

SYNTHESIS AND CHARACTERIZATION OF A NOVEL FLUORINE-CONTAINING HYDROPHOBICALLY ASSOCIATING POLYMER*

Jin Yang and Wei-yuan Huang**

*Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences, Shanghai 200032, China*

Abstract In this article, the synthesis and characterization of a novel fluoromonomer and its copolymer with acrylamide is reported. 2-perfluoroamyl-4-hydroxylquinoline **2** was synthesized from ethyl 2, 2-dihydroperfluoroheptanoate in high yields. The monomer **4** was then synthesized from **2** in two steps readily in high yields. Synthesis and characterization of copolymers of acrylamide (AM) and the fluoromonomer were investigated. The composition and intrinsic viscosity of these copolymers were studied. It was found that the rheological properties of aqueous solutions of polyacrylamide were modified significantly when a small proportion of the fluoromonomer **4** was incorporated on investigating the viscosity-concentration profiles, pseudoplasticity of these solutions and the effect of the presence of surfactant. These results could be explained by the hydrophobic association of the fluorocarbon segments in the aqueous solutions of these copolymers.

Keywords Hydrophobically associating polymer, Fluorine-containing acrylate, Perfluoroalkylation with $R_fI/Na_2S_2O_4$

INTRODUCTION

Hydrophobically associating polymers (HAP) have been investigated widely and thoroughly as it is a new approach to aqueous fluid mobility control and its interesting rheological properties, especially for its potential application in oil drilling and coating etc^[1-3]. Fluorocarbons possess substantial hydrophobicity in comparison with the corresponding hydrocarbons, which is reflected in the low values of their cohesive energy density and surface energy. In recent years, fluorine-containing hydrophobically associating polymers (FHAP) have been studied extensively^[4, 5]. It was found that the hydrophobic associations occurring between the fluorocarbon groups were much stronger than the interaction of the corresponding hydrocarbon groups and depended on the length of the fluorocarbon chain. This also indicated that the microstructure of fluorine-containing hydrophobically associating polymer in aqueous solution may be different from its counterpart. Therefore it is interesting to study the microstructure of FHAP's aggregation and association in aqueous solution, in order to further understand the behavior of the fluorine-containing hydrophobically association in aqueous solution.

Fluorescence spectroscopy has been widely used in studying the microstructure of polymer in solution^[6-8]. The methods of fluorescence spectrum research have concentrated on the synthesis of

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** Corresponding author: Wei-yuan Huang (黄维垣), E-mail: wyhuang@pub.sioc.ac.cn

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HAP bearing fluorescence probe in the backbone or doping the HAP aqueous solution with a fluorescence probe. Until now there are only a few reports on the study of fluorescence spectroscopy on fluorine-containing hydrophobically associating polymers in aqueous solution, in which a fluorine-containing fluorescence probe was synthesized and used to dope the FHAP aqueous solution^[9]. In this article, we present the detailed results on the synthesis and some of the properties of a novel fluorine-containing hydrophobically associating polymer bearing a fluorescence probe.

EXPERIMENTAL

General, Reagents and Solvents

Acrylamide (ultra pure electrophoresis grade) was used after recrystallizing twice from acetone. IR spectra were recorded with a Shimadzu IR-440 spectrometer using liquid films and KBr pellets for solids. ¹H-NMR spectra were recorded on Varian EM-360A and AMX-300 spectrometers using TMS as the internal standard. ¹⁹F-NMR spectra were recorded on an EM-360L spectrometer at 56.4 Mz using TFA as the external standard. In ¹⁹F-NMR spectra, chemical shifts were positive for upfield shifts. Mass and HRMS spectra were taken on a Finnigan GC-MS-4021 spectrometer. Elemental analysis data were obtained by the Elemental Analysis Group of SIOC.

Synthesis of Ethyl 2, 2-dihydroperfluorooctanoate(1)^[10]

A mixture of 50 mmol C₆F₁₃I, 6 g ethyl vinyl ether (83 mmol), 12 g Na₂S₂O₄, 6 g NaHCO₃, 100 mL CH₃CN and 100 mL water was reacted to give 2-perfluorohexylacetaldehyde which was used directly without purification in the following synthesis.

