

Effects of Ethylene Oxide Spacer Length on Solution Properties of Water-Soluble Fluorocarbon-Containing Hydrophobically Associating Poly(Acrylic Acid-co- R_f -PEG Macromonomer)

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Poly(acrylic acid)s (PAAs) modified with a series of fluorocarbon group (R_f) end-capped Poly(ethylene glycol) (PEG) macromonomers (number of ethylene oxide unit: 1, 9, 23, 45) and corresponding copolymers without fluorocarbon end groups were synthesized. It was found that the effect of the hydrophobic association of fluorocarbon groups on the solution viscosity prevailed over that of the hydrogen bond between grafted PEG and the backbone. Rheological measurement on the aqueous solutions of these poly(acrylic acid-co- R_f -PEG macromonomer)s demonstrated that the best thickening performance was shown when the number of ethylene oxide unit (EO number) was 23.

Keywords fluorocarbon-containing, PEG macromonomer, spacer, rheological property, hydrophobic association

Introduction

Hydrophobically modified water-soluble polymers (HMWSPs) can be used as associative thickeners (AT's) in industry due to their amphiphilic property and inclination of hydrophobic association in water. Because of their unique rheological properties, HMWSPs have received increasing attention over the past two decades.¹⁻⁴ Versatile HMWSPs have been produced by copolymerization of water-soluble monomers with the hydrophobe-containing comonomers or the hydrophobically modified natural ingredients. The synthesis of novel and high performance HMWSPs becomes the emphasis of many researches.⁵⁻⁹

In fact, the associating ability of all hydrophobes is not completely fulfilled because many hydrophobic groups are associated into intramolecular aggregates which have no contribution to apparent viscosity.^{9,10} In HMWSP solutions there also exist a certain amount of free hydrophobes, which are inhibited to associate with each other mainly due to being localized by the rigid hydrophilic backbone. Introduction of one or more flexible groups between hydrophobes and polymer backbone, such as ethylene oxide unit (EO), as a spacer can improve the viscosity of the solution. Hwang *et al.*¹¹ had demonstrated that with the EO

number increasing from 1 to 3, the solution viscosity of the hydrophobically modified poly(acrylamide) increased continuously. The spacer was considered to provide more flexibility for hydrophobes to associate and alter the hydrophobicity of the macromonomers.

On the other hand, it has been available to design and synthesis a variety of comb, star, brush and graft polymers by using macromonomers as potential building blocks.¹² Especially, poly(ethylene oxide) (PEO) macromonomer is the most promising comonomers to afford high performance HMWSPs.^{1,5,13-15} Jenkins *et al.*^{1,5} have used methacrylic acid, ethyl acrylate and acrylate with a long PEO segment end-capped by a long hydrocarbon hydrophobe as comonomers and synthesized a series of AT's, which can be classified as hydrophobically modified alkali swellable/soluble emulsions (HASE). Many factors can promote the thickening efficiency of this type of AT's. Among them, the length of ethylene oxide spacer is a very important factor. Tam *et al.*⁵ investigated the solution properties of HASEs modified with different EO number ($n = 2.5, 10, 40$) but end-capped with the same hydrophobe ($C_{32}H_{65}$). The best thickening efficiency was obtained when the spacer holds 10 EO units.

Since fluorocarbon hydrophobe was used in the associating polymers for the first time,⁴ there have been many publications on fluorocarbon hydrophobically modified associating polymers. The association formed by fluorocarbon hydrophobes is stronger than that formed by corresponding hydrocarbon hydrophobes.¹⁶ Light scattering and fluorescence study have confirmed the existence of hydrophobic microdomains made up with fluorocarbon groups in aqueous solutions.¹⁷⁻¹⁹ Although Hwang *et al.*¹¹ investigated the solution properties of fluorocarbon-containing poly(acrylamide)s with different spacer lengths (EO number: 1, 2, 3), the influence of the spacer length ($n > 3$) on rheological properties of fluorocarbon-containing associating polymers have not been reported so far. Recently, we have synthesized different lengths of fluorocarbon group

