

Rheological Investigation on the Interaction of a Fluorocarbon and Hydrocarbon Comodified PAA with a Nonionic Surfactant in the Presence of Salt

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ABSTRACT: Derivatives of poly(acrylic acid) hydrophobically modified with hydrocarbon group (PH) and both hydrocarbon and fluorocarbon groups (PHF) were synthesized and the association of these copolymers with nonionic surfactant Np7.5 in 0.1M NaCl aqueous solutions was investigated. Microdomains formed in the system of PHF/Np7.5 consist of both hydrocarbon (HC) and fluorocarbon (FC) groups, which is similar to Winnik's mixed model (Kujawa, P. C.; Goh, C. E.; Calvet, D.; Winnik, F. M. *Macromolecules* 2001, 34, 6387). The hybrid structure of FC and HC groups on the polysoap backbone was proposed to interpret why

the miscibility between FC and HC groups was improved. The effect of salt and Np7.5 on PHF and PH solutions was carried out and compared. When the concentration of Np7.5 reaches 0.1 wt % in 0.3 wt % polymer solution especially, physical network junctions become greatly stabilized. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1279–1285, 2004

Key words: rheological; poly(acrylic acid); fluorocarbon; nonionic surfactant; associative

INTRODUCTION

Tremendous attention has been paid to hydrophobically modified water-soluble polymers (HMWSPs) or associative polymers featuring an excellent ability to make hydrophobic groups, grafted or end-capped on the hydrophilic backbone, associate into micelle-like aggregates.^{1–8} The addition to their versatile applications in industry and the potential compatibility with biosystem complexes with well-defined structures formed in the systems of HMWSPs and a variety of surfactants afford both polymer scientists and colloid scientists a promising approach to design and develop novel functional materials.

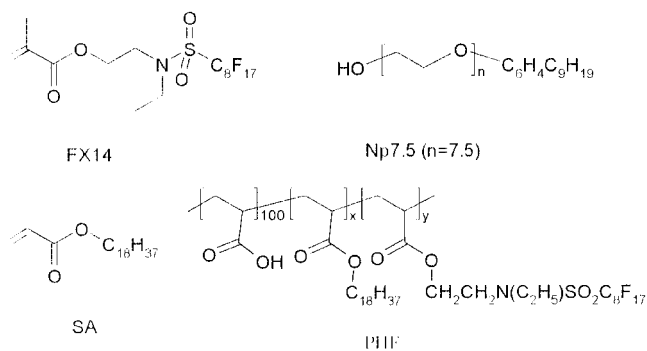
As the associating strength is concerned, the advantage of fluorocarbon groups over hydrocarbon ones has been evaluated by Racey and Stebe⁹ in a small molecular system and demonstrated by Zhang et al.¹⁰ in the HMWSP system. Now documents devoted to the fluorocarbon-modified water-soluble polymers (WSPs) are appearing more and more frequently.^{10–15} On the other hand, research on interactions between HMWSP and surfactants with different natures still

appear sparsely in contrast to teeming article on the interaction between hydrocarbon-modified WSPs and hydrocarbon surfactants.^{16–21} In most cases, mingling of two types of surfactant solutions often results in nonideal and demixing phase behaviors, that is, the coexistence of both hydrocarbon-rich microphases and fluorocarbon-rich microphases.²² In terms of polysoap, the poor compatibility occurs in the association of fluorocarbon-modified polyelectrolyte (F-PE) with hydrocarbon surfactants.

