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Interaction of fluorocarbon and hydrocarbon hydrophobically co-modified PAA with a nonionic surfactant: rheological properties of polymer solutions in the absence of salt

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Abstract

The interaction of a new hydrocarbon (HC) and fluorocarbon (FC) co-modified poly(acrylic acid), SA-1-FX14-1, with a HC nonionic surfactant, Np7.5, was investigated by rheological measurements. Its solution property was compared with HC or FC modified counterpart. It was found that the incompatibility between HC and FC groups in the micellization process was improved in the solution of SA-1-FX14-1. The terpolymer SA-1-FX14-1 associated with Np7.5 more like SA-2 rather than FX14-2. The latter interacted weakly with the HC surfactant due to the lipophobic tendency of the FC hydrophobe. The random distribution of FC and HC hydrophobes along the polyelectrolyte backbone was confirmed to be responsible for the compromised miscibility of HC and FC hydrophobes demonstrated in the system of SA-1-FX14-1 and Np7.5. Several affecting factors, such as backbone rigidity, polymer concentration, surfactant concentration, and FC modifying degree of the terpolymers, were also taken into account. In terms of hybrid surfactants, this type of hybrid polysoap is promising to serve as novel media improving the miscibility of HC and FC groups just as those hybrid small molecule surfactants have done.

Keywords: Hydrophobic association; Polyelectrolyte; Rheological properties

1. Introduction

Noncovalent interactions, such as hydrogen bond, ionic interaction, van der Waals interaction as well as hydrophobic interaction, have invoked tremendous interests in the research on supramolecular construction and molecular self-assembly, especially for biologically compatible aqueous media [1–4]. Among them, hydrophobic association has been deeply investigated by colloid scientists in nucleating the micellization process of small amphiphilic molecules [5]. From the 80s, accompanied with the burgeoning and prosperity of hydrophobically modified water-soluble polymers (HMWSPs), documents devoted to the hydrophobic interaction among HMWSPs and between HMWSPs and small molecular surfactants have come out increasingly [6–12]. Most of them are focused on hydrocarbon group grafted or end-capped water-soluble polymers (H-WSP) [6–10]. As for fluorocarbon modified water-soluble polymers (F-WSP), however, few papers can be retrieved [11,12].

Compared to their hydrogenated counterparts, fluorinated chains are more hydrophobic, which endows FC group stronger associative potential. As the associative ability is concerned, a CF_2 is equal to 1.7 CH_2 [13]. Zhang et al. [14] have initiated the introduction of FC groups into water-soluble polymers. A gel-like solution can be obtained at low polymer concentration and it was ascribed to the formation of a 3D network physically bridged by strong intermolecular association of FC groups. The association induced thickening phenomenon of the HMWSP solution can also be implemented at lower polymer concentration by adding external surfactants. Once the critical aggregate concentration (CAC), which is usually at least one decade lower than critical micelle concentration (CMC), is reached, mixed micelle-like aggregates form and serve as junctions to maintain viscoelastic network reversibly. Especially for hydrophobically modified polyelectrolytes (HMPE), oppositely charged surfactants will promote the interaction due to the

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additional electrostatic attraction between HMPE and surfactants while surfactants with the same charge prohibit the interaction owing to the disfavored electrostatic repulsion.

For fluorocarbon hydrophobically modified polyelectrolytes (F-PE), Iliopolous et al. [7] first reported the association of $CH_2C_7F_{15}$ randomly grafted PAA with corresponding hydrogenated PAA by postpolymerization and found that the evident association between these two hydrophobic groups occurred only when the polymer concentration was high enough. It was thought in line with the nonideal mixing behavior of fluorinated surfactant and hydrogenated one [15]. The association in this case can also be accounted as the interaction between FC and HC polysoaps, where two interacting hydrophobic groups are of different nature.

Due to the simultaneously hydrophobic and lipophobic nature, mingling of FC surfactant (F-surf) and HC surfactant (H-surf) leads to either compatibility or incompatibility [15]. In a mutually compatible system, only one kind of mixed micelle comprised of two types of surfactants exists. While two categories of micelles, fluorocarbon-rich and hydrocarbon-rich micelles co-exist in a mutually incompatible system. However, both systems are usually nonideal and their constitutions are dependent on molecular structures, concentrations and ratios of two surfactants, and media environments. Novel approaches have been developed for mixed surfactant systems in two directions: either improving the miscibility of two hydrophobiles to obtain only one kind of mixed micelle or improving their segregation to obtain two co-existing pure micelles. Kunitake et al. [16] prepared various double- and triple-chain hybrid amphiphiles of FC and HC chains, which all form bilayers despite the poor miscibility of their precursors. On the contrary, Candau's group [17] successfully synthesized multicompartment polymer with HC and FC surfmers copolymerized onto the same polymer chain and distributed in the form of microblock. The key technique lies in improving the incompatibility between H- and F-surfmers and thus to prepare well-segregated surfmer micelles.

Our group has synthesized FC and HC groups co-modified PAA via solution copolymerization. Two types of hydrophobic groups are randomly distributed along the macromolecular backbone of the terpolymer. There seems to be little opportunity for two types of randomly distributed hydrophobic groups to selectively form segregated microdomains by themselves. Meanwhile, the terpolymer solution shows evident thickening effect, which should be ascribed to the network of hydrophobic microdomains. Therefore, mixed micelle-like aggregates are present and responsible for the particular solution behaviors. When the improvement of the miscibility of two hydrophobes is concerned, our system is opposite to Candau's system and more similar to Kunitake's hybrid amphiphiles, except that the linkage combining the two neighboring hydrophobic groups is not a short and regular spacer but various lengths of water-soluble PAA segments. In this paper, we intend to investigate the interaction of this hybrid polysoap with a small molecular surfactant.

For PAA is a pH-sensitive polyelectrolyte, avoiding the complexity induced by the ionic interaction between PAA and ionic surfactant, we choose a nonionic surfactant. Two bipolymers exclusively modified by HC or FC group with the same feed fraction as in terpolymer are synthesized to serve as control. Preliminary results, obtained from the interaction between these two control bipolymers with two nonionic surfactant Np7.5 (H-surf) and FC171 (F-surf), show that the two surfactants, respectively, prefer to associate with copolymers modified by the same type of hydrophobic group. That is, H-PE interacts more strongly with H-surf (Np7.5) but weakly with F-surf (FC171), and F-PE behaves just the opposite [18]. For the hybrid terpolymer, however, the interactions between H-surf and F-surf are comparable. It is of interest and therefore we systematically investigate rheological properties of these polymer solutions and the disparity in them is emphasized. For brevity, this paper only deals with the interactions of HMPE with H-surf (Np7.5).

