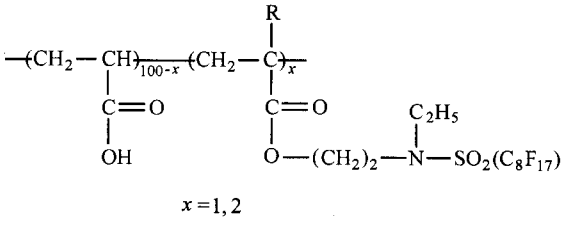
Experimental

Materials

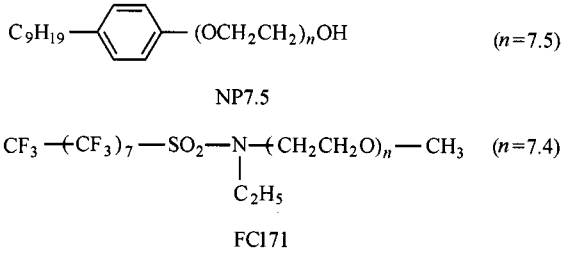
The fluorocarbon-containing hydrophobically modified poly(acrylic acid) was synthesized via precipitation copolymerization of acrylic acid with hydrophobic comonomer (FMA, Scheme 1) in benzene. Details of the synthesis were described previously.[6] The aqueous solution of above copolymers was alkalized to pH = 10 with NaOH (1.0 mol/L), precipitated in ethanol (95%) and dried at 50 ℃ under vacuum for 24 h to afford the copolymer sample in its sodium salt form The copolymers are represented as FMA followed with a number. For instance, FMA-200 means that FMA was used as the hydrophobic comonomer and its feed fraction was 2.0 mol% (Elemental analysis: FMA 1.84 mol% in copolymer). FC171 [*N*-ethyl-*N*-polyoxyethylene ethanol perfluorooctane sulfonamide (n = 7.4)] is used as received from 3M Co.. NP7.5 [polyethylene glycol mono-*p*-nonylphenyl ether (n = 7.5)] is donated by TCL Co.. Molecular structures of two surfactants are shown in Scheme 2.

Scheme 1 Structure of FMA copolymer



x = 1, 2

Scheme 2 Structure of nonionic surfactant



Characterization

The compositions of neutralized copolymers were determined by anionic chromatography on a Dionex 2010I instrument and elemental analyses. All the Brookfield viscosity measurements were performed with a Brookfield viscometer with a shear rate of 0.4 s^{-1} at (25 ± 0.1) ℃. Rheological experiments of polymer solutions were carried out on a Haake Rheostress RS 75 rheometer equipped with a 2°/(6 cm) cone-plate geometry. A C60/2Ti sensor was adopted and the gap was kept at 0.108 mm. In the oscillatory stress sweeps, the frequency was fixed at 1 Hz, All measurements were conducted at (25 ± 0.1) ℃.

Results and discussion

Effect of surfactants on viscosity

As shown in Fig. 1, surfactant concentration has a significant effect on the viscosity of coplymer solution. Very weak interaction is found in FMA-100 + FC171 systems, which is ascribed to the low content of fluorocarbon groups in FMA-100. For 0.5 wt% FMA-200, solution viscosity becomes more sensitive to the addition of FC171.

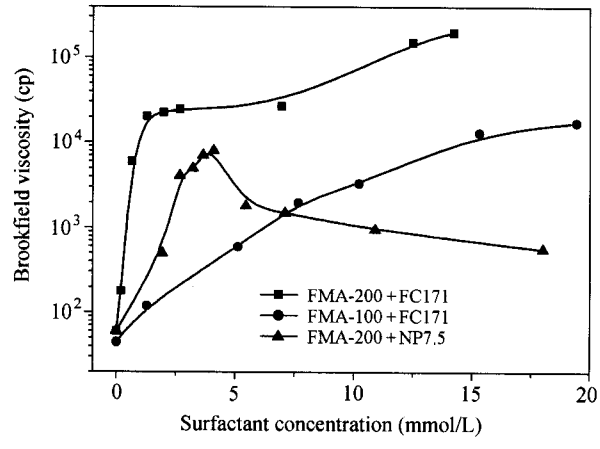


Fig. 1 Effect of nonionic surfactant on the Brookfield viscosity of the copolymer at 0.5 wt% in aqueous solution (shear rate: 0.4 s^{-1}).