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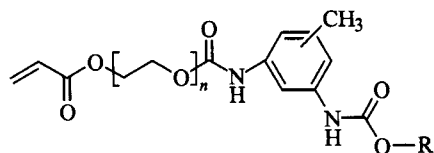
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end-capped PEG (M_w : 1000) macromonomers by isocyanate mediated crosslinking.¹³ Solution copolymerization of these macromonomers with acrylic acid supplied a novel series of fluorocarbon modified associating polymers. These polymer solutions showed more distinguishing thickening ability compared with those without PEG spacers. In this paper, our interest is focused on the effect of the length of the PEG spacer on solution properties of fluorocarbon modified associating polymers. Three fluorocarbon group end-capped PEG monoacrylate macromonomers (R_f -PEG macromonomer) with molecular weight of 400, 1000 and 2000 were synthesized and incorporated into poly(acrylic acid) (PAA) backbone. Hydrogen bond is thought to be an important factor responsible for the solution viscosity when the solution pH value is below 7.²⁰ Therefore, control polymers without fluorocarbon groups were synthesized to distinguish the H-bond effect from the hydrophobic effect. Our research is aimed to find a suitable range of the spacer length, which endues the best thickening effect to fluorocarbon modified associating polymers.

Experimental

Materials

R_f -PEG macromonomers (EO number: 1, 9, 23, 45) used in this research were synthesized in our laboratory. Details on the synthesis have been reported in our previous paper.¹³ α -Monoacrylate- ω -monohydroxy PEG ($n = 9, 23, 45$) were purchased from Monomer-Polymer & Dajac Labs, Inc. The structures of these monomers are listed in Fig. 1. Acrylic acid (AA, A.R.), toluene (A.R.) were redistilled before use. Azobisisobutyronitrile (AIBN) was recrystallized from methanol.

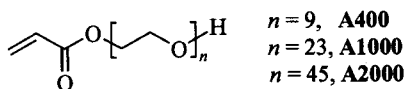


$R = \text{CH}_2(\text{CF}_2\text{CF}_2)_3\text{H}$

$n = 1, \text{FA40}$ $n = 23, \text{FA1000}$

$n = 9, \text{FA400}$ $n = 45, \text{FA2000}$

Fluorocarbon end-capped PEG macromonomer



HO end-capped PEG macromonomer

Fig. 1 Chemical structures of fluorocarbon modified and unmodified macromonomers.

Polymerization

Into a round-bottom flask acrylic acid (2 g), 2 mol%

of comonomers (fluorocarbon end-capped macromonomers or hydroxyl end-capped macromonomers) and toluene (2 mL) were added. The flask was capped with a rubber stopper. Acetone solution (1 mL) of AIBN (2 g/L) was injected into the flask (the ratio of the initiator to monomers was about to 0.1 wt%). The solution was purged with dry pure nitrogen in an ice-water bath for 1 h and then moved into an oil bath with vigorous stirring. The precipitated polymerization was left to proceed for 24 h. The precipitate was dissolved by the mixed solvent (methanol/toluene) and was reprecipitated by decanting the solution into diethyl ether. The product was dried (under vacuum) at 50 °C for at least 20 h to give white powder. These copolymers are referred to as A400, A1000, A2000, FA40, FA400, FA1000 and FA2000 respectively corresponding to the product containing PEG monoacrylate ($n = 9, 23, 45$) and fluorocarbon end-capped PEG monoacrylate (EO number: 1, 9, 23, 45).

Polymer characterization

The fluorine contents (wt%) of copolymers were determined by anionic chromatography and recorded on a Dionex2010I instrument. To fluorocarbon containing macromonomers, the molar ratios of macromonomers to AA can be obtained by comparing the theoretical fluorine contents in feed with the measured ones in copolymers. But to the control polymers not containing fluorocarbon groups, the direct measurement of the macromonomer conversions is difficult. In our research, the approximate macromonomer contents were estimated from the total conversion of all the monomers. In the homopolymerization of acrylic acid, the conversion of acrylic acid is very close to 100%. According to this, it is assumed that acrylic acid in copolymerization was also totally converted, thus the weight loss in copolymerization can be attributed to the incomplete conversion of macromonomers and the corresponding macromonomer contents can be calculated. The actual values should be somewhat higher than calculational ones if the loss of acrylic acid was considered. As shown in Table 1, the conversions of three macromonomers containing fluorocarbon groups are all close to 50%. It seems that the difference in the length of ethylene oxide spacer has no effect on the reactivity of macromonomers in our system. To three control copolymers, the macromonomer conversions are higher than those containing fluorocarbon groups, which are not less than 80%. Therefore the macromonomer contents are close to 1.6%.