Into a solution of 20 mmol 2-perfluorohexylacetaldehyde in 40ml acetone was added a mixture of 4.0 g (40 mmol) chromium trioxide, 4 mL concentrated sulfuric acid and 20 mL water while maintaining the temperature of the reaction mixture below 10°C with external cooling. After an overnight stirring at room temperature, 5 mL 2-propanol was added dropwise to destroy the excess oxidizing reagent. Then 5 mL hydrochloric acid (6 mol/L) was added to the resulting mixture which was extracted with ether. The etheric extract was dried over anhydrous Na₂SO₄. On removal of the solvent by distillation, the residual mass was not purified and was used in the next step directly.

A mixture of 20 mmol 2-perfluorohexylacetic acid, 10 mL EtOH, 20 mL benzene and 0.5 g *p*-toluenesulfonic acid was stirred under reflux for 6 h. The reaction mixture was diluted with 40 mL water and extracted with ether. The combined organic layer was washed with 5% NaHCO₃ and saturated aqueous NaCl solutions and then dried over anhydrous Na₂SO₄. The crude product was distilled under reduced pressure to give ethyl 2, 2-dihydroperfluorooctanoate with 65% yield.

¹H-NMR (CDCl₃): δ_H = 1.28 (3H, *t*, —CH₃), 3.15 (2H, *t*, ³J_{HF} = 18.0Hz, —CF₂CH₂—), 4.22 (2H, *q*, —CH₂O—); ¹⁹F-NMR (CDCl₃): δ_F = 4.8 (3F, *s*, CF₃), 36.2 (2F, *s*, —CF₂—), 45.9(4F, *m*, —CF₂—), 49.8(2F, *s*, —CF₂CF₃)

Preparation of Compound 2 (2-Perfluoroamyl-4-Hydroxyl Quinoline)

A mixture consisting of 5 mmol of ethyl 2, 2-dihydroperfluorooctanoate, 7.5 mmol of aniline, 15 mmol of Et₃N and 5 mL of CH₃CN was stirred at 70°C for 6 h. The mixture was then neutralized with aqueous 1 mol/L HCl solution and extracted with ether. The etheric layer was washed with saturated NaCl solution and dried over anhydrous Na₂SO₄. After the removal of the solvent, the mixture of enamine and imine is not purified and is used in the next step directly.

The mixture of enamine and imine (1 g) and polyphosphoric acid (PPA) (10 g) was stirred at 170°C for 2 h. After cooling to room temperature, it was neutralized with aqueous 2 mol/L NaOH solution and extracted with ether. The organic layer was washed with saturated NaCl solution and dried over anhydrous Na₂SO₄. The removal of solvent followed by recrystallization from ethanol

gave the pure 2-perfluoroamyl-4-hydroxyl quinoline with 82% yield.

$^1\text{H-NMR}$ ($\text{DMSO-}d_6$): $\delta_{\text{H}} = 7.04$ (1H, s, C3-H), 7.52 ~ 8.24 (4H, m, ArH); $^{19}\text{F-NMR}$ ($\text{DMSO-}d_6$): $\delta_{\text{F}} = 4.8$ (3F, s, CF_3), 36.2 (2F, s, $-\text{CF}_2-$), 45.9 (4F, m, $-\text{CF}_2-$), 49.8 (2F, s, $-\text{CF}_2\text{CF}_3$). MS (m/e): 413 (M^+ , 74.33), 394 (M^+-OH , 15.93), 194 (100). IR (film): 3440 (OH), 1620, 1520, 1220, 1120; HRMS ($\text{C}_{14}\text{H}_6\text{ONF}_{11}$): cal.: 413.0274; found: 413.0240

Preparation of Compound 3

0.8 g of $\text{BrCH}_2\text{CH}_2\text{OH}$ was added dropwise to a mixture of 2-perfluoroamyl-4-hydroxyl quinoline 1.2 g (3 mmol), K_2CO_3 1.5 g (6 mmol) and NaI (1 mol%) in 20 mL acetone with stirring at room temperature. The mixture was then stirred under reflux. TLC monitoring showed that the reaction was completed in 7 h. After cooling to room temperature, 20 mL water was added and the mixture was extracted with ether. The organic layer was washed with saturated NaCl solution and dried over anhydrous Na_2SO_4 . Removal of solvent followed by column chromatography separation gave compound 3 with 87% yield.