2. Theory

It has been confirmed [10,19] that the viscoelastic properties of associative polymer solutions can be described in terms of the single element Maxwell model, as shown by Eqs. (1) and (2):

$$G' = G_0\omega^2\lambda_0^2/\left(1 + \omega^2\lambda_0^2\right) \tag{1}$$

$$G'' = G_0\omega\lambda_0/\left(1 + \omega^2\lambda_0^2\right) \tag{2}$$

Through typical oscillatory rheological measurements, high-frequency modulus or plateau modulus G_0 and largest relaxation time or terminal relaxation time λ_0 can be determined. As shown in Fig. 1, the curves of $G'(\omega)$ and $G''(\omega)$ intersect at the point corresponding to the critical angular

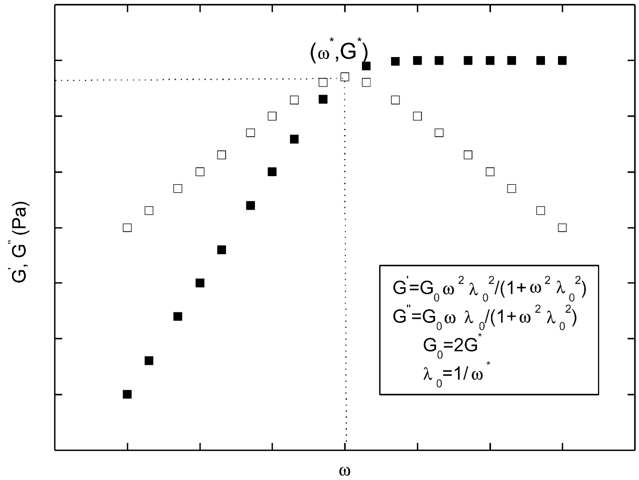

Fig. 1. Maxwell model of viscoelastic fluid. (■) Storage modulus curve: $G'(\omega) \sim \omega$; (□) loss modulus curve: $G''(\omega) \sim \omega$. Two curves intersect at a critical point (G^*,ω^*).

frequency (ω^*) and critical modulus (G^*), G_0 and λ_0 can be inferred from Eqs. (1) and (2) as follows:

$$G_0 = 2G^* \tag{3}$$

$$\lambda_0 = 1/\omega^* \quad \text{or} \quad \lambda_0 = 1/2\pi f^* \tag{4}$$

According to Green and Tobolsky's transient network theory extended from the simple theory of rubber elasticity [20], the magnitude of plateau modulus is proportional to the number density of network junctions ν_{eff}.

$$G_0 = \nu_{\text{eff}} kT \tag{5}$$

Since the critical modulus G^* obtained at the cross point of $G'(\omega)$ and $G''(\omega)$ is just half of the plateau modulus, G^* can be conveniently used to characterize the junction density of the transient network. That is,

$$G^* \sim \nu_{\text{eff}}. \tag{6}$$

Terminal relaxation time λ_0 is interpreted as the average lifetime of association of an end group in a junction and then is the reciprocal of the dissociation rate of an end group from a junction. Tanaka and Edwards [21] assume that the dissociation process needs to overcome a bonding potential with a well depth of E_{m}. Therefore,

$$\lambda_0 = 1/\beta_0 = \exp(E_{\text{m}}/kT)/\omega_0 \tag{7}$$

where ω_0 is the characteristic frequency of thermal vibration and estimated to be of the order of 0.1 ns, k is the Boltzmann constant, and T is usually kept unchanged in experiments. Giving the critical angular frequency ω^* is the reverse of λ_0 and is equal to 2π times the critical frequency f^*, we adopt f^* to estimate the junction stability. That is,

$$\ln f^* \sim 1/E_m. \tag{8}$$

3. Experimental

3.1. Materials

Acrylic acid (AA), AR, was redistilled under reduced pressure. Cyclohexane, AR, was redistilled before use. AIBN and 2-(*N*-ethylperfluorooctanesulfoamido)ethyl methacrylate (FX14, 3M) were recrystallized twice from methanol. Stearyl acrylate (SA) was first dissolved in ethyl acetate and then washed with 0.1N NaOH twice succeeded with washing by water and removal of the solvent. Nonionic surfactant Np7.5 from Fluka was used as received. The chemical structures of FX14 and Np7.5 are shown in Fig. 2.

3.2. Preparation of polymer samples

Typical solution copolymerization was carried out in a 50 ml egg-shape bottle equipped with a magnetic stirrer and a rubber stopper, where 4.0 ml AA, 20 ml cyclohexane, certain amounts of hydrophobic monomer (SA and/or FX14), and 4.0 mg AIBN were added. Then this solution was purged with pure N_2 in ice-water bath for 45 min. Finally, the reactor was immersed in oil bath with temperature keeping at 50 ± 1 °C for 24 h. The initiation of polymerization can be inspected from the onset of white precipitates. After the polymerization was stopped, ethyl ether was added to wash the polymer and the product was further suction-filtered with ether three times on a 3# grit-stone funnel to remove the unreacted monomers. The resulted white powder was vacuum dried overnight at 50 °C.

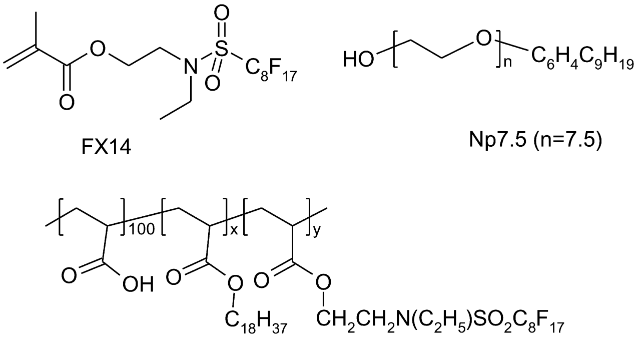

Fig. 2. Chemical structures of FX14, Np7.5 and typical polymer sample.