Dilute solution properties were characterized in the 2 mol/L NaOH aqueous solutions by using an Ubbelohde capillary viscometer at the temperature of (25 ± 0.1) °C. The Mark-Houwink constants K and α for this system were 42.2×10^{-3} mL/g and 0.64, respectively.²¹ The apparent viscosity of the polymer solution was measured by using a Brookfield LVT 100188 viscometer equipped with a Polyscience Series 8000 constant temperature circulator. The HAAKE Rheostress RS 75 rheometer fitted with a F6/

8 thermosetter and a C60 2Ti sensor was used to measure dynamic rheological properties of polymer solutions. A 6 cm/2° cone and plate geometry with a gap of 0.108 mm was adopted. In the oscillatory measurement, the frequency sweeps were carried out at constant stress 1 Pa, and the stress sweeps were performed at a fixed frequency of 1 Hz. All the measurements were conducted at (25 ± 0.1) °C. Usually, the pH value of polymer solutions was adjusted to be in the range of 6.0–6.5 by adding 10% NaOH solution, except that the research was on the effect of pH on the viscosity of polymer solutions.

Table 1 Synthesis and characterization of polymers

Samples	n^a	Ratio in feed (%) ^b	Ratio in products (%) ^c
PAA	—	—	—
FA40	1	2	1.5
FA400	9	2	0.9
FA1000	23	2	1.1
FA2000	45	2	0.9
A400	9	2	1.6
A1000	23	2	1.6
A2000	45	2	1.6

^a Number of ethylene oxide units (or mol of ethoxylation). ^b Molar ratios of macromonomer to acrylic acid in feed. ^c Molar ratios of macromonomer to acrylic acid in products calculated from measured fluorine content.

Results and discussion

Estimation of the molecular weight

The viscosity-average molecular weights (M_η) of the homopolymer and copolymers used in our research were estimated from the intrinsic viscosity data obtained by Ubbelohde capillary viscometer. It should be pointed out that the estimation is only suitable to the homopolymer. For fluorocarbon-containing copolymers, the hydrophobic groups associate with each other in the dilute solutions to form aggregates. The intermolecular aggregates will cause the increase of the hydrodynamic volume of molecules and intrinsic viscosity, so the molecular weights estimated from it are exaggerated. The intramolecular aggregates will make the molecule coils compact, therefore the molecular weight data obtained are underestimated. For molecules with graft structure will take a more compact conformation than the linear molecules of the same molecular weight,¹² the viscosity-average molecular weights of control copolymers in our system obtained by this method are also imprecise, generally underestimated. Besides, the Mark-Houwink constants were obtained based on the pure PAA system. As the increase of the ethylene oxide spacer length, the fraction of ethylene oxide units in the polymers increased, too. For sample, FA2000, the ratio of EO unit to AA unit amounted to about 90/100. Such high EO concentration in polymers will also affect the precise evaluation of the molecular weight obtained in this system.

The reduced viscosity profiles of polymers used in our research are plotted in Fig. 2. It can be seen that all plots show good linearity below 1 g/L. According to the equation of $C^* = 1/[\eta]^{15}$ and data shown in Table 2, it can be determined that the overlap concentration of all solutions is over 1 wt%, and all solutions in measurement are in their dilute solutions range. The intrinsic viscosity $[\eta]$ of the homopolymer, PAA, is larger than those of modified copolymers. Samples containing fluorocarbon groups possess larger $[\eta]$ compared with those without fluorocarbon groups. Meanwhile, the longer the PEG grafted onto the copolymer, the smaller the intrinsic viscosity of the copolymer, whatever the PEG is end-capped by fluorocarbon groups or not.

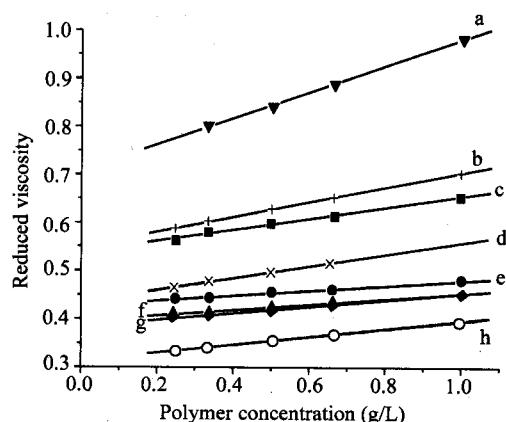


Fig. 2 Reduced viscosities of polymers with different structure as a function of polymer concentration in 2 mol/L NaOH. Polymers: PAA (a), FA40 (b), FA400 (c), A400 (d), FA1000 (e), FA 2000 (f), A1000 (g), A2000 (h).