$^1\text{H-NMR}$ (CD_3OD): $\delta_{\text{H}} = 3.75$ (2H, t, $-\text{CH}_2\text{O}-$, $^3J_{\text{HH}} = 4.1$ Hz), 4.20 (2H, t, $-\text{CH}_2\text{O}-$, $^3J_{\text{HH}} = 4.1$ Hz), 6.9 (1H, s, C3-H), 7.3~8.24 (4H, m, ArH); $^{19}\text{F-NMR}$ (CD_3OD): $\delta_{\text{F}} = 3.0$ (3F, s, CF_3), 34.8 (2F, s, $-\text{CF}_2-$), 44.8 (4F, m, $-\text{CF}_2-$), 49 (2F, s, $-\text{CF}_2\text{CF}_3$). MS (m/z): 457 (M^+ , 4.33), 411 ($\text{M}^+-(\text{CH}_2)_2-\text{OH}+1$, 23.93), 194 (100). IR (film): 2900, 1600, 1580, 1240, 1180 cm^{-1} .

Elemental analysis ($\text{C}_{16}\text{H}_{10}\text{NO}_2\text{F}_{11}$): calc.: C 42.03, H 2.20, N 3.06, F 45.70; found: C 44.38, H 2.24, N 2.82, F 43.08.

The product was not further purified and was used directly for the synthesis of the monomer 4.

Preparation of Compound 4

A mixture of 2 mmol compound 3 and 2.4 mmol anhydrous Et_3N dissolved in 20 mL anhydrous THF was stirred with external ice-water bath cooling. 2.4 mmol acryloyl chloride dissolved in 5 mL anhydrous THF was added dropwise. After addition, the mixture was stirred at 0°C for 15 h. TLC monitoring showed that the reaction was completed, 20 mL water was then added and the mixture was extracted with ether. The organic layer was washed with saturated NaCl solution and dried over anhydrous Na_2SO_4 . Removal of solvent followed by column chromatography separation gave the pure compound 4 with 55% yield.

$^1\text{H-NMR}$ (CD_3OD): $\delta_{\text{H}} = 4.45$ (2H, t, $-\text{CH}_2\text{O}-$, $^3J_{\text{HH}} = 4.1$ Hz), 4.65 (2H, t, $-\text{CH}_2\text{O}-$, $^3J_{\text{HH}} = 4.1$ Hz), 5.82 (1H, dxd, $=\text{CH}_2$, $^3J_{\text{HH}} = 10.3$ Hz), 6.1 (1H, m, $-\text{CH}=\text{CH}_2$), 6.45 (1H, dxd, $=\text{CH}_2$, $^3J_{\text{HH}} = 10.3$ Hz), 7.0 (1H, s, C3-H), 7.3 ~ 8.24 (4H, m, ArH); $^{19}\text{F-NMR}$ (CD_3OD): $\delta_{\text{F}} = 3.0$ (3F, s, CF_3), 34.8 (2F, s, $-\text{CF}_2-$), 44.8 (4F, m, $-\text{CF}_2-$), 49 (2F, s, $-\text{CF}_2\text{CF}_3$). MS (m/z): 511 (M^+ , 0.86), 438 ($\text{M}^+-\text{OCCH}=\text{CH}_2+2$, 1.17), 99 (100). IR (film): 2900, 1730, 1600, 1240, 1200, 1160, 1120 cm^{-1} .

Elemental analysis ($\text{C}_{16}\text{H}_{10}\text{NO}_2\text{F}_{11}$): calc.: C 44.63, H 2.37, N 2.74, F 40.87; found: C 45.09, H 2.50, N 2.51, F 40.61.

Copolymerization of Monomer 4 and Acrylamide

The polymerization was carried out by dispersion of 2.1 g acrylamide and varying amounts of fluorine-containing comonomers 4 in a 50 mL capped round-bottom flask containing 20 mL deionized water, 2 mL acetone and 0.12 ~ 0.25 wt% of the surfactant, ammonium perfluorooctanoate. After purging the solution with nitrogen for 30 min, 0.5 mol% of an ammonium persulfate solution was injected into the rapidly stirred contents in the flask. Each polymerization was carried out for 24 h at $50 \pm 1.0^\circ\text{C}$. The contents of the flask was diluted with several volumes of deionized water to dissolve the gels which was then precipitated out by pouring the resulting aqueous solution into 200 mL acetone. The precipitate was filtered and dried in a vacuum oven at 40°C for 24 h to give the polymers.

