

# Rheological Properties of Semidilute Solutions of Poly(acrylic acid) Modified with Hydrocarbon and Fluorocarbon End-Capped Poly(ethylene glycol) Macromonomer

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**ABSTRACT:** Hydrocarbon and fluorocarbon end-capped poly(ethylene glycol) (PEG) macromonomers with 9, 23, and 45 ethylene oxide units were synthesized by the esterification method. Copolymerization of these macromers with acrylic acid (AA) resulted in hydrophobically grafted poly(AA)s (PAAs) containing different lengths of PEG spacers. Their solution properties were investigated by rheological measurements and compared to those without hydrocarbon and fluorocarbon groups and without PEG spacers. Evident hydrophobic association was found to exist in the aqueous solution of these hydrophobically grafted copolymers, and the associating

efficiency was improved by the flexible PEG spacer compared to those counterparts without them. However, the intramolecular association became predominant with the spacer length increase and the solution viscosity decreased. A wide viscosity plateau was observed for macromer modified polyelectrolytes in the alkalization process, which was unavailable for hydrophobically modified ones without PEG spacers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2777–2783, 2003

**Key words:** hydrophobic association; graft; end capping; polyelectrolyte; viscosity

## INTRODUCTION

In recent years, much attention has been paid to associative polymers,<sup>1–3</sup> especially, hydrophobically grafted water-soluble polymers, because of their easy preparation and practical prospects as associative thickeners.<sup>4–6</sup> It is found that the associating potential of the hydrophobic groups for grafted water-soluble polymers is partially inhibited by the restriction of the polymer backbone. NMR and microscopy results<sup>7,8</sup> show that a large part of the hydrophobes do not participate in the aggregation or just contribute to the intramolecular association, which has nothing to do with the improvement of the thickening performance. The introduction of a flexible group as a spacer between the polymer backbone and the hydrophobic graft is found to effectively diminish the restriction from the backbone and thus favor the rheological properties of the aqueous solutions.<sup>9–11</sup> Hydrophobically modified alkali swellable emulsion polymers have been commercialized as a category of hydrophobically grafted water-soluble polymers. A series of poly(ethylene oxide)s (PEOs) with different chain

lengths are used as spacers to improve the accessibility of the hydrophobes to form aggregates.

Macromonomer techniques are adopted in the preparation of the hydrophobic comonomer containing PEO spacers.<sup>12,13</sup> In our earlier work, end capping via an isocyanate was used to synthesize fluorocarbon end-capped poly(ethylene glycol) (PEG) macromonomers.<sup>14</sup> Copolymerization of these macromonomers with acrylic acid (AA) resulted in polymers with improved rheological properties in aqueous solution. This article reports a more convenient end-capping method, esterification, to prepare the desired macromonomer. Studies suggested that the best thickening effect was displayed when a suitable length of PEG spacer was chosen.<sup>9,15</sup> Herein macromers with different numbers ( $n$ ) of EO units were synthesized and the effect of the spacer length on the solution properties was investigated. Because the polymer backbone was a polyelectrolyte chain and the hydrophobic association could be modulated by adding surfactants, the effects of the pH and surfactants on the solution properties were also discussed.

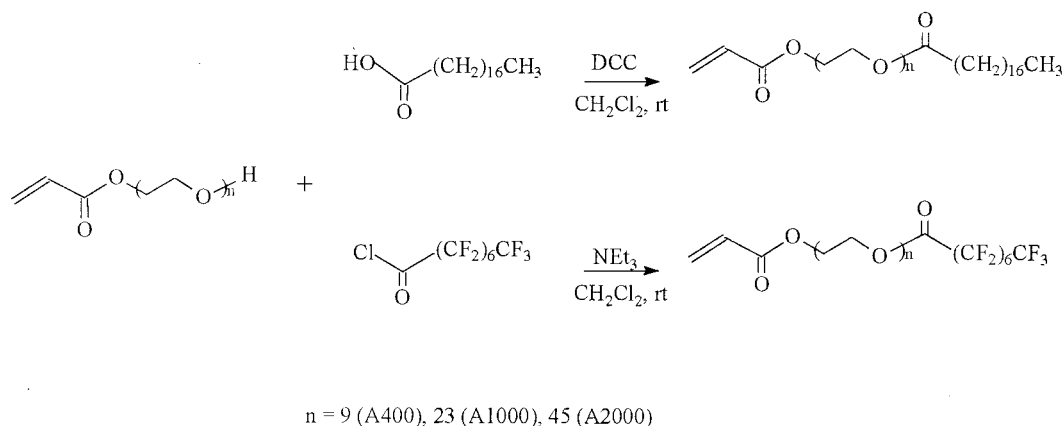
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## EXPERIMENTAL