Table 2 Dilute solution properties of polymers in 2 mol/L NaOH solutions

Samples	$[\eta]$ (dL/g)	κ	EO/AA ^a	$M_v (\times 10^{-4})^b$
PAA	0.6868	0.5405	—	10.422
FA40	0.5443	0.5395	—	7.2482
FA400	0.5315	0.4084	8/100	7.0361
FA1000	0.4246	0.2936	24/100	4.9161
FA2000	0.3873	0.4000	40/100	4.2590
A400	0.4255	0.6638	14/100	4.9331
A1000	0.3801	0.4605	35/100	4.1359
A2000	0.3093	0.8288	72/100	2.9971

^a Molar ratio of ethylene oxide to acrylic acid units. ^b Apparent viscosity average molecular weight calculated from the intrinsic viscosity.

A high chain transfer constant, which is known to be held by EO units, will decrease the molecule weight of PEG containing copolymers. It can lead to a substantial chain branching, crosslinking and the decrease of molecular weight in polymerization according to the different reaction conditions.²² This should be another important reason

for the decrease of $[\eta]$.

It is proved that the hydrophobic association in dilute solution will cause a high Huggins coefficient.²³⁻²⁵ From Table 2, we can see that there is no obvious difference between the Huggins coefficients of these polymers and all are close to the theoretical values in ideal solvents. So the hydrophobic association should be weak in our system. Hydrogen bond should also be rare, because the carboxylic units of polymers were neutralized totally in 2 mol/L NaOH solutions. Thus, the key factor that reduce the intrinsic viscosity in our system should be the high chain transfer constant of ethylene oxide unit which reduced the molecular weight of polymers.

Semidilute solution properties

Dependence of complex viscosities on the oscillatory stress (comparison of FA1000 with A1000, A400 and PAA)

Fig. 3 shows the result of oscillatory rheological measurement on the 8 wt% solution of homopolymer, PAA. It is typical for a Newtonian fluid. Stress at a fixed frequency (1 Hz) has no effect on the storage modulus, G' , loss modulus, G'' , and complex viscosity, η^* , and they are all very low. The solution behavior of A400 under oscillatory stress sweep is similar to the homopolymer, as shown in Fig. 4. Nevertheless, the solution of A1000 displays pseudo-elastic behavior demonstrated by the complex viscosity decreasing with the increase of oscillatory stress. The difference between A400 and A1000 should be attributed to intermolecular hydrogen bond. Although the solution is neutralized to pH value between 6 and 6.5, where hydrogen bonds are partially destroyed, hydrogen bonds still play a key role in influencing the solution properties. For FA1000, a complex viscosity plateau keeps at a high value with the stress increasing to 3 Pa. The plateau of FA1000 is different from PAA and A1000. A highly viscoelastic network is formed in the solution of FA1000 and maintains a high viscosity plateau till the stress is high enough (over 3 Pa for 1 wt% solution of FA1000) to destroy it.

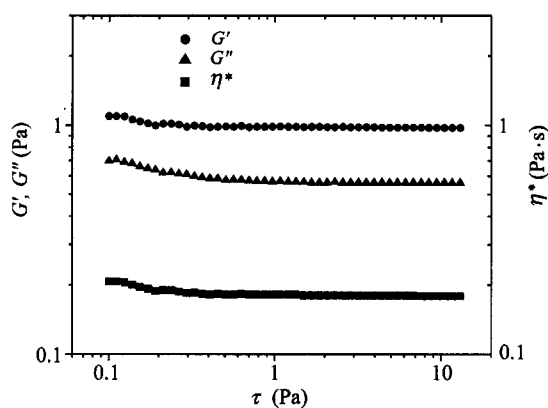


Fig. 3 Oscillatory stress sweep on 8wt% homopolymer PAA.

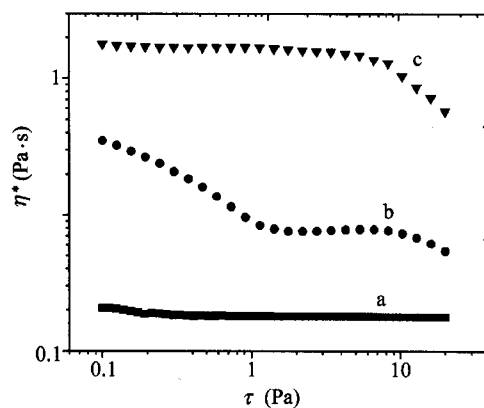


Fig. 4 Oscillatory stress sweep on 1 wt% copolymers: A400 (a), A1000 (b), and FA1000 (c).