Five different copolymer samples, SA-1, SA-2, FX14-1, FX14-2, and SA-1-FX14-1, were afforded, of which the feed fractions of hydrophobic monomers are 1.0, 2.0 mol% SA, 1.0, 2.0 mol% FX14 and 1.0 mol% SA plus 1.0 mol% FX14, respectively. Their general structure is depicted in Fig. 2. The conversion of FX14 in polymerization was determined by anionic chromatography on a Dionex2010I instrument and found almost 100%. However, the precise determination of the content of SA in the copolymer by element analysis was unavailable. After suction-filtration three times, filtrates of the earlier mentioned SA-1 and SA-2 were concentrated and further vacuum dried. Since ethyl ether and AA is easily evaporated, the amount of unreacted SA can be assessed by weight and the rough conversion of SA is about 65–70 mol%. The characterizing data, altogether with the concentration of hydrophobes in 0.6 wt% polymer solution and their molar ratios to 0.04 wt% Np7.5, are listed in Table 1. The CMC of Np7.5 is about 0.004 wt% [22]. The reactivity ratios of SA and FX14 to AA have been measured in our previous work [23]. FX14 is more reactive than AA while SA more inert. The lower conversion of SA relative to FX14 in copolymerization is thus reasonable. Furthermore, the block composition of the hydrophobic monomer along the backbone is inferred by its reactivity ratio to AA and accounts for not more than 2 mol% when its feed fraction is below 10 mol% [23].

3.3. Molecular weight determination

In order to obviate the effect of the hydrophobic association on the determination of the molecular weight, SA-2,

Table 1
Characterization of polymers and hydrophobe concentration of 0.6 wt% polymer solution

Samples	Yield (wt%)	SA/FX14 conversion (%)[a]	$[\eta]$ (dl/g)	M_η (10^4)	[Hydrophobe] (mol/l)[b]	[Hydrophobe]/[Np7.5][c]
SA-1	88	67			5.4×10^{-4}	0.74
SA-2	92	67	4.44	31.7	1.0×10^{-3}	1.4
FX14-1	96	93			7.2×10^{-4}	1.0
FX14-2	97	99	5.60	43.1	1.4×10^{-3}	1.9
SA-1-FX14-1	95	67/98	5.28	39.9	1.2×10^{-3}	1.6
PAA	90		6.27	50.1		

[a] It means the conversion of SA for SA-1 and SA-2, of FX14 for FX14-1 and FX14-2, and SA and FX14, respectively, for SA-1-FX14-1.

[b] The average molecular weight of the repeat unit is calculated as: $72(1-x)+M_w x$, where M_w is 324 for SA and 639 for FX14 and x is the feed fraction. The concentration of all repeat units in copolymer SA-1, SA-2, FX14-1, FX14-2, and SA-1-FX14-1 is 8.05×10^{-2}, 7.79×10^{-2}, 7.72×10^{-2}, 7.20×10^{-2}, and 7.48×10^{-2} mol/l, respectively.

[c] Used is 0.04 wt% Np7.5 and the molar concentration is 7.3×10^{-4}.

FX14-2 and SA-1-FX14-1 were hydrolyzed by 1.0N NaOH at 80 °C in the 4:1 mixture of water and ethanol for 2 days prior to the measurement of the intrinsic viscosity. For FX14-2 and SA-1-FX14-1, the hydrolyzing degree was determined by fluorine content to be close to 80%. The intrinsic viscosity $[\eta]$ of these hydrolyzed samples in 0.1N aqueous NaBr at 25 °C were measured by Ubbeldohe capillary viscometer. Eq. (9) was used to obtain $[\eta]$:

$$\eta_{sp}/c = [\eta] + k\eta_{sp}[\eta], \qquad \eta_{sp} = (t - t_0)/t_0 \tag{9}$$

Mark–Houwink equation [24]:

$$[\eta] = KM_\eta^\alpha, \qquad K = 31.2\times10^{-5}\ \text{dl/g}, \qquad \alpha = 0.755 \tag{10}$$

was used to calculate the M_η. Although K and α values in Eq. (10) are inferred from unmodified PAA, here they are applied to modified PAA because the effect of the hydrophobic association on the determination of M_η of these hydrolyzed samples is very weak and negligible. Measured M_η were found to be comparable with each other and with homopolymer as shown in Table 1. Therefore it is as expected that the introduction of small amounts of hydrophobic monomer in copolymerization does not affect the average molecular weight of the copolymer evidently.

3.4. Rheological measurements

The typical process is stated in the following. A solution with desired polymer concentration was prepared by dilution of a concentrated polymer solution and the pH value was adjusted by 1.0N NaOH. Then Np7.5 was carefully added to the solution so that desired surfactant concentration was reached. The small amount of Np7.5 almost has no diluting effect on the concentration of polymer solution. Prepared polymer solution was kept at least 2 days before rheological measurements to ensure the equilibrium state reached. Oscillatory frequency sweep experiments were carried out on a controlled HAAK Rheostress RS75 rheometer equipped with a geometry of 2°/6 cm cone and plate. A C60/2Ti sensor was used and the gap was set 0.108 mm. Temperature was kept at 25 ± 0.5 °C by a F6/8 temperature device. Prior to oscillatory frequency sweeps on the solution, an oscillatory amplitude sweep at 1 Hz was performed in order to determine the linear viscoelastic region. Then oscillatory frequency sweeps were performed with applied oscillatory stress located in the linear viscoelastic region.

4. Results and discussion

4.1. Mixed micelle-like aggregates

The overlap concentration C^* of five polymer samples can be evaluated in the range from 0.15 to 0.2 wt% by the relationship between C^* and intrinsic viscosity $[\eta]$: $C^* = 1/[\eta]$ [25,26]. For 0.6 wt% solutions of SA-1 and FX14-1, as exhibited in Fig. 3, the viscoelastic behaviors of the polymer solutions change little upon the addition of Np7.5. The pH value of these two solutions was modulated to 10 and the Np7.5 concentration (0.04 wt%) is 10 times its CMC. It indicates that not only FC groups but also HC groups along the polymer chain obviously do not associate with Np7.5 molecules to form mixed micelles. It is partially due to the low graft density and partially due to the rigidity of the polymer chain. At pH 10, almost all carboxyl groups are neutralized and the electrostatic repulsion makes the chain inflexible and thus unfavorable for hydrophobic groups to associate with each other to form viscoelastic network.