### Materials

Analytical reagent (AR) grade AA was distilled. PEG monoacrylate (EO  $n = 9, 23,$  and  $45,$  denoted as A400,



**Scheme 1** The synthesis of hydrocarbon and fluorocarbon end-capped PEG macromonomers.

A1000, A2000, respectively; Aldrich), 1,3-dicyclohexylcarbodiimide (DCC, 99%, AR, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, AR), stearic acid (AR, BASF), sodium dodecyl sulfate (SDS, AR), potassium perfluorooctanate (FC143, 3M), perfluorooctanic acid, and NaOH (AR) were used as received. Azobisisobutyronitrile (AIBN) was recrystallized in methanol. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ , AR), cyclohexane (AR), ethyl ether (AR), and methanol (AR) were used as received. Deionized water was used to prepare the polymer solution.

#### Synthesis of stearic acid end-capped PEG monoacrylate macromonomers

The synthesis of hydrocarbon and fluorocarbon end-capped monoacrylate is depicted in Scheme 1. Typically, preparation of the stearic acid end-capped A1000 ( $n = 23$ ) monoacrylate, which we named 1000h, is described as follows. Into a 50-mL egg-shaped bottle were added 2.0 g (2.0 mmol) of A1000 monoacrylate, 1.14 g (4.0 mmol) of stearic acid, 0.82 g (4.0 mmol) of DCC, and small amounts of DMAP with 30 mL of dry  $\text{CH}_2\text{Cl}_2$ . A powderlike precipitate occurred, indicating dehydration. The reaction was stirred at ambient temperature for 24 h. The product was purified on silica gel columns and eluted first with ethyl acetate and then with  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (10:1, v/v). For perfluorooctanic acid end-capped A1000 (termed 1000f), perfluorooctanoyl chloride is used instead of acid. Conversion of the esterification was determined by  $^1\text{H-NMR}$ , and the values are listed in Table I.

#### Synthesis of macromonomer modified poly(AA) (PAA)

Into a 50-mL egg-shaped bottle were added 2.0 mL (29.2 mmol) of AA, 394 mg (0.29 mmol) of 1000h monoacrylate, 20 mL of cyclohexane, and 0.5 mL (50 mM) of a benzene solution of AIBN. The solution was

bubbled with pure  $\text{N}_2$  for 40 min. Then the bottle was placed in a  $60 \pm 1^\circ\text{C}$  oil bath for 24 h. A white precipitate occurred during the reaction. The product was suction filtered and washed several times with  $\text{CH}_2\text{Cl}_2$  and ethyl ether. Finally, the products were vacuum dried at  $50^\circ\text{C}$  overnight.

The conversions of the hydrocarbon macromonomers were determined by vacuum drying and weighing the residues in the filtrate obtained after washing. The conversions of the fluorocarbon macromonomers were determined by fluorine analysis. By controlling the feed ratio of the macromonomer to AA, an almost equimolar content of macromonomer (0.5–0.6 mol %) was copolymerized into the resulted products. These polymer samples containing A400, A1000, and A2000

**TABLE I**  
Single End-Capping Ratios of Macromonomers

| Macromer | Cal <sup>a</sup> | Found <sup>b</sup> | End-Capping Ratio <sup>c</sup> (%) |
|----------|------------------|--------------------|------------------------------------|
| 400h     | 35/36            | 35/48              | 75                                 |
| 1000h    | 35/92            | 33/75              | 84                                 |
| 2000h    | 35/180           | 14/54              | 67                                 |
| 400f     | 33%              | 27.5%              | 83                                 |
| 1000f    | 19.5%            | 15.8%              | 81                                 |
| 2000f    | 11.6%            | 11.1%              | 96                                 |

<sup>a</sup> For hydrocarbon end-capped macromers, the calculated values are the numerical ratios of alkyl hydrogens to ethylene oxide hydrogens; for fluorocarbon end-capped macromers, the calculated values are the weight percentage of fluorine.