The FMA-200 solution without surfactant has a viscosity of about 60 cp. The solution viscosity starts to increase with NP7.5 added, up to a pronounced maximum value at about 8000 cp, and then decreases at concentration higher than 3 mmol/L, where the molar ratio of fluorocarbon group to NP7.5 is about 1/4. However, different phenomenon appears for the FMA-200 + FC171 system. In the investigated range of FC171 concentration, no maximum viscosity value can be found. In addition to the

relatively sharp increase of solution viscosity with the FC171 concentration increasing to the 2 mmol/L, a successively relatively slow increase in viscosity was observed. As the FC171 concentration continuously increases to 15 mmol/L, where the molar ratio of FC171 to fluorocarbon group reaches about 20, the solution viscosity is higher than 200000 cp, which is about thousands times of the starting value.

The enhancement in viscosity can be ascribed mainly to the strong interaction in FMA-200-surfactants system and three-dimensional networks formed. NP7.5 and FC171 seem to follow different interacting mechanism as their concentrations reach high values. The aggregation for copolymer-surfactant system was proposed as shown in Fig. 2. The viscosity of FMA solution (0.5 wt%) without any surfactant may be originated from hydrophobic associations of fluorocarbon groups. Upon the addition of NP7.5 or FC171, the surfactant moleculars absorbed onto the fluorocarbon groups induce the formation of mixed micelles, which cross-link the copolymer chains physically and result in the increased viscosity.

Further addition of surfactant leads to two different consequences for NP7.5 and FC171, respectively. When the molar ratio of NP7.5 to fluorocarbon group is over 4, perfect surfactant micelles are inclined to form, which replace the hydrophobic groups locating on the polymer chain. Hence the effective cross-linking between polymer chains is destroyed and the viscosity of the system decreases. However, larger micelles are speculated to form in the FC171 system, giving fluorocarbon groups more association sites. Thus hydrophobic associations with greater strength are formed resulting in the increase of viscosity. All above can be confirmed with the data shown in Fig. 3.

Effect of surfactants on modulis

Oscillatory stress sweep on the above solution supplies us the storage and loss moduli G′ and G″, which correspond to elasticity and viscosity of viscoelastic solution respectively.[4] Figs. 4 and 5 compare the difference in dynanmic rheological behavior for NP7.5 and FC171. As shown in Fig. 4, the storage moduli G′ of FMA-200 + NP7.5 (2.2 mmol/L) system is much larger than that of FMA-200 + NP7.5 (1.1 mmol/L), which indicates the number of joint increasing with NP7.5 added in the low surfactant range. However, when the NP7.5 is added further over a certain level (> 3 mmol/L), the number of joints decreases with increasing NP7.5 concentration. While for FMA-200 + FC171 systems, G′ and G″ of FMA-200 + FC171 (15.6mmol/L) are larger than those of FMA-200 + FC171 (2.2 mmol/L). It demonstrates that the number of junctions in the FMA200 + FC171 systems increases with FC171 added. The FMA-200 + FC171

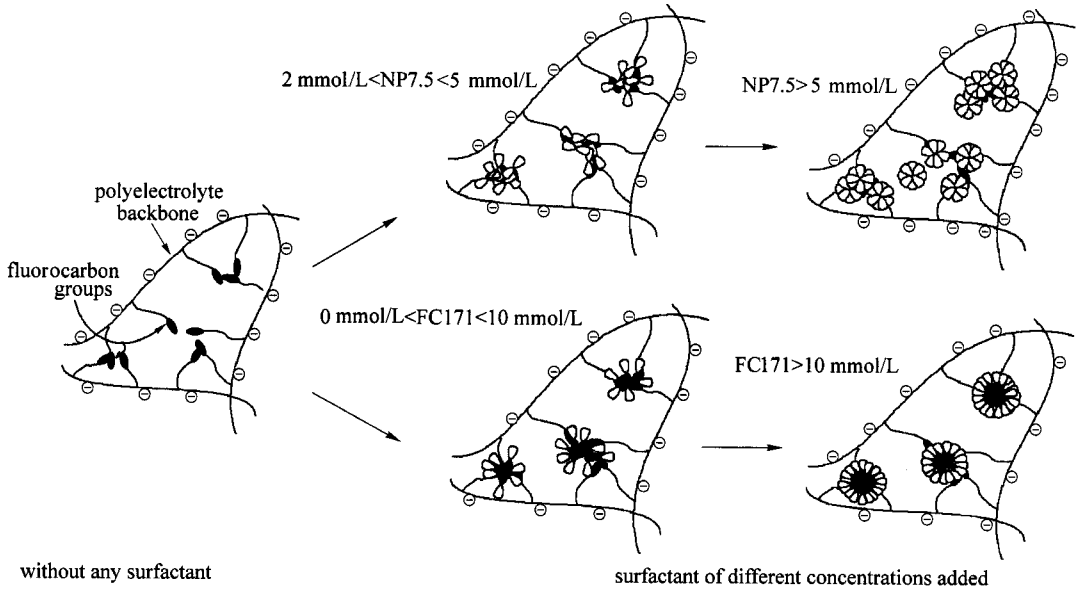


Fig. 2 Interactional mechanism of copolymer with surfactants NP7.5 and FC171.