However, the solution of the terpolymer SA-1-FX14-1 displays distinguishingly different rheological behaviors. Upon oscillatory frequency sweep, as shown in Fig. 4, it is found that the critical modulus G^* of SA-1-FX14-1 is two times that of SA-1 and FX14-1 and the critical frequency f^* is almost two orders of magnitude lower. The increase in G^* and decrease in f^* mean that both junction density and junction strength of the terpolymer solution are higher than those of two bipolymer solutions. Although the terpolymer solution without Np7.5 serving as control is

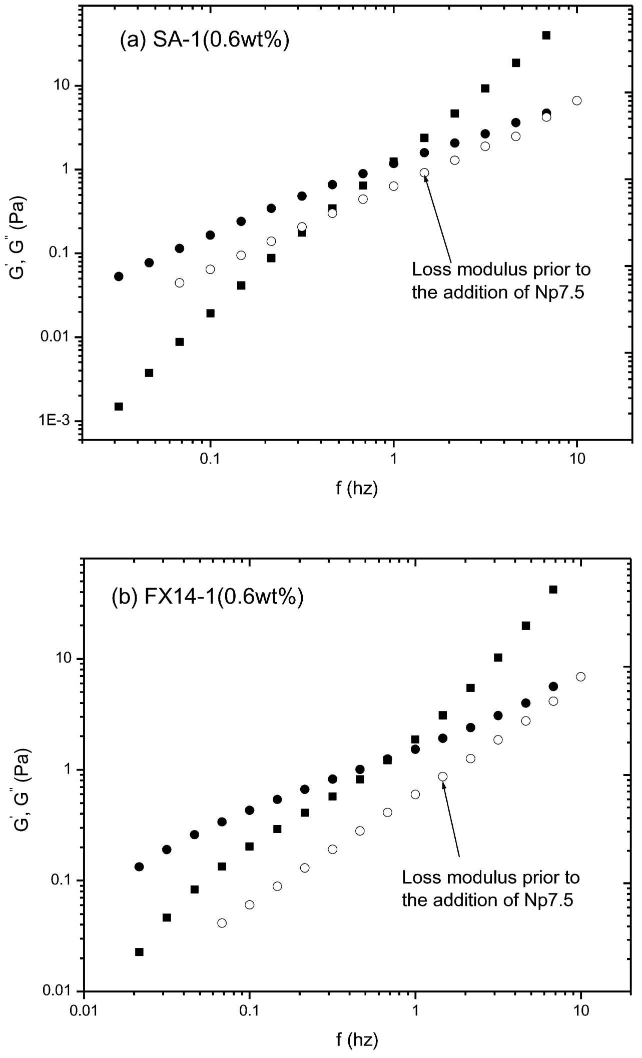

Fig. 3. Storage modulus (G') and loss modulus (G'') of 0.6 wt% SA-1 (a) and FX14-1 (b) in the presence of 0.04 wt% Np7.5. Applied oscillatory stress is 1 Pa. (■) G', (●) G''.

more viscous than two corresponding bipolymer SA-1 and FX14-1, the strengthening effect of Np7.5 on terpolymer network is unplausibly more efficient than two bipolymer networks. Especially convincing fact lies in the drastic deduction in f^*. That is, greatly stabilized junctions are formed, which should only be contributed to the participation of Np7.5 in the association of hydrophobic groups.

More noteworthy is that whether FC groups are involved in the composition of mixed micelle-like aggregates. Because the SA content in terpolymer solution is the same as in SA-1 solution, the f^* between SA-1-FX14-1 and SA-1 should be unexpected of much difference if the structure of junctions formed in the system of terpolymer and Np7.5 is similar to that of SA-1 and Np7.5 solution. Hence, the preliminary contrast between Figs. 3 and 4 hints us that mixed microdomains, comprised of the hydrophobic moieties of SA, FX14 and Np7.5, exist in the terpolymer solution.

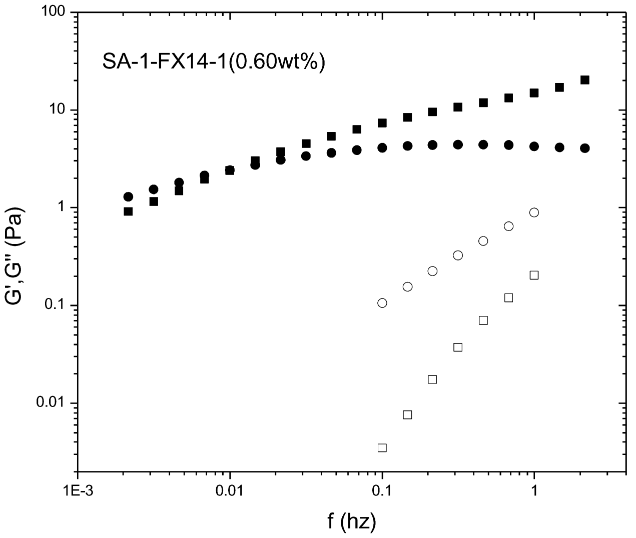

Fig. 4. Oscillatory frequency sweep on 0.6 wt% SA-1-FX14-1. Applied oscillatory stress is 3 Pa. (■) G', (●) G'' with 0.04 wt% Np7.5 (□) G', (○) G'' without Np7.5.

Further comparing with Fig. 5 which depicts the rheological behaviors of the other two bipolymer solutions, SA-2 and FX14-2, more impressive results can be easily grasped. As shown in Fig. 5, the G^* and f^* of the system of SA-2 and Np7.5 are far different from those of SA-1 and Np7.5 while the G^* and f^* of the system of FX14-2 and Np7.5 are very close to those of FX14-1 and Np7.5. From the contrast in the rheological correspondence of SA-2 and FX14-2 to the addition of Np7.5, it is concluded that the hydrocarbon surfactant Np7.5 is inclined to associate with the HC moiety of SA but reluctant to aggregate with the FC moiety of FX14. Kaestner et al. [27] observed strong interaction between their fluorocarbon hydrophobically modified hydroxyethyl celluloses (F-HMHEC) and hydrocarbon surfactants SDS. However, the low miscibility of alkyl with perfluoroalkyl groups is indicated in the displacement between the maxima of the viscosity and the storage modulus G' for the solutions of F-HMHEC with added SDS [27]. In the present study, the similarity between the solution behaviors of SA-1-FX14-1 and SA-2 indicates that the FC moiety of FX14 plays a role as the HC moiety of SA in association with Np7.5, concerning that the content of FX14 in the terpolymer solution almost compensates the content of SA in the terpolymer solution relative to SA-2. This confirms the point of view, which has been speculated earlier, that in hybrid polysoap solution mixed aggregates or strong junctions induced by the addition of Np7.5 contains FC groups. The improvement of rheological properties of the solution of SA-2 before and after the addition of Np7.5 is far less evident than that of SA-1-FX14-1. Therefore, the compromising effect on the mingling of FC and HC groups is improved by the introduction of HC hydrophobe. Compared with Kunitake's small hybrid molecules, the linkage has been replaced by water-soluble polymer