<sup>b</sup> For the hydrocarbon series, the found values are the ratios of the peak areas of alkyl hydrogens (chemical shift: 0.7–1.7 ppm) to ethylene oxide hydrogens (chemical shift: 3.3–4.0 ppm) on the  $^1\text{H-NMR}$  spectrum, which was obtained on a 300M NMR spectrometer. For the fluorocarbon series, the data are the results of fluorine element analysis.

<sup>c</sup> For 1000h and 2000h, double end-capped products may exist. Therefore, the peak areas for alkyl hydrogens are larger than those for ethylene oxide hydrogens. Only the ratios of single end-capped products are calculated here.

TABLE II  
Characterization of Macromer Modified Poly(acrylic acid)

| Sample   | Macromer | Feed ratio | Yield (%) | Conversion <sup>a</sup> (%) | Grafting ratio <sup>b</sup> | [ $\eta$ ] <sup>c</sup> | $M_{\eta}$ <sup>c</sup> |
|----------|----------|------------|-----------|-----------------------------|-----------------------------|-------------------------|-------------------------|
| 400-0.6  | A400     | 0.0067     | 92        | 80                          | 1/192                       | 3.86                    | 26.3                    |
| 1000-0.6 | A1000    | 0.006      | 97        | 92                          | 1/181                       | 2.99                    | 18.8                    |
| 2000-0.6 | A2000    | 0.006      | 100       | 100                         | 1/167                       | 1.68                    | 8.8                     |
| 400h-1   | 400h     | 0.01       | 97        | 52                          | 1/190                       | 3.59                    | 23.9                    |
| 1000h-1  | 1000h    | 0.01       | 93        | 64                          | 1/156                       | 1.60                    | 8.2                     |
| 2000h-1  | 2000h    | 0.01       | 88        | 63                          | 1/160                       | 2.23                    | 12.7                    |
| 400f-2   | 400f     | 0.02       | 90        | 28                          | 1/177                       | 2.89                    | 17.9                    |
| 1000f-2  | 1000f    | 0.02       | 89        | 27                          | 1/193                       | 1.26                    | 6.0                     |
| 2000f-2  | 2000f    | 0.02       | 63        | 24                          | 1/211                       | 1.30                    | 6.2                     |

<sup>a</sup> The conversions of fluorocarbon end-capped macromers were determined by the fluorine contents in the polymers and those of hydrocarbon end-capped and unmodified macromers were determined by the gravimetric method.

<sup>b</sup> The ratio of macromer to monomer AA.

<sup>c</sup> The intrinsic viscosity [ $\eta$ ] was obtained in 0.1M NaBr aqueous solution, where the K and  $\alpha$  of the Mark-Houwink equation at 25°C is  $31.2 \times 10^{-4}$  dL/g and 0.755, respectively. For all hydrophobically modified polymers, hydrolysis was carried out prior to the measurement of the intrinsic viscosity. It was found that the hydrolysis degree was above 95% for fluorocarbon modified samples as determined by element analysis.

spacers were named 400h-1, 1000h-1, 2000h-1 and 400f-2, 1000f-2, 2000f-2 for the hydrocarbon and fluorocarbon macromonomers, respectively. Three control copolymers with PEG monoacrylate but without hydrophobic end groups were also synthesized and denoted as 400-0.6, 1000-0.6, and 2000-0.6. Table II shows the data for the synthesis of polymer samples and the properties of their dilute solutions. For the fluorocarbon end-capped series, the conversion is between 20 and 30%. This is similar to both Piculell et al.'s<sup>16</sup> and our<sup>15</sup> previous results.