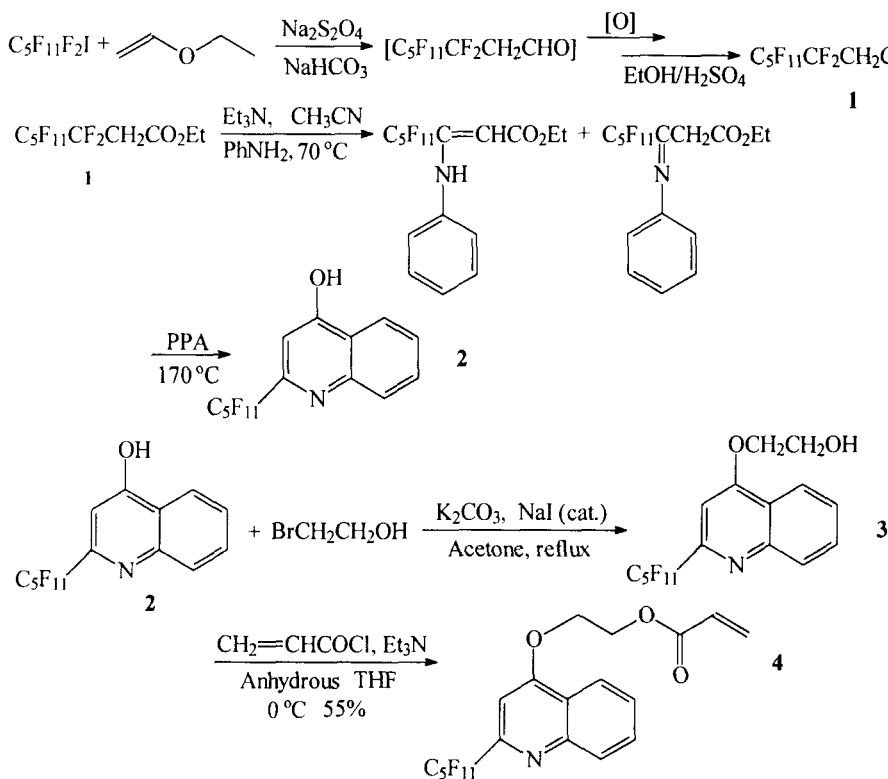
Measurement and Characterization

The fluorine contents of these copolymers were determined by anionic chromatography, the instrument is Dionex 2010i.

The solid polymers were dissolved in deionized water for subsequent viscosity measurement. The intrinsic viscosity was determined using a capillary viscometer at $30 \pm 0.5^\circ\text{C}$. The Brookfield viscosity was determined using a Wells Brookfield viscometer at room temperature. The Brookfield viscosity (cp) and shear rate were obtained by directly using the range table supplied by the manufacturer.

RESULTS AND DISCUSSION

In our laboratory, we developed a convenient method for the perfluoroalkylation of vinyl ether with perfluoroalkyl iodides initiated with $\text{Na}_2\text{S}_2\text{O}_4/\text{NaHCO}_3$ reagent system as a key step in the synthesis of 2, 2-dihydroperfluoroalkanoic acid ester **1**, which was then used as the starting material for the synthesis of the novel fluorine-containing monomer, as showed in Scheme 1^[11], thus:



Scheme 1

According to Schulz *et al.*^[12], the presence of a hydrophilic spacer between the polymer backbone and the hydrophobic group in the side-chain is essential to side-chain hydrophobically associating polymers. The hydrophilic spacer can promote the association of hydrophobic group in aqueous solution. So the hydrophilic spacer $-\text{OCH}_2\text{CH}_2-$ was introduced by reacting $\text{BrCH}_2\text{CH}_2\text{OH}$ with compound **2** in the presence of a base to give compound **3**. In the reaction, the use of catalytic amount of NaI is essential for the formation of O-alkylation product rather than the

N-alkylation. The titled fluoromonomer **4** was then synthesized by esterification of compound **3** with acryloyl chloride in the presence of Et₃N in high yields.

Then we studied the copolymerization of fluoromonomer **4** with acrylamide. A series of copolymers were obtained using ammonium perfluorooctanoate as an added surfactant. The detailed results are shown in Table 1.

Table 1. The results and condition of polymerization

Entry No.	The content of fluoromonomer 4 in the monomer feed (mol%)	Conversion (%)	The fluorine content of the polymer (wt%)*	The content of Fluoromonomer 4 in the polymer (mol%)**
CP-F5-A	1	96	1.25	0.44
CP-F5-B	0.5	98	0.82	0.28
CP-F5-C	0.1	100	0.26	0.09
CP-F5-D	0.05	100	0.16	0.05
PAM	---	100	---	---

* The fluorine content (wt%) was determined by anionic chromatography

** The content of fluoromonomer **4** in the polymer was calculated based on: the content of monomer **4** in the polymer (mol%) = (71F%)/(209~440F%), F% = the fluorine content of the polymer (wt%)

These results indicated that under the above polymerization condition, fluoromonomer **4** could be introduced into the copolymer successfully, The conversions of fluoromonomer **4** were quite good.