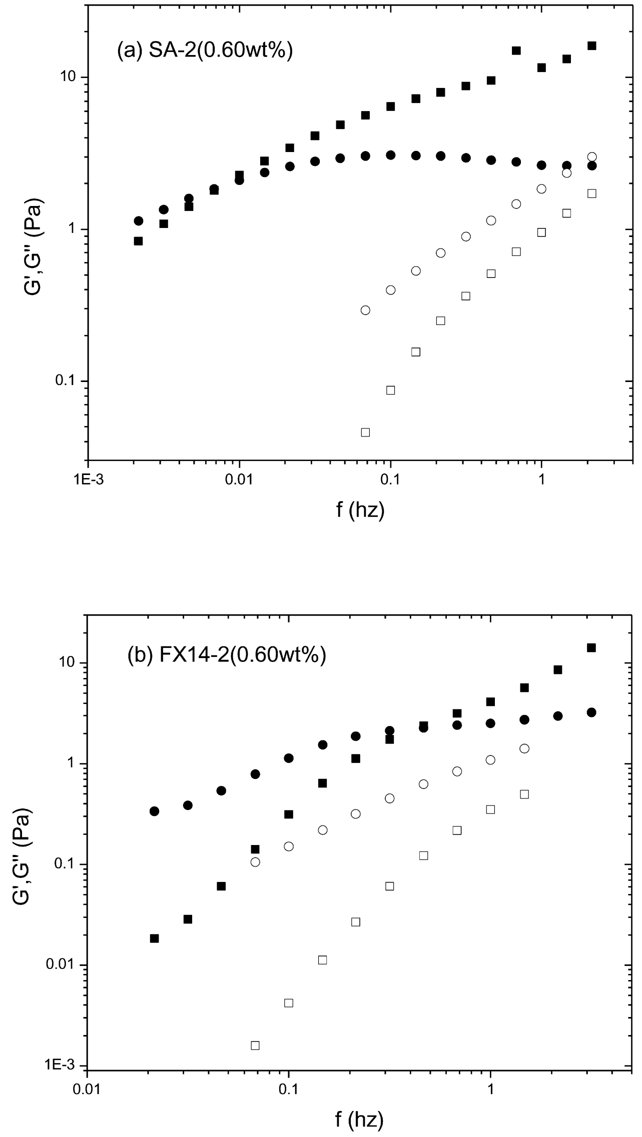

Fig. 5. Oscillatory frequency sweep on 0.6 wt% SA-2 (a) and FX14-2 (b). Applied oscillatory stress is 3 Pa. (■) G', (●) G'' with 0.04 wt% Np7.5; (□) G', (○) G'' without Np7.5.

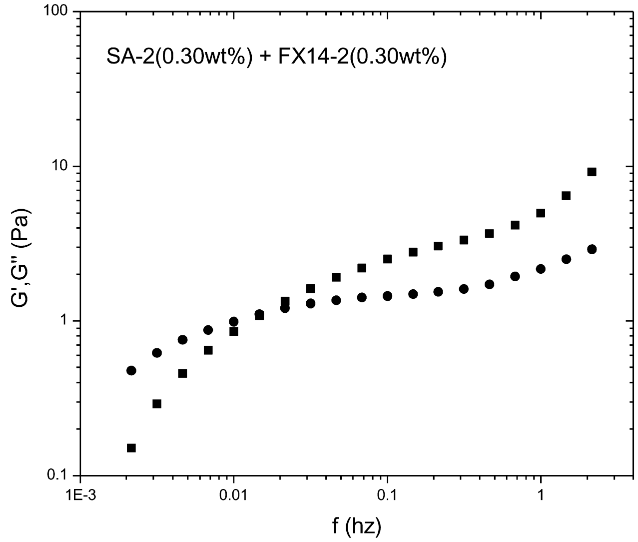

Fig. 6. Oscillatory frequency sweep on the mixture of 0.3 wt% SA-2 and 0.3 wt% FX14-2 with 0.04 wt% Np7.5 added and applied oscillatory stress at 3 Pa. (■) G', (●) G''.

segments, which makes hybrid polysoap and promises to be derived into a novel type of hybrid surfactant. By the way, when a FC nonionic FC171 is used, the viscoelasticity of SA-2 solution improves little while SA-1-FX14-1 solution becomes even more viscoelastic than FX14-2 [18]. This should also be ascribed to the excellent compatibility induced by the compromising effect.

Mingling of two equi-volume of 0.6 wt% SA-2 and FX14-2 leads to a solution with concentrations of both HC and FC hydrophobes equal to those of 0.6 wt% SA-1-FX14-1. After addition of 10 times CMC of Np7.5, however, the G^* is lower and the f^* is higher compared with SA-2 and SA-1-FX14-1, as shown in Fig. 6. It seems more like the consequence of diluting the precursor solution of SA-2 to its half concentration. We deduce that there exist hydrocarbon-rich and fluorocarbon-rich microdomains prior to the addition of Np7.5, and then the surfactant selectively associates with those hydrocarbon-rich microdomains thus resulting in the loss of viscoelastic contribution from the microdomains consisting of a small portion of SA and a great portion of FX14. Contrarily, in the preformed hydrophobic microdomains of SA-1-FX14-1, two types of hydrophobic groups are distributed more even due to the randomly hybrid structure and thus the preference of Np7.5 to hydrocarbon microdomains is discouraged.

Now we summarize above results as follows: the random distribution of both FC and HC groups along the macromolecular backbone of the terpolymer is advantageous to form mixed aggregates where two hydrophobic groups are not microphase separated as found in the mixture of two pure bipolymers. When certain amounts of Np7.5 are added, different viscoelastic behaviors upon the oscillatory frequency sweep are observed compared with two pure bipolymer solutions. Drastic increase in solution viscoelasticity occurs for the HC modified bipolymer (SA-2) solution because the hydrocarbon nonionic surfactant prefers to stay within microdomains of the same kind. Meanwhile, changes for FC modified bipolymer (FX14-2) are almost neglectable. However, random grafting of both FC and HC groups along the terpolymer chain imparts the formed mixed aggregates good compatibility to HC surfactant. Compromising effect of FC and HC groups make the rheological behavior of SA-1-FX14-1 very close to SA-2 when Np7.5 is added. On the other hand, several factors would affect the rheological behaviors of this hybrid polysoap solution. In the following, we will discuss, respectively, the effect of solution pH, hydrophobic group concentration, and especially the feed fraction of FX14 in copolymerization, on rheological properties of polymer solutions.