### Solution preparation and rheological measurements

Different concentrations of polymer solutions were prepared by diluting the 1 wt % semidilute solutions. The pH value of the solution was modulated by adding 10 wt % aqueous NaOH. The solution was turbid below pH 4 and became clear above it. Because the ester bonds were prone to hydrolysis in basic environments, the pH values of the investigated solutions were adjusted to around 5. These solutions were kept 2 days prior to the measurements. In the investigation of the effect of pH on the solution properties, the acidic solutions were alkalized stepwise and the whole process was not longer than 2 h so that the hydrolysis of the hydrophobic PEG macromer was not enough to affect the measurements of the solution properties. SDS and FC143 were added directly to the desired weight percentage concentrations. Rheological measurements of the polymer solutions were performed on a Haake Rheostress RS75 rheometer equipped with a geometry of 2°/6-cm cone and plate. A C60/Ti 2 sensor was used and the gap was set to 0.105 mm. The temperature was kept at  $25 \pm 0.5^\circ\text{C}$  by a F6/8 temperature device. In the dynamic stress

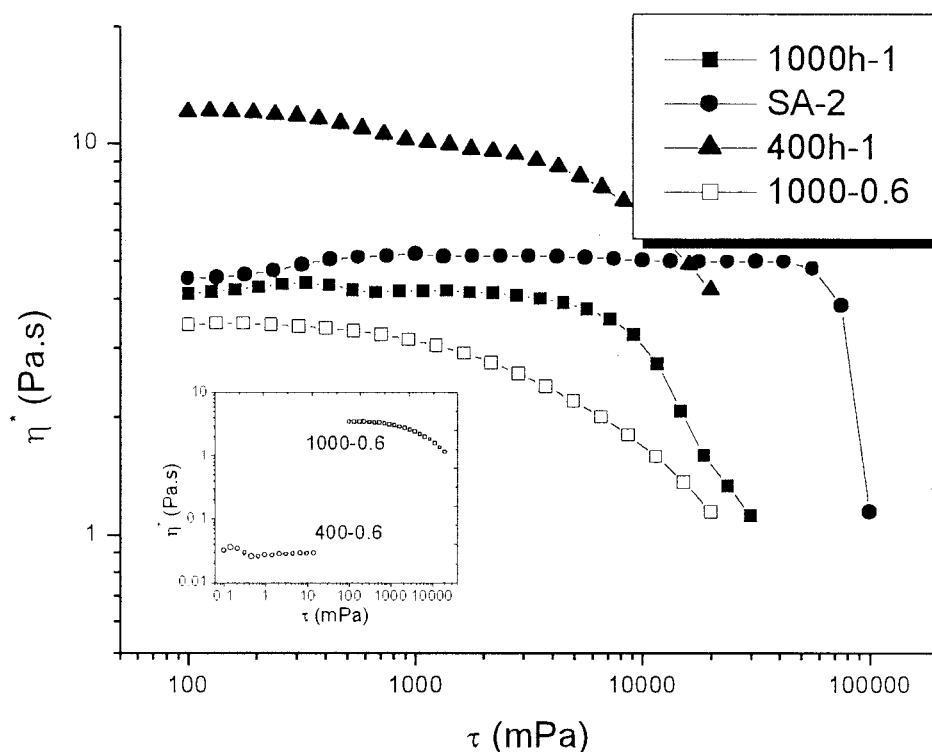
sweep measurements, the oscillatory frequency was kept at 1 Hz. For the 400-0.6 sample, the solution viscosity was too low to be measured by the RS75 rheometer. The viscosity measurements were performed on an Ares Rheometric Scientific rheometer with a 34-mm cup diameter, 32-mm bob diameter, and 33.34-mm bob length. The temperature was controlled at 25°C with a Neslab RTE130 thermocontroller.