Dependence of Brookfield viscosities on the pH (comparison of FA1000 with A1000 and FA40)

The difference of Brookfield viscosities between FA1000 and control solutions of A1000 and FA40 upon the change of pH was investigated and shown in Fig. 5. Despite of the lowest concentration (0.7 wt%) in three polymer solutions, the Brookfield viscosity of FA1000 is the highest when the pH value overpasses 7. With hydrogen bond is gradually destroyed by the increasing pH, the Brookfield viscosity of 1.4 wt% solution of A1000 decreases dramatically. In contrast, Brookfield viscosity of FA1000 has small dependence on pH value when the pH value is below 10. Evidently it is due to the strong hydrophobic association between fluorocarbon groups that the solution viscosity maintains with the increasing pH. Given the relatively lower polymer concentration of FA1000 (0.7 wt%) compared with that of A1000 (1.4 wt%), hydrophobic association plays a more important role in thickening the solution than hydrogen bonds. On the other hand, the indispensable contribution from PEG spacer is embodied by comparing the viscosity of FA1000 with that of FA40. The Brookfield viscosity of FA1000 is several

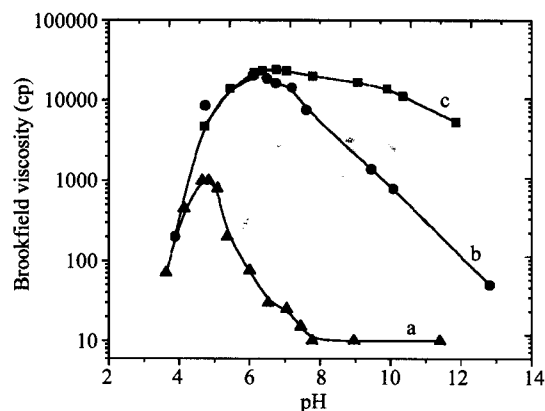


Fig. 5 Effect of pH on apparent viscosities of the copolymers: (a) FA40 (4.0 wt%); (b) A1000 (1.4 wt%), (c) FA1000 (0.7 wt%).

magnitude higher and the spacer of **FA1000** holds more EO units than that of **FA40**. Comparison of **FA1000** with **A1000** has shown that the effect of hydrogen bond on viscosity can be ignored. Thus it is corroborated that the flexibility of a long PEG spacer facilitates very effectively the association of fluorocarbon groups. Additionally, the introduction of a long PEG spacer improves the tolerance of solution viscosity to pH change as shown by a broad and high viscosity range.

Effect of the PEG length on solution viscosities of hydrophobically modified polymers

The length of the PEG spacer is a controllable parameter in controlling solution viscosity. Finding out a suitable length of PEG, which brings with the maximum viscosity, is of interest to researchers. Tam *et al.*⁵ investigated the rheological behavior of three HASE solutions with EO number of 2.5, 10 and 40 respectively and found that the HASE with 10 moles of EO units shows the most eminent thickening ability. In our system, PEG spacers with molecular weight of 400, 1000, 2000 were investigated. Fig. 6 shows the dependence of Brookfield viscosity of three solutions on polymer concentration. It is interesting that the thickening ability increased in the order of **FA2000**, **FA400** and **FA1000**. Short PEG is thought to be not able to supply enough flexibility and extensibility to promote the hydrophobic groups to form intermolecular junctions. Nevertheless, the longest spacer (EO number: 45) may benefit the association among one or several molecules and prevent them from aggregating into greater junctions. There are two ways for long PEG spacer chain to affect the rheological properties of polymer solutions. First, they allow the hydrophobes to move more flexibly. The steric hindrance effects of the charged backbone restrict the accessibility of hydrophobes to association. Longer PEG spacer chains release the hydrophobes from the backbones and promote the association of hydrophobes. Beyond a critical length of the PEG spacer could remove the effect of backbones on the hydrophobes, and compact and constant micelles independent of the length of PEG chain will be formed.²⁶ Second, changing the length of the spacer will alter the hydrophobicity of macromonomers. The longer the PEG spacer length, the lower hydrophobicity the side chains, and the easier the dissolution of side chains in water homogeneously and freely. So the longer PEG spacer will also decrease the tendency of hydrophobes to associate. The maximum thickening efficiency should be achieved by appropriately balancing these two factors. Surely the most suitable length of PEG must be varied for different systems. The effect of oscillatory stress on the complex viscosity of 1 wt% solution of **FA400**, **FA1000**, and **FA2000** is shown in Fig. 7. **FA1000** with best thickening ability exhibits the highest viscosity plateau. **FA400** is similar to **FA1000** except that its plateau is relatively low. Both complex viscosities decrease suddenly when the oscillatory stress exceeds 6 Pa.