A considerable number of reports have been devoted to tackling the miscibility, namely, controlling the mixing behavior of fluorocarbon (FC) and hydrocarbon (HC) surfactants, by either comicellization or phase separation.^{23–25} Candau et al.²⁵ managed to obtain separated microdomains in the solution of WSP modified with both fluorocarbon and hydrocarbon groups in the form of block. Recently, Winnik's group published their investigation¹¹ on a fluorescent PNIPAM terpolymer (PNIPAM-F/HPy) carrying both fluorocarbon and hydrocarbon groups. They found that the presence of fluorocarbon groups did influence the fluorescence spectra of pyrene and make it different from those of copolymer PNIPAM-HPy with no fluorocarbon groups grafted. Hence, the F-chains affect the association of the H-chains in aqueous PNIPAM-F/HPy even when present only in minute levels. However, as the authors said, whether or not the two hydrophobic segments are actually associated

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Scheme 1 Structures of SA, FX14, Np7.5, and the terpolymer PHF.

within single hydrophobic microdomains cannot be ascertained from the fluorescence data alone.

In our previous article,²⁶ we develop a polysoap system that is similar to Winnik's hybrid system. The hydrophobically modified polyelectrolyte PHF [poly(acrylic acid) modified with hydrocarbon and fluorocarbon groups], on which both fluorinated and hydrogenated comonomers are randomly grafted, could be regarded as a hybrid polysoap with ionized polymer segment serving both as head groups of surfactants and as spacers linking two hydrophobes, which are of the same or different type. We have illustrated that the solution behavior of the terpolymer PHF with the HC nonionic surfactant Np7.5 is similar to the HC-modified copolymer PH [poly(acrylic acid) modified with hydrocarbon group] in the absence of salt.^{26,27} FC groups of PHF play a role as HC groups rather than FC groups. Here, we would compare the rheological properties of the solutions of PHF/Np7.5, PH/Np7.5, and PF/Np7.5 in the presence of salt (0.1M).

EXPERIMENTAL

Preparation of polymer samples and solutions

Convenient solution copolymerization is used to synthesize hydrophobically modified polyelectrolyte (HMPE) samples. Details on the synthesis and charac-

terization have been described in our previous article.²⁶ The structures of hydrocarbon and fluorocarbon monomer SA (BASF, Germany) and FX14 (3M) and nonionic surfactant Np7.5 (Fluka, Japan) as well as the structure of PHF are presented in Scheme 1. The critical micelle concentration (CMC) of Np7.5 is about 0.004 wt %.²⁸ Polymer samples used in the current investigation and their characterizing data are listed in Table I.

Polymer solutions containing 0.1M NaCl were prepared by diluting those salt-free polymer solutions with equivolume 0.2M aqueous NaCl. Prior to the dilution, pH values of these solutions were adjusted to 10 by adding 10 wt % aqueous NaOH. Np7.5 was carefully added so that the desired surfactant concentration was reached and the small amounts of Np7.5 have almost no diluting effect on the concentration of polymer solution. The overlapping concentration C^* of the three polymer samples can be evaluated in the range of 0.15–0.2 wt % by the relationship between C^* and intrinsic viscosity $[\eta]$: $C^* = 1/[\eta]$.²⁹ Therefore, all solutions used in our study with concentrations over C^* can be regarded as semidilute solutions.

Rheological measurements

Prepared polymer solutions were kept at least 2 days before rheological measurements to ensure the establishment of equilibrium state. Rheological experiments were carried out on a controlled HAAK Rheo-stress RS75 rheometer equipped with a geometry of 2°/6 cm cone and plate. A ⁶⁰C/2Ti sensor was used and the gap was set at 0.108 mm. Temperature was kept at 25 ± 0.5°C by a F6/8 temperature device except in steady shear temperature ramp experiments. Prior to oscillatory frequency sweeps on the solution, an oscillatory amplitude sweep at 1 Hz was performed to determine the linear viscoelastic region. Then, oscillatory frequency sweeps were performed with applied oscillatory stress located in the linear viscoelastic region.