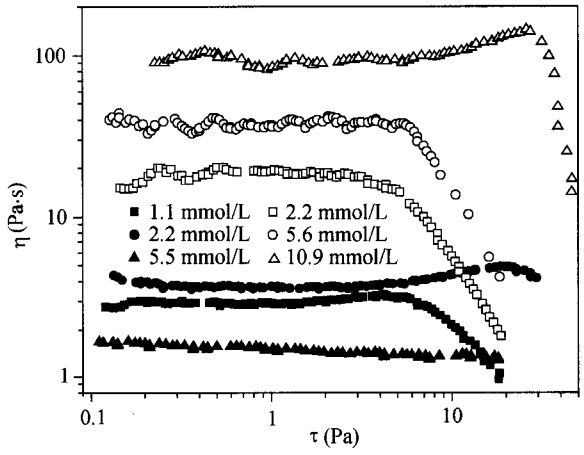


Fig. 3 Steady shear viscosity of the FMA-200 in FC171 (open points) and NP7.5 (filled points) solution at 0.5 wt% as a function of shear stress.

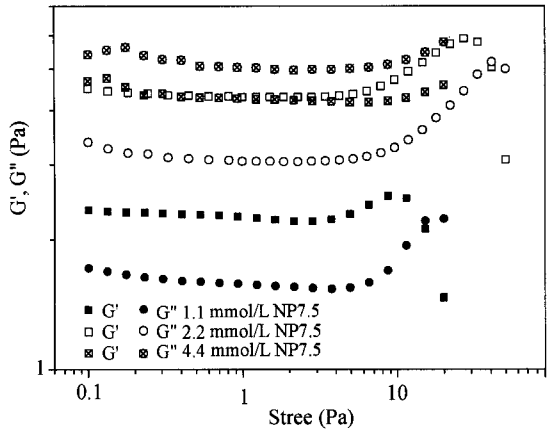


Fig. 4 Storage and loss modulus at 1 Hz of the FMA-200 solution (0.5 wt%) with surfactant NP7.5 as a function of stress.

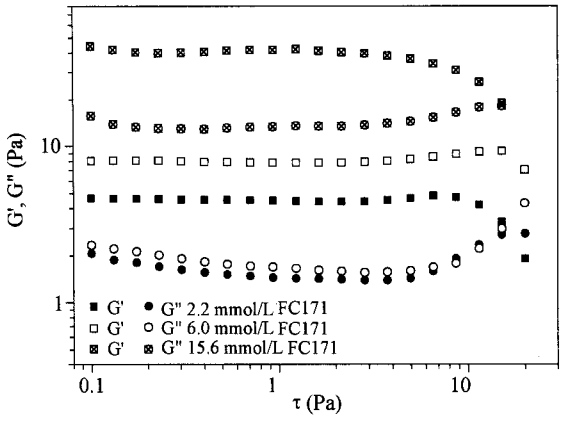


Fig. 5 Storage and loss modulus at 1 Hz of the FMA-200 solution (0.5 wt%) with surfactant FC171 as a function of stress.

system (Fig. 5) displays a typical viscoelastic fluid behaviorfor G′ being higher than G″ in the entire range of stress meseasured. Based on rubber elasticity that is extended to transient networks or reversible physical bonds, the G′ value is related to the density of mechanically active junctions, thus the increase of G′ value indicates an augment in the number of joint due to the interpolymer associations increased. On the other side, the increase of G″ value indicates an increase in the effective volume occupied by the network structure in solution.

Therefore, the oscillatory sweep experiments well confirm the proposed mechanism depicted in Fig. 2. Aggregates with wormlike micelles structure are formed at high concentration of FC171 because of their strongly viscoelastic and optically clear micellar phase. While for NP7.5, sequential addition of NP7.5 just induces the junction-breaking and a structural transformation into surfactant micelles may be formed for their low viscosity. This is just what the difference between NP7.5 and FC171 lies in the association with FMPAA.

Conclusions

The results mentioned above show the interaction of fluorocarbon-modified poly(sodium acrylate) with nonionic surfactants (hydrogenated and fluorinated). The fluorocarbon surfactants have stronger interaction with copolymers than with hydrogenated surfactants. The effects of two kinds of surfactants are quite different from each other, espicially at high surfactant concentration, which are likely related to the mechanism of forming micelles due to the different substituents.

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