It can be attributed to the catastrophic disassociation of the viscoelastic network. However, the behavior of **FA2000** upon the increase of the oscillatory stress is different. The η^* of **FA2000** decreases continuously. It seems that the network, if exist prior to measurements, is very weak and ready to be destroyed even at a very low stress of 0.1 Pa. Therefore, the results got from oscillatory measurements in Fig. 7 is agreement with the results in Fig. 6. It was suggested that the suitable range of molecular weight of PEG is between 400 and 2000.

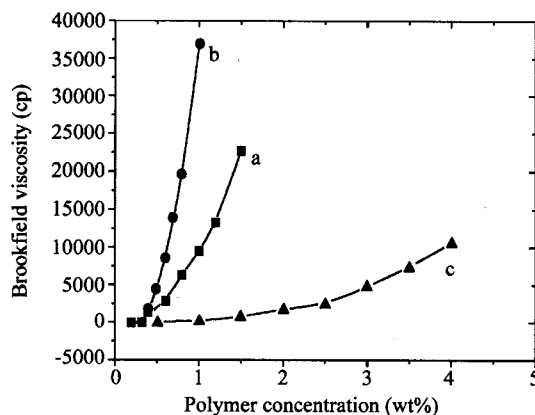


Fig. 6 Effect of spacer length on the apparent viscosity-concentration curves of fluorocarbon modified PAAs. Polymer: **FA400** (a), **FA1000** (b), **FA2000** (c).

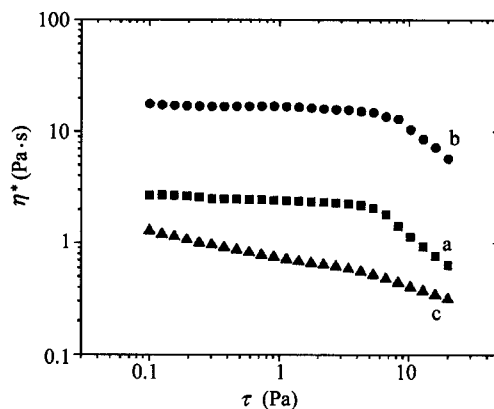


Fig. 7 Oscillatory stress sweep on 1 wt% fluorocarbon modified PAA with different spacer length. Polymer: **FA400** (a), **FA1000** (b), **FA2000** (c).

*Rheological properties of **FA1000** under oscillatory stress sweep*

The evolution of storage modulus, G' , and loss modulus, G'' , with the oscillatory stress in the range from 0.1 Pa to 20 Pa was further investigated. As shown in Fig. 8, the changing pattern is very similar to Jenkins' s HASE system.^{27,28} At a fixed oscillatory frequency of 1 Hz, the storage modulus predominates over the loss modulus when the stress is not high enough and the solution behaves like an elastic fluid. The restoring rate of the hydrophobic mi-