TABLE I
Characterization of Hydrophobically Modified Poly(Acrylic Acid)

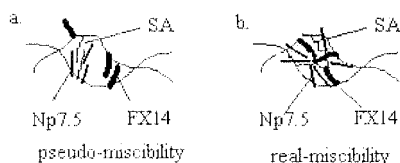
| Sample | Yield (wt %) | Feed fraction of comonomer (mol %) | Comonomer conversion (%) | $[\eta]^a$ (10 ⁴) | $[M_w]_w^b$ (10 ⁴) | N_g^c (10 ⁴) |
|--------|--------------|------------------------------------|--------------------------|-------------------------------|--------------------------------|----------------------------|
| PH | 92 | 0.02 | 67 | 4.44 | 31.8 | 56 |
| PF | 97 | 0.02 | 99 | 5.60 | 43.1 | 103 |
| PHF | 95 | 0.01, 0.01 ^d | 67, 98 ^d | 5.28 | 39.9 | 33, 50 ^d |

^a Hydrolyzed samples were used for the intrinsic viscosity measurements in 0.1M aqueous NaCl at 30°C.

^b M—H equation used to calculation the molecular weight is $[\eta] = KM_w^\alpha$, where $K = 3.12 \times 10^{-3}$ ml/g, $\alpha = 0.755$.

^c N_g , the average number of grafts per chain. The average molecular weight of monomer is calculated as: $72 \times (1 - x) + M_w \times x$, where M_w is 324 for SA and 639 for FX14 and x is the comonomer fraction in polymer.

^d The first number is for SA and the second number for FX14.



Scheme 2 Model (a) and (b) for the miscibility of three compartments: FC group; polymeric HC group; and surfactant HC group.

RESULTS AND DISCUSSION

Effect of 0.1M NaCl on solution properties

Results about the interaction of HMWSP with surfactant in the absence of NaCl, reported in our previous article, suggest that the poor miscibility between FC groups of the polyelectrolyte and HC groups of Np7.5 can be improved via a specially hybrid structure where two different natures of hydrophobiles are randomly linked by various lengths of polymer segments. It can be supposed that the structure of the microdomain formed in our PHF-Np7.5 system is similar to that of Winnik's system¹¹ except that the pyrene group is replaced by the HC surfactant Np7.5. However, in Winnik's system, the fluorescent group is covalently bonded to the backbone and close to the HC group. While in our system, the surfactant Np7.5 was added and associated into the microdomain. The surfactant may mingle unselectively with HC and FC hydrophobiles of the terpolymer. Here we draw the two models, pseudomiscibility and real miscibility, into Scheme 2 (a, b), respectively. In the case of pseudomiscibility, a hydrophobic microdomain or mechanically effective junction is made up of microphase-separated hydrocarbon moiety and fluorocarbon moiety, although in the case of real miscibility, hydrocarbon and fluorocarbon groups are molecularly mixed with each other. No matter which case is true for our system, the structure of the microdomain formed in PHF/Np7.5 is different from that in PH/Np7.5. Further investigation is performed in the presence of 0.1M aqueous NaCl.

As shown in Figure 1, a shear-thickening region is found for the system of PHF/Np7.5 in both the presence and the absence of NaCl. The changing pattern of G' is similar to Tam and Jenkins' HEUR³⁰ and HASE³¹ systems and it is interpreted as the shear-induced transformation from intramolecular association to intermolecular association or shear-induced shortening of superbridges. Namely, the thickening is caused by the net increase of the density of mechanically active chains, whereas in the Newtonian region, the solution elasticity in 0.1M NaCl is a little less than that without salt, as compared with G' . It should be noted that the preparing sequence is an alkalization of the original polymer solution to pH value of 10, followed by the addition of NaCl, and finally, the addition of Np7.5. It