4.2. The solution pH

Poly(acrylic acid) used in our study is a polyelectrolyte when the carboxyl protons dissociate from the backbone. The dissociation degree can be easily modulated by external addition of alkali solution. The importance of proton dissociation degree lies in its dominating effect on the rigidity of the polymer chain, which consequently has influence on the hydrophobic association. It can be imaged that when intramolecular association happens between two hydrophobic groups, the chain segment between them bends into a loop. Once the charge density of the segment increased enough, it would be difficult for the end groups to loop together. For all intramolecular microdomains and many intermolecular microdomains containing intramolecular associations, increased pH value clearly results in the increased loop tension and thus increased difficulty to exist stably. As shown in Fig. 7(a) and (b), when the solution pH increases from 5.5 to 10, the elastic parameter G' of SA-1-FX14-1 at low frequency range decreases evidently. Simultaneously, increased f^* indicates that the junction stability becomes lower when the polymer chain carries more charge. It can be inferred that the curvature of the hydrophobic microdomain in high pH solution is smaller and hence the aggregate is looser, more unstable and disorderly than in low pH solution.

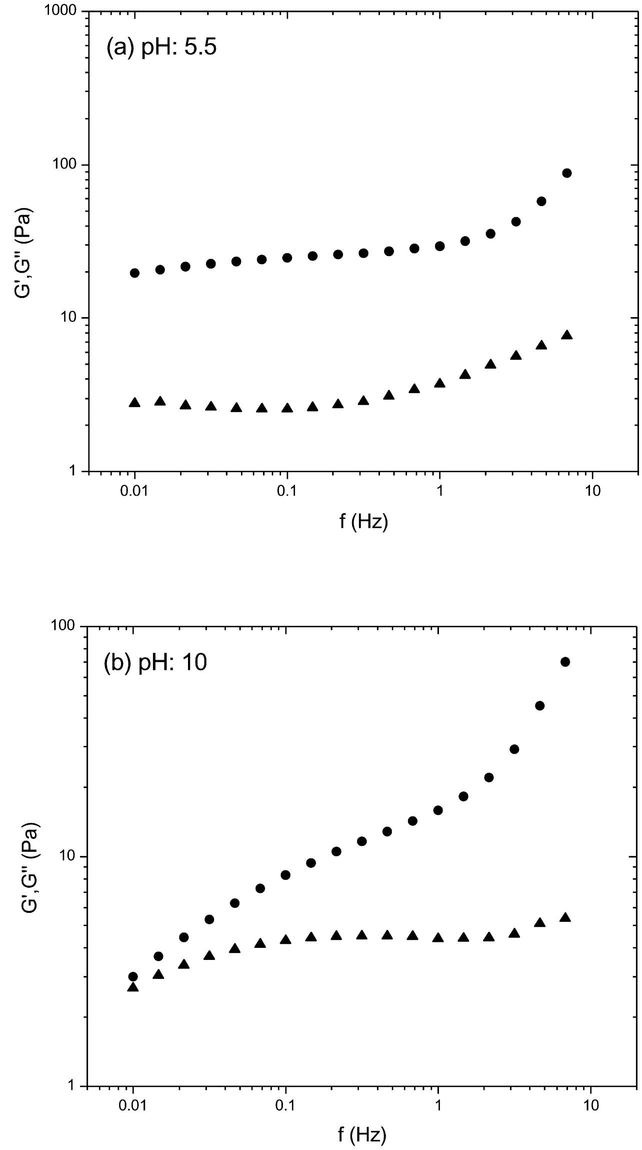

Fig. 7. The effect of pH on rheological properties of SA-1-FX14-1. The pH is (a) 5.5 and (b) 10. The polymer concentration is 0.6 wt% and Np7.5 concentration is 0.04 wt%. Applied oscillatory stress is 10 Pa. (●) G', (▲) G''.

As determined by Kaestner et al. [27] through rheological measurements and more recently by Petit-Agnely et al. [28] through ^{19}F and ^{13}C NMR, only a few alkyl side chains are eventually aggregated to form the network. For Kaestner's F-HMHEC samples, approximately one quarter of the hydrophobic chains form the transient network while the other chains form intramolecular contact points. Increased rigidity of the backbone induced by the increased pH seems to favor the dissociation of intramolecular association of high tension and thus favor the formation of intramolecular association through these released side chains. However, the increased charge density of the backbone increases the intermolecular repulsion. Thus the enhanced electrostatic repulsion induced by high pH inhibits the intermolecular association of hydrophobic groups when two polymer segments approach each other during aggregation. Therefore, increasing charge density through alkalization does not create more opportunities for the transition from intramolecular to intermolecular association.

As presented in Fig. 8, f^* of the FX14-2 solution at pH 5.5 is at least one order of magnitude greater than that of SA-1-FX14-1 (as shown in Fig. 7(a)) and this is coincident with the results at high pH solution (pH 10). This shows that,

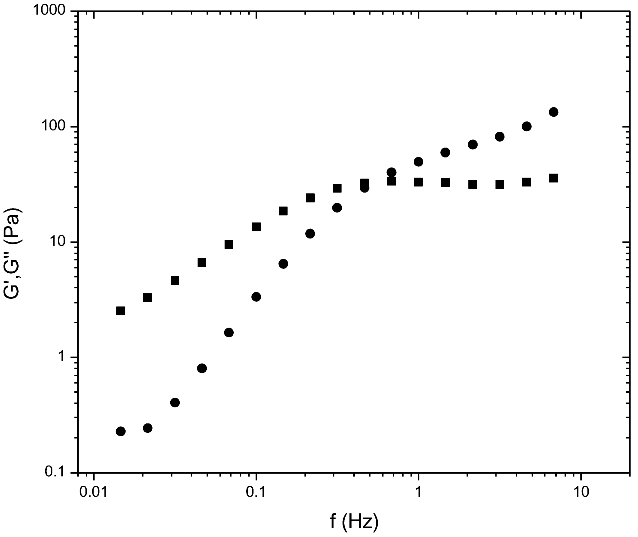

Fig. 8. Oscillatory frequency sweep on 0.6 wt% FX14-2 at pH of 5.5 with 0.04 wt% Np7.5 is added. Applied oscillatory stress is 10 Pa. (●) G', (■) G''.

even if the polymer backbone was held more flexibly, the association between Np7.5 and FC groups was still unsatisfactory. This fact confirms once again that the poor compatibility between Np7.5 and FX14-2 covered earlier is not derived from the ionic effect but rooted in the mutual incompatibility of two types of hydrophobic groups. Although the viscoelasticity in this case has been improved compared to Fig. 5(b), it can be explained as the result that the viscoelasticity of pure FX14-2 solution itself has been improved by the decreased pH before Np7.5 is added.