## RESULTS AND DISCUSSION

### Effect of spacer length on thickening ability

Tam et al. found that for their hydrophobically modified alkali swellable emulsion polymers with a  $\text{C}_{32}\text{H}_{65}$  hydrophobile, the best thickening behaviors were presented when there were 10 EO units in the PEG spacer.<sup>9</sup> In our previous work, better thickening ability was also shown by the solution of PAA modified with fluorocarbon end-capped PEG monoacrylate ( $n = 23$ ) than with the other two ( $n = 6$  and 45).<sup>15</sup> As shown in Figure 1, the complex viscosity of the 0.8 wt % solution of the 400h-1 copolymer is higher than that of 1000h-1, although for the corresponding copolymers modified without hydrophobic end groups, the solution of 1000-0.6 is more viscous than that of 400-0.6. However, the solution viscosity of the 2000h-1 copolymer is very low and is not shown in Figure 1, which means that a longer PEG spacer disfavors the formation of a strong physical network when macromonomers are prepared by esterification.

It can also be seen in Figure 1 that, when the macromonomer is hydrocarbon end-capped, the thickening efficiency of the corresponding copolymer is improved. However, the increase of the solution viscosity from 400-0.6 to 400h-1 is greater than that from 1000-0.6 to 1000h-1. With the decrease of the chain

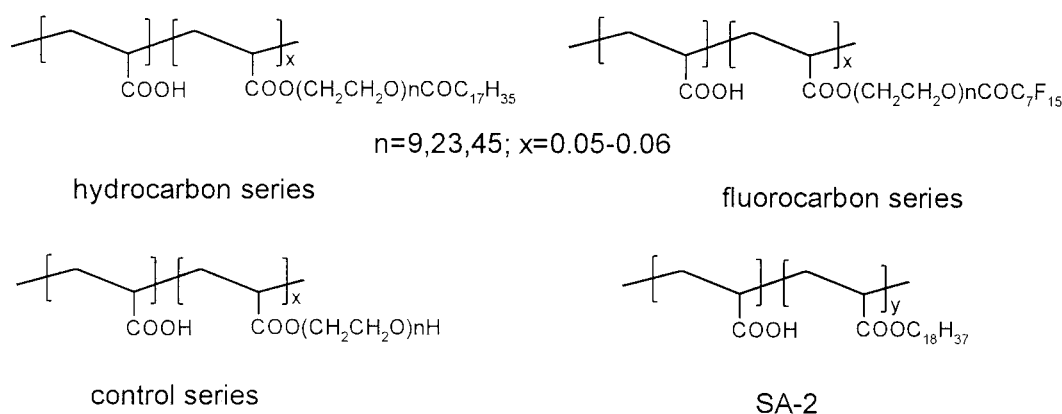


**Figure 1** The complex viscosities of 0.8 wt % 1000-0.6, 1000h-1, 400h-1, and SA-2 under an oscillatory stress sweep.

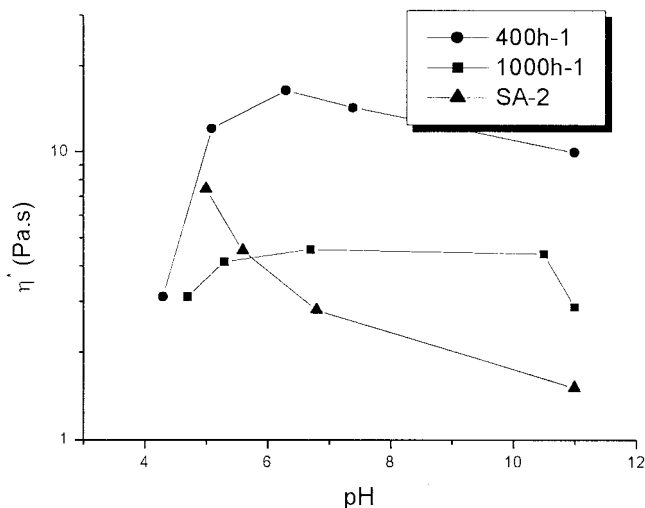
length of the PEG spacer, the contribution of the hydrogen bond to the whole solution viscosity is diminished because the viscosity of copolymer 400-0.6 is lower than that of 1000-0.6. Therefore, the fact that the viscosity of 400h-1 is higher than that of 1000h-1 indicates that the hydrophobic interaction predominates the solution viscosity of 400h-1 more than that of 1000h-1. The grafting hydrophobic end groups of copolymer 400h-1 are more efficient in forming intermolecular associations.