is expected that the added counterions (Na^+) shield the electrostatic repulsion of the charged backbone and reduce the rigidity of polymer.³² This enlarges the possibility of forming intramolecular association upon the addition of Np7.5, and thus, leads to the reduction of the density of the intermolecular junctions. However, it also brings more opportunity for salted solution to transform the intramolecular-to-intermolecular associations upon the shear. As determined by Kaestner et al.³³ through rheological measurements and by Petit-Agnely et al.³⁴ through ¹⁹F- and ¹³C-NMR, only a few of alkyl side chains are eventually aggregated to form the network. Most of the hydrophobic chains exist in the form of intramolecular association and this make shear-thickening possible by transforming the intramolecular into intermolecular association. When the shear stress increases, more stable intermolecular association is preferably formed. Compared to the solution without salt, an earlier and more drastic thickening is observed for the solution of 0.1M NaCl, as expected. Similar situations are found for PH solution. Nevertheless, for 0.4 wt % PF, macroscopic phase separation emerges concomitant with the turbidity of the solution because of the strong hydrophobic associating ability, which is first forbidden by the chain rigidity and then released by the electrostatic shielding through adding salt. The phase separation indicates that the association in the case of PF/Np7.5 is substantially different from that of the other two. In the following, attention will be focused on the comparison between the system of PH/Np7.5 and PHF/Np7.5.

The oscillatory frequency measurements of the solution of 0.4 wt % PH and 0.004 wt % Np7.5, as shown in Figure 2, shows the structural change of the associative junctions before and after the addition of NaCl. Conspicuously, the junction life, as shown by the crit-

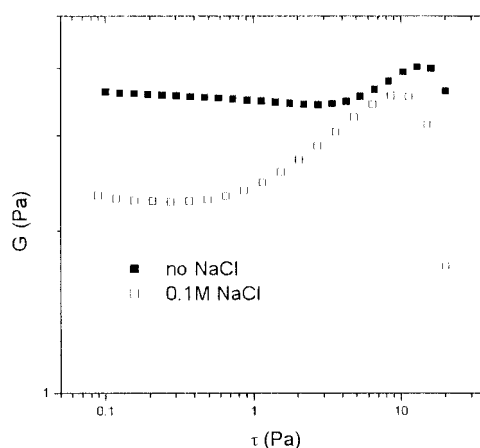


Figure 1 Oscillatory stress sweeps on 0.4 wt % PHF with and without 0.1M NaCl. Into the solution, 0.04 wt % Np7.5 is added and the sweep frequency keeps 1 Hz.

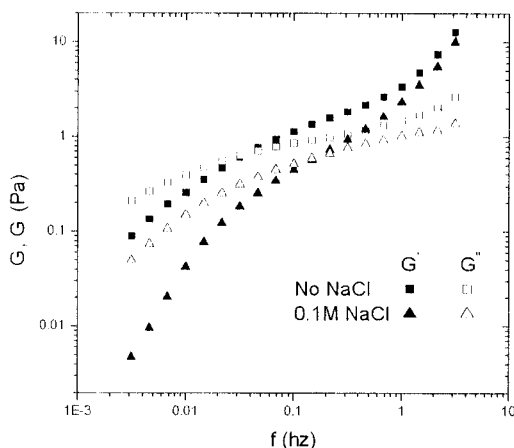


Figure 2 Oscillatory frequency sweeps on the solution of 0.4 wt % PHF and 0.04 wt % Np7.5 with and without 0.1M NaCl. The applied stress is 1 Pa.

ical frequency f^* , is shortened when the electrostatic repulsion is screened. In the absence of NaCl, the rigid chain hinders the formation of the micellelike aggregate with a high curvature. A low curvature inevitably results in the aggregate with relatively large size, which is stable enough to experience the disfavored circumstances. As the salt is added, the flexibility of the polymeric chain makes it possible for more hydrophobes to form a small size of aggregate with high curvature. From the viewpoint of mechanical effect, the addition of the salt seems to break the great aggregates into small ones. The decrease of aggregate functionality leads to the reduced viscoelasticity of the solution. The variation of rheological behaviors of PHF/Np7.5 is similar to that of PH/Np7.5.