4.3. The concentration of the polymer solution

Besides the earlier-mentioned ionic effect, the concentrations of hydrophobic groups themselves are certainly the factors that affect the rheological properties of polymer solutions. One factor is the polymer concentration (C_p). As displayed in Fig. 9, when the polymer concentration decreases from 0.6 to 0.4 wt% while Np7.5 content is kept constant (0.0 4 wt%), changes occurred for the solution of terpolymer SA-1-FX14-1 are different from bipolymer SA-2. As far as G^* is concerned, it decreases from 2 to 0.6 Pa for SA-1-FX14-1 solution and from 2 to 0.3 Pa for SA-2 solution. However, the f^* of SA-1-FX14-1 solution increases from 0.01 to 0.04 Hz while almost no variation is observed for SA-2 solution (0.07 Hz). First, the decrease of C_p with the concentration of added Np7.5 keeping constant alters the molar ratio of hydrophobic groups grafted on the polymer to the nonionic surfactant. The ratios decrease to 2:3 for both SA-2 and SA-1-FX14-1. Second, when the C_p decreases from 0.6 to 0.4 wt%, total hydrophobic contents have been lessened. If each aggregate formed in 0.4 wt% solution in average contains the same amount of hydrophobic groups of the hybrid polysoap, the quantity of aggregates would be less than that of a 0.6 wt% solution and thus a less G^* would be measured for a 0.4 wt% solution. In addition, the transformation from mechanically active junctions or intermolecular microdomains to mechanically inactive junctions or intramolecular microdomains is another cause for the decrease of G^*. The transformation will consume more Np7.5 and less polysoap hydrophobes and hereby level off the excess of Np7.5 relative to polysoap hydrophobes. For SA-2, the unchanged f^* can be ascribed to the structural semblance between Np7.5 and SA. Therefore, the compositional change in junction aggregates before and after the decrease of C_p has little influence on the junction strength. However, the case for SA-1-FX14-1 is different, the evident increase of f^* for SA-1-FX14-1 means the junctions are weakened by increasing the fraction of Np7.5 in junctions. It should be ascribed to the structural difference between Np7.5 and FX14 in the formed mixed junctions. Furthermore, a less decreased G^* suggests that the diminishing extent of junction density in SA-1-FX14-1 is not as drastic as in SA-2. Upon the decrease of polymer concentration from 0.6 to 0.4 wt%, the decreased G^* of SA-1-FX14-1 indicates that the average aggregate functionality of polysoap hydrophobes is somewhat diminished so that more aggregates and thus a higher G^* for SA-1-FX14-1 is presented compared to SA-2. More Np7.5 molecules are then involved into the mixed aggregates in the solution of SA-1-FX14-1 and it just consumes the plethoric Np7.5 and thus in turn contributes to the weakening of junctions and a higher f^* compared to the SA-2 solution. In these aggregates, SA and FX14 seem to be easier to exit as shown by an increased f^*.

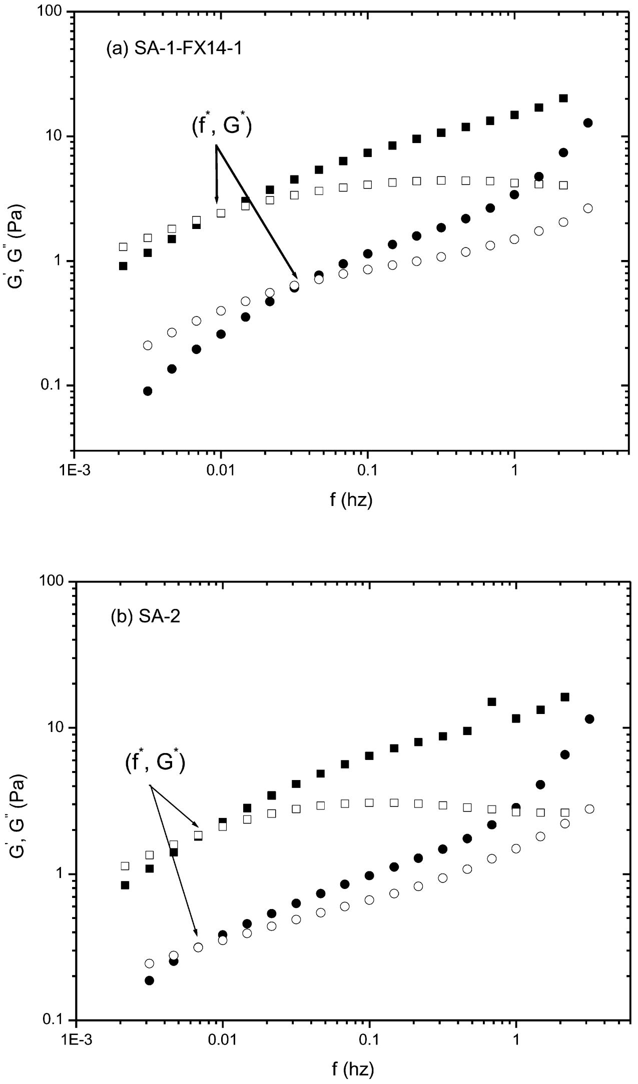

Fig. 9. Dependence of critical modulus (G^*) and freqency (f^*) on polymer concentration of SA-1-FX14-1 and SA-2 (b) with 0.04 wt% Np7.5 added. Applied oscillatory stress is 3 Pa for 0.6 wt% and 1 Pa for 0.4 wt% solution. Cp: 0.4 wt% (●: G', ○: G''); 0.6 wt% (■: G', □: G'').

4.4. The concentration of the added surfactant

Surely, the concentration of the added surfactant Np7.5 is the other factor influencing solution properties. Upon the increase of the fraction of Np7.5 in total hydrophobes with polymer concentration keeping constant, the comparison of

Table 2
Rheological properties of the solution of SA-1-FX14-1 and Np7.5 (Stresses applied on the oscillatory frequency sweep are 3 Pa for 0.6 wt% and 1 Pa for 0.4 wt% solution)