Under low shear stress, the solution viscosity of 1000h-1 is comparable to that of SA-2, which is a PAA modified with twofold contents of hydrophobes but without a PEG spacer. Its structure is shown in

Scheme 2, but its characterization is stated elsewhere.<sup>17</sup> The solution of 400h-1 is more viscous than SA-2. This confirms that the associating efficiency of the grafting hydrophobes without PEG spacer is low and the introduction of a flexible PEG spacer evidently improves it. However, we found that the solution viscosity of the 400h-1 copolymer decreases continuously with the increase of the shear stress when the stress is above 10 Pa. Meanwhile, the viscosity of SA-2 is unchanged with the shear stress and becomes larger than that of 400h-1 when the shear stress passes 20 Pa. This indicates that, in the SA-2 solution, the network is mainly maintained by small amounts of very large and stable aggregates, which can endure greater shear



**Scheme 2** The chemical structures of the investigated copolymers.



**Figure 2** The effect of pH on the complex viscosities of 0.8 wt % 400h-1, 1000h-1, and SA-2.

stress. When a stress is applied, the intermolecular association breaks on the one hand and the intramolecular association is transformed to intermolecular association on the other hand.<sup>17</sup> Therefore, the solution viscosity can stay at a plateau till the stress is large enough. In the solutions of 400h-1 and 1000h-1, sufficient association existed and conversion of the intramolecular association into an intermolecular association cannot compensate the inverse process. Therefore, the solution viscosity decreases with increasing shear stress.

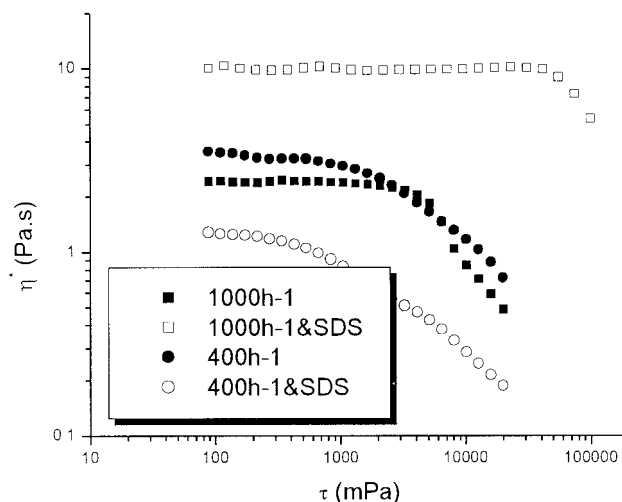
**Effect of pH on rheological behaviors of polymer solutions**

Because PAA is a typical polyelectrolyte, its chain conformation is related to the solution pH. In acidic solution, the polymer chain is flexible and similar to a coil; but in basic solution, it becomes rigid and extended like a rod. The conformation of the backbone has obvious impact on the association of the hydrophobic graft. Thus, the whole solution viscosity can be modulated with the pH value.<sup>18</sup> This feature also makes the modified PAA a promising pH responsive hydrogel for various applications. Studies have shown that, for a hydrophobically modified PAA without a PEG spacer, the hydrophobic aggregates are greatly dissociated when the solution pH is modulated to 7.<sup>15</sup> It is ascribed to the strong restriction of the polymer chain to the hydrophobic graft. When the polymer chain is extended, the association of the grafts becomes difficult. The case of SA-2, as shown in Figure 2, is typical. However, for our macromonomer modified PAA, two different phenomena occur. The first is that a higher pH value is needed to make copolymers 1000h-1 and 400h-1 reach their highest viscosity. The second is that the viscosity plateau is wider than that