Effect of hydrophobe concentration on solution properties of PHF/Np7.5 in the presence of salt compared with PH/Np7.5

As discussed above, although it is same for PH and PHF that the addition of NaCl improves the flexibility of polysoap and alters the morphology of the microdomains formed through association with Np7.5, the composition of the aggregates is different for the two polymer solutions. By studying the effect of the salt on the rheological properties of PHF/Np7.5 and PH/Np7.5, however, we cannot determine which form of association, as shown in Scheme 2(a, b), is preferably taken by these aggregated FC and HC groups. Some steady fluorescence measurements using pyrene as the probe were also taken for the two solutions. When the concentration of Np7.5 is far below its CMC, with the increase of the concentrations of PH and PHF, the degree of hydrophobicity of the microdomain for PHF/Np7.5 is lower than that for PH/Np7.5, as characterized by the spectrum of the

pyrene. It can be interpreted as the effect of the lipophobicity of the FC groups in the microdomain on the location of the HC probe to the hydrophobic microdomain. Therefore, results from the steady fluorescence measurements can only strengthen the opinion as revealed by aforementioned rheological results that in PHF/Np7.5 the microdomain consists of both HC and FC groups.

The effect of hydrophobe concentration, both polymer concentration and surfactant concentration, on the compositional evolution of mixed aggregates is also investigated. The oscillatory stress sweep on PHF and PH, as shown in Figure 3, leads to the similar behaviors as reported by Tam et al. for their HASE system.³⁰ That is, after the shear-thickening region, the storage modulus G' begins to decrease drastically but the loss modulus G'' still increases. This general phenomenon for associative polymers has been explained as the result of transformation of intramolecular association into more stable intermolecular association with the increase of shear stress, as shown by the increase of G' .^{30,31} Beyond a critical stress, the intermolecular aggregates break into smaller and smaller aggregates, which decreases the G' on one hand and extends the polymer network on the other hand. Elasticity turns into viscosity and G'' increases concomitantly with the decrease of G' during this process until the stress is high enough to break all network junctions. The solution behaviors of PHF and PH upon the oscillatory frequency sweep are studied; the results are listed in Table II. Explicitly, both the critical modulus G^* and the critical frequency f^* of the two solutions increase with the increasing stress. The aggregate is ready to become smaller under higher stress as aforementioned. The increase of polymer concentration, for instance from 0.3 to 0.4 wt %, decreases the f^* , which is ascribed to the formation of greater aggre-

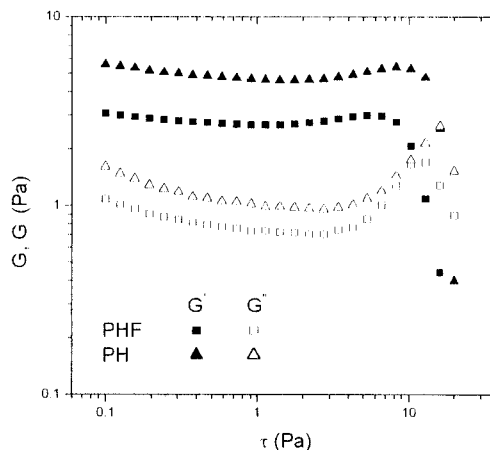


Figure 3 Oscillatory stress sweeps on 0.4 wt % solution of PHF and PH. Other conditions: pH: 10, [NaCl]: 0.1M, [Np7.5]: 0.04 wt %, frequency: 1 Hz.