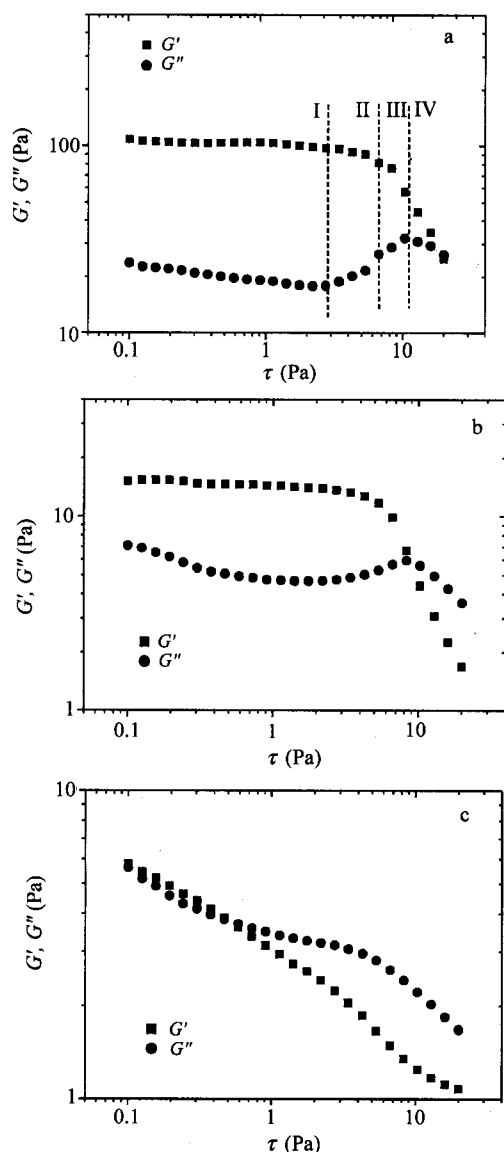


Fig. 8 Storage moduli (G') and loss moduli (G'') of 1 wt% FA1000 (a), FA400 (b), and FA2000 (c) under oscillatory stress sweep.

crodomains serving as network junctions can keep up with the destroying rate. Low shear stress has little effect on these hydrophobic junctions. With oscillatory stress increasing beyond a critical value (5 Pa), the dissociation of hydrophobic groups from network junctions becomes faster than association and the network becomes disrupted. In this process, the amount of hydrophobic junctions diminishes quickly, first the weak junctions, and then the strong junctions. A certain part of weak junctions should be composed of intramolecular hydrophobic microdomains. It is believed that loss modulus, the viscous component of dynamic shear modulus, correlated with the effective volume of the network formed in solutions.²⁸ In Fig. 8 it could be seen that the onset point of the increase of loss modulus is earlier than the point where storage modulus starts to decrease. When the shear stress is over 3 Pa, the molecular coils, including weak junctions, are extended,

and then the volume of the network is enlarged. Dissociation of weak junctions has no evident effect on the elasticity of the polymer solution, as shown by the almost unchanged G' and η^* , but surely results in the enlarged hydrodynamic volume as shown by the increased G'' . The phenomenon that the increase of G'' appears prior to the decrease of G' suggests that disassociation of the weak junction favors the augment of the hydrodynamic volume. The increase of G'' continues to 10 Pa where most of strong junctions break down and G' decreases. The disassociation of remaining junctions diminishes the elasticity (G') as well as the viscosity (G'') when the shear stress is over 10 Pa. Finally, the four regions could be distinguished as shown in Fig. 8. In region 1, where the stress is below 3 Pa, both G' and G'' keep constant, but when the stress grows from 3 Pa to 5 Pa into region 2, G'' increases while G' still keeps on the plateau. Region 3 is located in the range from 5 Pa to 10 Pa, where G' decreases and G'' keeps increasing. However, when the stress exceeds 10 Pa, both G' and G'' decrease as shown in region 4. The situation for FA400 is the same except the relatively low G' and G'' . The same critical stress (7 Pa) needed to disrupt the network structure. It means that the strength of the junctions in the solution of FA400 is comparable with that of FA1000. In the system of HEUR (hydrophobically-modified ethoxylated urethane) associative polymers studied by Tam *et al.*,² there exists a stress-thickening region (region TK), which does not appear in our system. For FA2000, no plateau and increase of G'' can be found due to its weak network junctions.

Rheological properties of modified polymers under oscillatory frequency sweep

Solutions with physically cross-linked network usually exhibit single-mode Maxwell rheological behavior depicted as Eqs. (1) and (2).^{2,28}

$$G'(\omega) = G_0 \omega^2 \lambda^2 / (1 + \omega^2 \lambda^2) \quad (1)$$

$$G''(\omega) = G_0 \omega \lambda / (1 + \omega^2 \lambda^2) \quad (2)$$

That is, the slope degree of $G'(\omega)$ curve is twice that of $G''(\omega)$ at low frequency. In such system, the terminal relaxation time λ holds the relationship with the stability of the network junctions described as the Eq. (3).²

$$\lambda = \beta_{\text{exp}}(-E_m/kT) \quad (3)$$

Therefore it means that the stronger network and the longer terminal relaxation time. The terminal relaxation time λ , whose reciprocal is the characteristic angular frequency ω ($\omega = 2\pi f$), can be determined at the intersection point of $G'(\omega)$ and $G''(\omega)$ curves.^{2,28} Although the λ determined by this method is usually thought to be underestimated, it is still plausible in scaling the strength of the network junction. From Fig. 9, it can be seen that the critical relax-