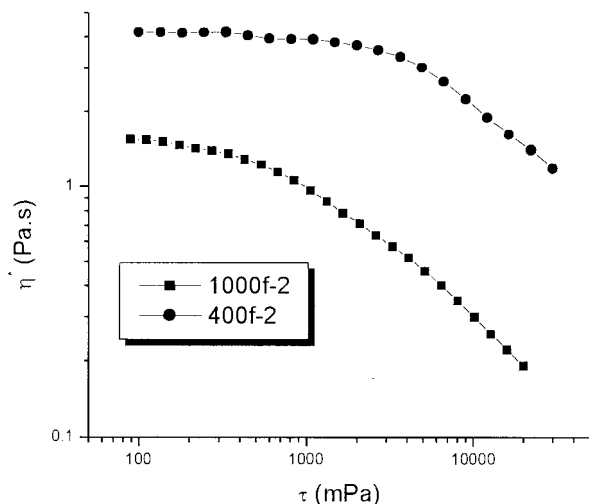
of SA-2. Both of these indicate that the PEG spacer buffers the unfavorable effect of the chain extension on the hydrophobic association of the grafts. A wide viscosity plateau is observed because the PEG spacer diminishes the restriction of the polymer backbone to the grafts and thus the effect of the chain extension on the grafts is weakened. In acidic solution, hydrogen bonds exist, to some extent, between PEG spacers within the acidic backbone. A higher pH is needed to decrease these hydrogen bonds and convert these grafts into intermolecular associations. Therefore, the occurrence of the maximum is delayed for macromonomer modified PAA.

**Effect of SDS on rheological behaviors of polymer solutions**

As shown in Figure 3, different responsive behaviors occur upon the addition of 0.2 wt % SDS into the 0.6 wt % aqueous solutions of 1000h-1 and 400h. For 1000h the solution viscosity is greatly enhanced and the tolerance for the shear stress is improved from 3 to 50 Pa. However, the solution viscosity decreases for 400h. The viscosity of 0.6 wt % 400h-1 is a bit higher than that of 1000h-1 prior to the addition of SDS. In the existence of 0.2 wt % SDS, the latter becomes far higher than the former. This means that the SDS stabilizes the aggregates of 1000h-1 but destabilizes those of 400h. Because the hydrophobic end groups grafting on copolymers 400h-1 and 1000h-1 are the same and their concentrations are close, the different effects of SDS on the aggregates of 1000h-1 and 400h-1 should be ascribed to the different lengths of the PEG spacers. We speculate that, in the solution of 400h, micelle-like aggregates formed and they were saturated. Adding SDS dissociated the aggregates into more mixed micelles consisting of both SDS and hydrophobic grafts.



**Figure 3** The effect of SDS on the complex viscosities of 0.6 wt % 1000h-1 and 400h-1.

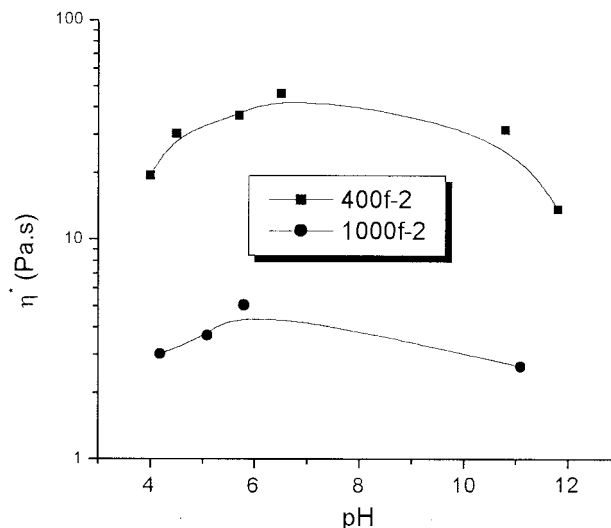


**Figure 4** The complex viscosities of 0.6 wt % 1000f-2 and 400f-2 under an oscillatory stress sweep.

Thus, the number of macromonomers per aggregate diminished and the network became weak. However, for 1000h, the formation of saturated aggregates would be inhibited because longer PEG chains induced the effect of shell-crowding when they acted as hydrophilic shells. By contrast, longer spacers would make it possible for more grafts to overcome the distribution irregularity and reach each other. By forming mixed micelles, the added SDS both decreased the shell-crowding effect and induced more grafts to associate into big aggregates. Thus, the network junctions were strengthened and increasing solution viscosity occurred; but for 2000h, no improvement of the solution viscosity was observed. Tam et al. thought that a longer spacer would have more opportunity to form intramolecular associations.<sup>9</sup> The effect of SDS on the intramolecular association cannot be reflected through the solution viscosity. Considering the shell-crowding effect induced by such a long spacer ( $n = 45$ ) in the solution of 2000h-1, the association of a hydrophobically end-capped PEG graft would be greatly disfavored.