TABLE II
Oscillatory Frequency Sweeps on Polymer Solutions
with Different Np7.5 Contents^a

| C_p (wt %) | [Np7.5] (wt %) | τ (Pa) | PHF | | PH | |
|-----------------|-------------------|-------------|------------|------------|------------|------------|
| | | | G^* (Pa) | f^* (hz) | G^* (Pa) | f^* (hz) |
| 0.3 | 0.04 | 2 | 0.4 | 0.2 | 0.5 | 0.02 |
| 0.3 | 0.10 | 10 | 2 | 0.09 | 4 | 0.2 |
| 0.4 | 0.04 | 2 | <1 | <0.01 | <1 | <0.01 |
| 0.4 | 0.04 | 10 | 1 | 2 | 2 | 2 |

^a G^* is the critical modulus and f^* is the critical frequency of the viscoelastic network.^{26,35,36} They are determined by the cross point of the storage and loss modulus curves. The value of G^* is proportional to the plateau modulus and the effective junction number of the transient network (ν_{eff}). The value of f^* is inversely proportional to the terminal relaxation time (λ_0) of the network and indicates the strength of the network junctions.

gates when the concentration of the polysoap hydrophobic increases. However, the effects of the alternation of Np7.5 concentration on rheological properties of the two 0.3 wt % polymer solutions are different. The difference lies more in f^* than in G^* . When the concentration of Np7.5 increases from 0.04 to 0.1 wt %, f^* decreases for PHF, meaning more stable aggregates are formed, but increases for PH when the same stress (10 Pa) is applied.

Results obtained from the steady-shear temperature ramp measurements on 0.3 and 0.4 wt % PH and PHF solutions with different Np7.5 contents are listed in Table III. As shown in Figure 3 and again in Figure 4, shear-thickening is observed for all the measured solutions. The dependence of zero-shear viscosity on temperature stems from the dissociation energy of hydrophobic groups from junctions. The solutions were generally kept a period prior to measurements to ensure the association equilibrium reached and were regarded as in the thermodynamic stable state. However, the shear-induced thickening can be referred to as a dynamic process. A maximal viscosity occurs

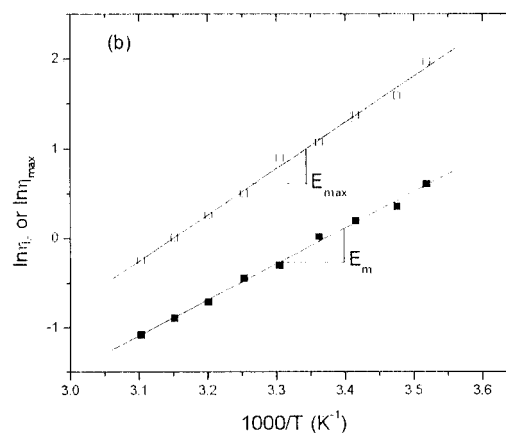
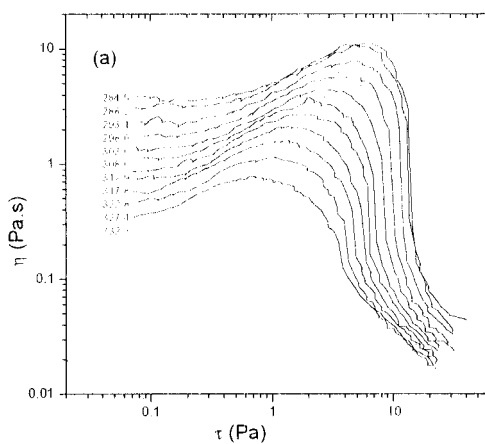


Figure 4 (a) Steady shear temperature ramp on the solution of 0.3 wt % PHF with 0.04 wt % Np7.5. pH: 10, [NaCl]: 0.1M. (b) The corresponding logarithmic zero shear viscosity and maximum viscosity as the function of the reciprocal of temperature.

before the network is destroyed by the shear. As shown in Figure 4, onset of the shear-thickening shifts to lower stress regions with the temperature stepwise