C_p (wt%)	[Np7.5] (wt%)	[Np7.5]/ [Hydrophobe]	G^* (Pa)	f^* (Hz)
0.6	0.04	0.6	2	0.01
	0.10	1.5	4	0.03
	0.33	4.5	10	1
0.4	0	0	0.03	0.2
	0.002	0.05	0.3	0.03

rheological properties of these solutions demonstrates more clearly the effect of added surfactant on hydrophobic association and network junctions. Table 2 shows the G^* and f^* for the solution of SA-1-FX14-1 at 0.4 wt% with and without Np7.5 and at 0.6 wt% with Np7.5 concentration of 0.04, 0.10, and 0.33 wt%, respectively. It can be seen that for 0.4 wt% SA-1-FX14-1 solution, when 0.002 wt% Np7.5 is added, both the junction number and the junction strength increase as exhibited by the change of G^* from 0.03 to 0.3 Pa and f^* from 0.2 to 0.03 Hz. Although the additive concentration is well below its CMC, mixed micelle-like aggregates form readily owing to the involvement of hydrophobes along the polysoap chain. When plethoric surfactants were added, it has been proposed [10,11,25] that mixed micelles would be dissolved or the 'bridge-making' process would change into 'bridge-breaking' process. Recently, Tam et al. [29] assumed a special mechanism for their HASE system where mixed micelles changed into more stable vesicles when the concentration of $C_{12}EO_4$ is high enough. Our system of SA-1-FX14-1 and Np7.5 seems to follow the former situations as seen by rheological spectra. As listed in Table 2, when more Np7.5 is added into the 0.6 wt% SA-1-FX14-1 solution, both G^* and f^* increase successively. It should be noted that the molar ratio of Np7.5 to polysoap hydrophobes changes from 0.6 to 1.5 and to 4.5, respectively. The decreasing extent in this case is greater than in the aforementioned case where C_p is changed and Np7.5 concentration keeps constant. Here the associating demand from the excessive Np7.5 can only be met by increasing total number of aggregates. Hence the average aggregate functionality of the polysoap hydrophobes further decreases and that of Np7.5 further increases, respectively. Therefore, junction strength is weakened, which is coincident with the above results by only decreasing C_p. As for the change of association energy E_m, it will be discussed in our next paper [30].

4.5. The FC modifying degree of the terpolymer

For the system consisting of a hybrid polysoap and a nonionic surfactant, the FC modifying degree of the polysoap is found to be another important factor affecting the association of polysoap hydrophobes with the surfactant. As plotted in Fig. 10, $G'(f)$ and $G''(f)$ curves of SA-1 and SA-1-FX14-0.5 are almost superposed with each other. It means that a low content of FX14 in the terpolymer cannot induce the formation of rheologically measurable network junctions. In Fig. 10, rheological curves of other three terpolymers with more viscoelastic behaviors are presented. The case of SA-1-FX14-1 has been discussed earlier in detail. Terpolymer SA-1-FX14-1.5 holds more content of FX14. For SA-0.5-FX14-1.5, the feed of hydrophobic monomers was modulated so that the augment of FX14 is almost equal to the subtract of SA. Under identical conditions of 0.4 wt% polymer and 0.04 wt% Np7.5, high fraction of FX14 is found to impart the polymer solution greater and stronger network junctions, as hinted by a lower f^* and a higher G^*. Meanwhile, when the FX14 fraction reaches 1.5 mol%, the deduction of SA fraction in polysoap from 1 to 0.5 mol% seems to have no influence on the solution property. The moduli curves of SA-1-FX14-1.5 and SA-0.5-FX14-1.5 are almost juxtaposed. It indicates that the junctions have condensing tendency as more FC groups are involved into the aggregation and the junction density and stability are mainly contributed from FC groups. It is also reminiscent of the aforementioned case that, when the C_p is decreased from 0.6 to 0.4 wt%, the f^* of SA-1-FX14-1 increased more evidently than SA-2. It should stem from the increase of Np7.5 content as well as the fractional decrease of FX14 in solution, for the latter decreases the junction density and stability greatly.

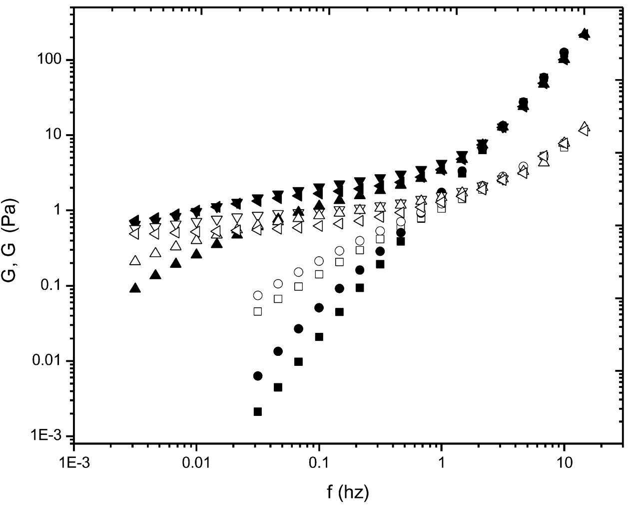

Fig. 10. Effect of FC modifying degree on rheological properties of 0.6 wt% SA-1, (■, □) 0.6 wt% SA-1-FX14-0.5 (●, ○) 0.4 wt% SA-1-FX-1 (▲, △), and 0.4 wt% SA-1-FX14-1.5 (▼, ▽), and 0.4 wt% SA-0.5-FX14-1.5 (◄, ◁). [Np7.5]: 0.04 wt%, applied oscillatory stress: 1 Pa.

5. Conclusion

Specific solution properties are found for a FC and HC jointly modified poly(acrylic acid) SA-1-FX14-1 by rheological study. When the HC nonionic surfactant Np7.5 is added, the semidilute terpolymer solution behaves rheologically more similar to HC modified bipolymer SA-2 rather than FC modified bipolymer FX14-2. The incompatibility between the FC hydrophobes of polysoap and HC groups of surfactant Np7.5 exists in the solution of FX14-2 but is evidently improved in the terpolymer solution. In the latter case, FC group is proposed to involve in the mixed aggregates and serves as more efficient associating counterpart of HC hydrophobic group. The random distribution of these two kinds of hydrophobes on the polymeric backbone is responsible for the advantageous compatibility between FC and HC groups. When hybrid surfactant is concerned, this polysoap of FC and HC co-modified terpolymer is promising to pioneer an easy approach to prepare polymeric surfactants performing as surface modifiers.

Low pH results in flexible backbone and facilitates the formation of perfect mixed micelles. Stronger association with Np7.5 is obtained for SA-2 as well as for SA-1-FX14-1. The decrease of polymer concentration from 0.6 to 0.4 wt% changes the ratio of hydrophobes of the polymer to the surfactant. It has different effects on the changing pattern of rheological properties of SA-2 and SA-1-FX14-1. The network junction density of both solutions decreases, however, the junction lifetime varies little for SA-2 but decreases obviously for SA-1-FX14-1. It is ascribed to the different composition of network junctions. The junctions consist of only HC groups for the system of SA-2 and Np7.5 but both HC and FC groups for the system of SA-1-FX14-1 and Np7.5. As the content of Np7.5 successively increases, the aggregate quantity increases accordingly but the aggregate lifetime decreases. It is also found that comicellization of the FC and HC group is dependent on the FC modifying degree of the terpolymers. A too low modifying degree cannot lead to rheologically measurable mixed aggregates.

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