Then the rheological properties of the polymers were investigated. First, the rheological properties of the dilute solutions of these polymers were investigated, the intrinsic viscosities of the polymers were determined by capillary viscometer at 30° and the results are shown in Table 2.

Table 2. The intrinsic viscosities of the polymers

Entry No.	$[\eta]$ (dL/g)
CP-F5-A	2.79
CP-F5-B	3.03
CP-F5-C	3.14
CP-F5-D	4.20
PAM	2.71

Comparison of copolymers and homopolymer, shown that under comparable condition of polymerization, the intrinsic viscosities of the copolymers were greater than that of the homopolymer. These higher values of $[\eta]$ may seem to reflect the presence of hydrophobic association even at a very low concentration of the copolymers. Dynamic light scattering investigations on some of fluorine-containing hydrophobically associating polymers appear to confirm residual association at concentration around 100^[13]. The intrinsic viscosity of the copolymers versus the fluoromonomer content in the copolymers was shown in Fig. 1.

The higher content of fluoromonomer in the copolymers was accompanied by the lower values of intrinsic viscosity. This indicated that the latter may not be related only to the difference in molecular weights of the copolymers but also related to the different types (intermolecular or intramolecular association) of hydrophobic association of the fluoroalkyl group in the copolymers in dilute solution. Namely, copolymers with lower fluoromonomer content seem to favor intermolecular association of the fluorocarbon segments, whereas that with increasing fluoromonomer content favor intramolecular association.

Then, the rheological properties of the polymers in semi-dilute solutions were investigated. The Brookfield viscosities versus the fluoromonomer content in the copolymers were studied. Figure 2 shows that the Brookfield viscosities decreased with increasing content of fluoromonomer in the copolymers. These results were similar to that shown in Fig. 1. Therefore this further

supports the assumption that there are two different models (intermolecular or intramolecular association) of hydrophobic association of fluoroalkyl group in dilute or semi-dilute solution.

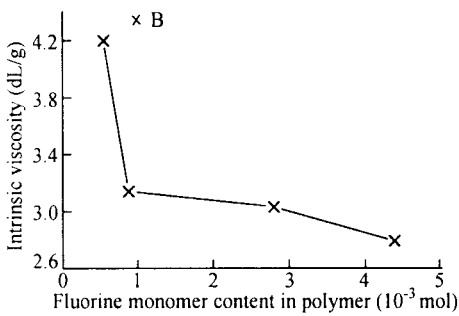


Fig. 1 The relationship between intrinsic viscosity and fluoromonomer content in polymer in dilute solutions

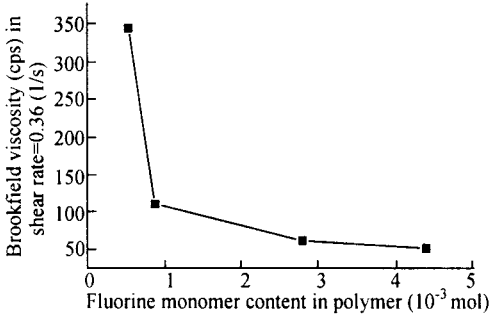


Fig. 2 The relationship between Brookfield viscosity and fluoromonomer content of the copolymers in semi-dilute solutions

As typical hydrophobically associating polymers, the Brookfield viscosities increased dramatically with the increasing of the concentration of the polymers in semi-dilute solution. The relationship between viscosity and concentration is non-linear in contrast to the linear one for the relationship for non-HAP. As shown in Fig. 3, All the copolymer solutions became more viscous with increasing concentration compared to that of the homopolymer (PAM, polyacrylamide) due to the presence of hydrophobic associations between fluoroalkyl groups in the copolymer. On the other hand, there was a linear relationship between the Brookfield viscosities and the concentration of the homopolymer (PAM). The viscosifying effect was most pronounced in the case of the copolymer with the lowest fluoromonomer content (CP-F5-D). This suggests that there is a higher tendency for the fluoroalkyl moieties of these copolymers to associate intermolecularly. The presence of hydrophobically association of fluoroalkyl groups is further supported by the viscosity-concentration profile.