TABLE III
Comparison of Plateau Dissociation Energy (E_m) and Maximum Dissociation Energy (E_{max})
of Two Polymers with Increasing Np7.5 Content^a

| C_p (wt %) | [Np7.5] (wt %) | [S]/[H] ^b | PHF | | PH | |
|-----------------|-------------------|----------------------|-------------------|------------------------------|-------------------|------------------------------|
| | | | E_m (kJ/mol) | E_{max} (kJ/mol) | E_m (kJ/mol) | E_{max} (kJ/mol) |
| 0.3 | 0.004 | 0.12–0.14 | 47.2 | 69.3 | 55.5 | 78.0 |
| 0.3 | 0.01 | 0.3–0.35 | 47.5 | 64.4 | 41.2 | 59.9 |
| 0.3 | 0.04 | 1.2–1.4 | 33.5 | 42.8 | 42.5 | 55.2 |
| 0.3 | 0.10 | 3.0–3.5 | 67.8 | 38.8 | 22.0 | 33.2 |
| 0.4 | 0.04 | 0.9–1.1 | 37.4 | 45.3 | 37.0 | 44.3 |

^a The ΔG of Np7.5 during micellization is 23.7 kJ/mol.

^b [H] stands for the concentration of hydrophobiles of polysoap and [S] for the concentration of Np7.5. The value of [S]/[H] is a little different for PHF and PH because the hydrophobes of PHF is a little more than that of PH. The upper limit of [S]/[H] corresponds to PH and the lower limit to PHF.

increasing, indicating that the strength of these junctions decreases continuously. Through steady-state shear measurements and the following equation^{30,31,35,36}

$$\ln \eta_0 \sim E_m/kT \quad (1)$$

$$\ln \eta_{\max} \sim E_{\max}/kT \quad (2)$$

where the plateau dissociation energy, E_m , and the maximum dissociation energy, E_{\max} , are obtained. The E_{\max} is similarly obtained from the dependence of the maximum viscosity on temperature and is thought to characterize the stability of those junctions dynamically induced by the shear force. From Table III, it can be seen that all E_{\max} are greater than the corresponding E_m except for the system of 0.3 wt % PHF and 0.1 wt % Np7.5. Because of the hindrance from the polymer backbone, more stable junctions can be formed only on conditions that the applied shear stress dynamically modulates the conformation and facilitates the formation of more stable association. In our system, the aggregates containing less Np7.5 are more stable, which can be inferred from the fact that the increase of Np7.5 fraction in the solution causes the lowering of E_m . The shear favors the association of hydrophobiles of the polysoap, which could only associate with more Np7.5 prior to the shear because of the dynamic hindrance. The variation of the Gibbs free energy (ΔG) during the micellization of Np7.5 is 23.7 kJ/mol. Dissociation energies of all junctions are generally higher than Np7.5 except for the system of PH and 0.1 wt % Np7.5. In this system, the ratios of Np7.5 to SA in the junctions are so high that the structure of mixed micelles is close to Np7.5 micelles.

For the solution of PHF, the E_m increases when the concentration of Np7.5 rises from 0.04 to 0.1 wt %. This is different from the trend that with the increase of Np7.5 concentration, E_m and E_{\max} decrease. Furthermore, the E_{\max} is lower than E_m . For PH, when the Np7.5 concentration is low enough (0.004 wt %), the E_{\max} (78 kJ/mol) approaches the documented value (85 kJ/mol) for C18 micelles in HEUR system.³¹ It means that the reformed junctions induced by the shear comprised mainly hydrophobiles of the polysoap. When the Np7.5 concentration reaches 0.1 wt %, the E_m is close to the ΔG of Np7.5 micelles, indicating that the main component of the junctions is Np7.5. With the concentration of Np7.5 increasing, the junctions both under thermodynamic equilibrium and under dynamic shear become less temperature sensitive. It is also the case for PHF when the Np7.5 concentration increases from 0.004 to 0.04 wt %. However, as the Np7.5 concentration reaches 0.1 wt %, the E_m increase surprisingly and the E_{\max} decreases continuously. For E_{\max} , the lower E_{\max} , compared to those obtained at