#### Solution properties of hydrocarbon modified PAA modified with fluorocarbon end-capped PEG monoacrylate

Similar to the results obtained for hydrocarbon modified polyelectrolytes, the solution viscosity of 400f-2 is higher than 1000f-2, as shown in Figure 4. Therefore, it is confirmed once again that the spacer length is the determining factor influencing the associating efficiency. Hwang and Hogen-Esch<sup>19</sup> found that insertion of 1–3 ethylene oxide groups between the hydrophilic backbone and fluorocarbon graft could improve the apparent viscosities of polymer solutions continuously. Here we increased the spacer length and found

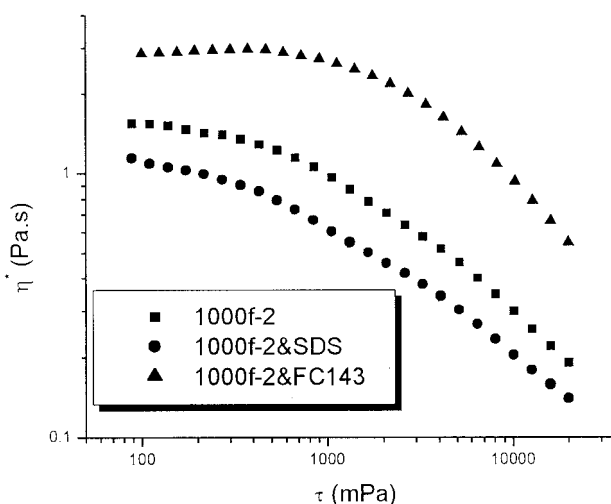


**Figure 5** The effect of pH on the complex viscosities of 0.8 wt % 400f-2 and 1000f-2.

the solution viscosity decreased if the length of the spacer exceeded a critical length range.

The effect of the pH on the solution viscosity is shown in Figure 5. Similar to 400h-1 and 1000h-1, both the 400f-2 and 1000f-2 solutions present viscosity plateaus. Therefore, the introduction of a PEG spacer can increase the endurance of the associating network to the solution pH, no matter which kind of hydrophobic junction it comprises.

As shown in Figure 6, the addition of 0.4 wt % FC143 into 0.8 wt % 1000f-2 solution results in increased viscosity. This is similar to the system of SDS and 1000h-1. However, when SDS is added into the 1000f-2 solution, the solution becomes less viscous. This can be ascribed to the poor compatibility between fluorocarbon and hydrocarbon groups.



**Figure 6** The effects of FC143 and SDS on the complex viscosity of 0.6 wt % 1000f-2.

### CONCLUSION

Through esterification, three stearic acid end-capped and three perfluorooctanic acid end-capped PEG monoacrylate macromonomers ( $n = 9, 23,$  and  $45$ ) were prepared. Copolymerization of small amounts of these macromonomers with AA resulted in macromonomer modified PAAs. Rheological measurements showed that the associating efficiency was improved for the solutions of 1000h-1 and 400h-1 compared to the corresponding hydrophobically modified PAA (SA-2) without a spacer. This was coincident with the proposal that a flexible spacer decreased the restriction of the polymer backbone to the hydrophobic end group. Polymers 400h-1 and 400f-2 displayed the best thickening ability among the hydrocarbon and fluorocarbon series, respectively. Upon the increase of the solution pH, a wide viscosity plateau was observed. The addition of SDS increased the solution viscosity of 1000h-1 but decreased that of 400h-1. Similarly, the solution viscosity of 1000f-2 was increased by adding FC143.

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