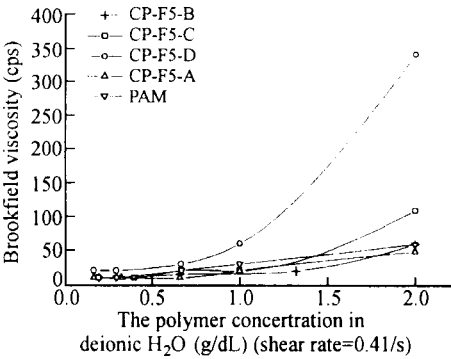


Fig. 3 The relationship between Brookfield viscosity and the polymer concentration in deionized water
Shear rate = 0.4 1/s

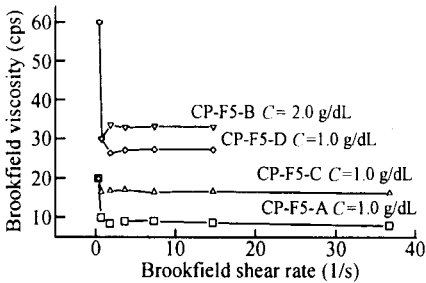


Fig. 4 The relationship between Brookfield viscosity and shear rate in aqueous solution

The solutions of all these copolymers appear to be quite pseudoplastic as shown in Fig. 4. The very sharp decrease in viscosity with shear rate is again consistent with the existence of network-like loose structures held together by the relatively weak hydrophobic interactions that would be expected to be disrupted readily upon application of shearing. Of special interest is the fact that upon removal of shearing the viscosity of the copolymers solutions completely recovers their

original low shear value. This result is consistent again with the reversible cleavage of the hydrophobic "bond" holding the network together.

Additional evidence for intermolecular hydrophobic association is provided by the effect on the Brookfield viscosity of a typical copolymer CP-F5-D by addition of fluorine-containing surfactant, which was shown in Fig. 5.

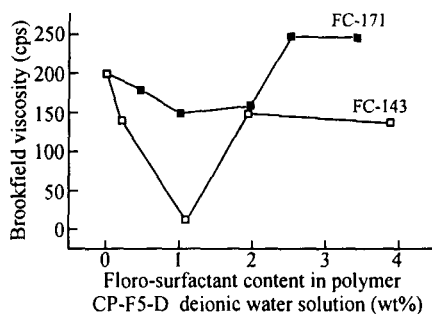
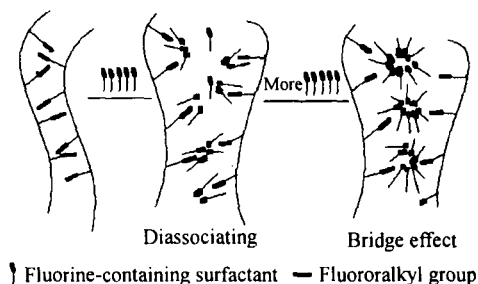


Fig. 5 The relationship between Brookfield viscosity and fluoro-surfactant content in aqueous CP-F5-D solution

The Brookfield viscosity of the aqueous solution of copolymer CP-F5-D decrease with increasing amounts of anionic and non-ionic fluoro-surfactant (FC-143: ammonium perfluorooctanoate; FC-171: $\text{CF}_3(\text{CF}_2)_n\text{O}(\text{CH}_2\text{CH}_2\text{O})_m\text{H}$) added into the copolymer solution, especially at a lower shear rate (0.4 s^{-1}). It is interesting to note that when more surfactant was added, the Brookfield viscosity of the aqueous CP-F5-D solution did not decrease further but increased to a value higher than that of the original solution without adding surfactant FC-171. This may be related to the bridge-breaking effect as shown in Scheme 2^[14].



Scheme 2

When the fluoro-surfactants was first added, it may dissociate the intermolecular hydrophobic association that reflected the decreasing of Brookfield viscosity. After more and more fluoro-surfactant were added, they may form micelles in aqueous solutions and these micelles may tend to build a bridge between two or more copolymer chains to form an association again that reflects the increasing of Brookfield viscosity of the copolymer solution. The difference between the former and FC-143 may be that the former has longer hydrophilic chain than the latter, so the bridge effect of FC-171 is much more significant.

In conclusion, the study on intrinsic viscosity, Brookfield viscosity, pseudoplasticity and effect of fluoro-surfactants on Brookfield viscosity of these copolymer solutions indicated the presence of hydrophobic associations in the aqueous solutions of the copolymers containing fluoromonomer 4.

The investigation of fluorescence spectrum is in progress.

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