low concentrations of Np7.5, suggests that the reformed junctions under shear stress become weaker because they contain more Np7.5. It is coincident with the increased fraction of Np7.5 in total hydrophobiles compared to the case of low Np7.5 concentration. However, for E_m , accompanied with the anomalous increase of the E_m , the decrease of f^* is also measured, as shown in Table II. We propose that when the Np7.5 concentration increases from 0.04 to 0.1 wt %, the size of formed aggregates is greatly increased. Although the fractions of Np7.5 in junctions increase, the enlarged aggregates in PHF become more stable as compared to those in PH with unchanged size. Furthermore, when shear stress is applied, the huge aggregates break into small ones. Although small aggregates become unstable as in PH as shown by the E_{\max} , the increased junction density compensates this disadvantage and ensures the occurrence of a higher viscosity (η_{\max}) than zero-shear viscosity for the system of PHF because the steady-shear viscosity is the product of the junction strength, expressed by the plateau modulus G_0 , and the junction density, expressed by the terminal relaxation time λ_0 ^{37,38}

$$\eta_0 = \lambda_0 G_0 \quad (3)$$

that aggregates with a large size do not form in PH but in PHF, to some extent, is correlated with the different composition of aggregates in PHF from that in PH. When the Np7.5 concentration is high enough, those microdomains consisting of HC and FC groups seem to be inclined to reaggregate into greater and more stable microdomains.

Investigation on the evolution of the network junctions upon the change of the ratio of added Np7.5 to polymer hydrophobiles gives us useful information about the structure of the microdomain. For PH/Np7.5, addition of Np7.5 only changes the fraction of two kinds of HC hydrophobiles, surfactant tail and HC grafts on poly(acrylic acid) (PAA). For PHF/Np7.5, the change of the ratio also means to vary the ratio of FC groups to HC groups and this would influence the composition of the aggregate no matter which model of association, pseudomiscibility or real-miscibility, is adopted by these groups. For network junctions, the functionality of HC hydrophobiles from the copolymer will decrease with the increase of the content of associated Np7.5 because of the bridge-breaking effect. Then, the association of FC hydrophobiles would also be affected because these FC groups are randomly grafted around HC groups and the association of FC groups is hindered by the backbone conformation, which is now affected by the released HC groups of the copolymer. As we found in our current study, when the concentration of Np7.5 reaches 0.1 wt %, the plateau dissociation energy is extraordinarily high, indicating that great aggregates

are formed in the solution. Before this, the plateau and maximum dissociation energies and their variation for PHF/Np7.5 upon the addition of Np7.5 are similar to those for PH/Np7.5. Although we could not tell whether the structure of the microdomain formed in PHF/Np7.5 resembles model (a) or model (b), the associating model before and after the concentration of Np7.5 reaches 0.1 wt % should be different. In other words, it is dependent on the concentration of the added surfactant, in which case miscibility is really adopted.

CONCLUSION

FC and HC comodified polyelectrolyte PHF has been synthesized readily by solution copolymerization of acrylic acid (AA) with two hydrophobic monomers SA and FX14. Its association with a nonionic surfactant Np7.5 is investigated by rheological measurements. Strong aggregates with the core containing both HC and FC hydrophobiles are produced in the solution of PHF by adding Np7.5. The poor compatibility between HC surfactant and FC containing polyelectrolytes is improved in PHF/Np7.5. When the Np7.5 content is high enough (over 0.04 wt % Np7.5), the structure of the formed aggregates in 0.3 wt % PHF solution and thus the endurance to the applied shear especially are different from HC modified counterpart PH.

To the best of our knowledge, the interaction of HC and FC comodified polyelectrolytes with added surfactant is first investigated in this article and the associative terpolymer, PHF, is dealt with as a macromolecular hybrid polysoap for the first time. Unique interactions of this hybrid polysoap with the added surfactant are promising to supply some insight on the mixed system of FC and HC groups.

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