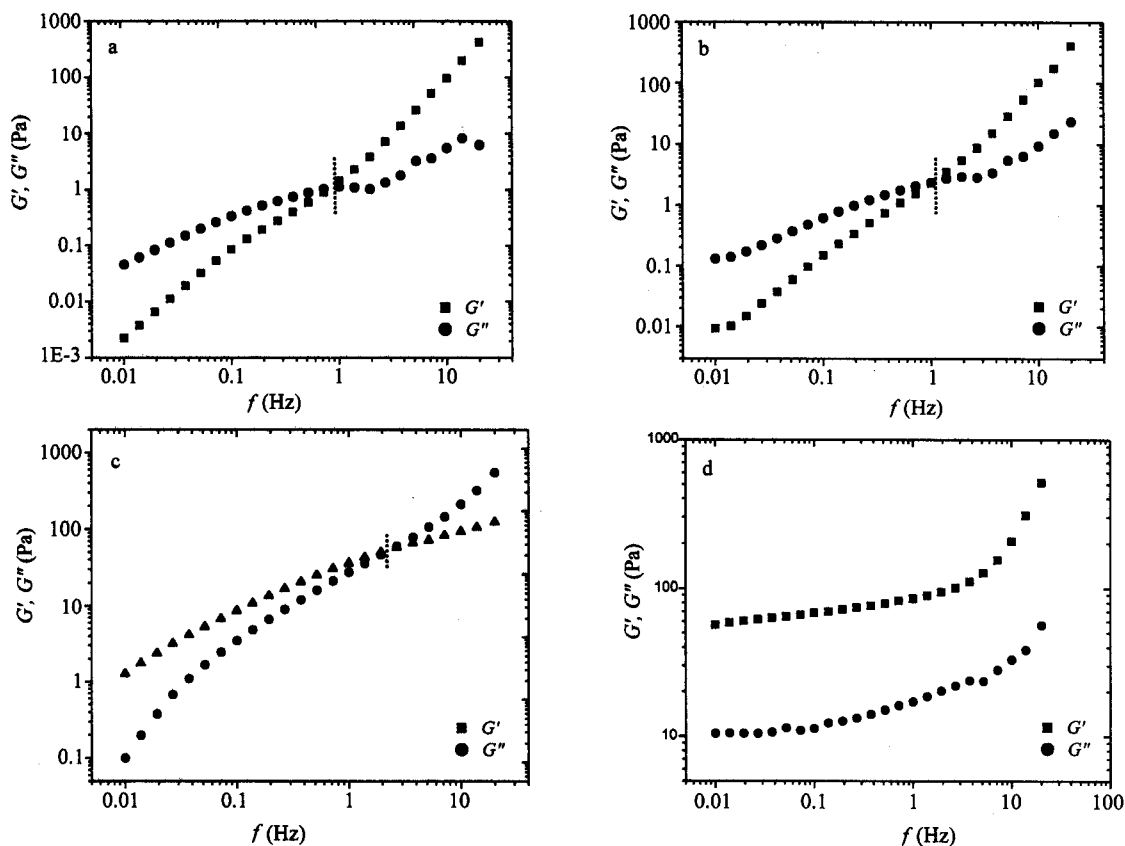


Fig. 9 Storage moduli (G') and loss moduli (G'') of 1 wt% **A400** (a), **A1000** (b), **FA40** (c), and **FA1000** (d) under oscillatory frequency sweep.

ation frequency for **A400**, **A1000** and **FA40** is on the order of 1–2 Hz. For **FA1000**, however, the characteristic frequency f can not be obtained even if the oscillation frequency of applied stress (1 Pa) is as low as 0.01 Hz. This indicates that a very strong elastic network exists in the polymer solution of **FA1000**. It seems that the PEG spacer endues the fluorocarbon groups enough freedom to build huge and stable hydrophobic microdomain. While in the solution of **A1000** only small amounts of hydrogen bonds are available and in the solution of **FA40** the hydrophobic groups are incapable to fulfill their association due to the hindrance from backbone inertia. **FA400** has an identical relaxation time λ to **FA1000**, meaning the microdomains in these two solution being of the same strength. But the G' and G'' of the **FA400** solution are relatively low. According to Green-Tobolsky theory of transient network,³⁰ as shown in Eq. (4), the relatively lower G' stands for a lower density of network junctions in **FA400** relative to that in **FA1000**:

$$G_0 = \nu RT \quad (4)$$

It should be noted that chemical crosslinks induced by the chain transfer effect of PEG chain in polymerization is out of the question. If the strong elasticity in the solutions of **FA1000** and **FA400** was predominated by chemical crosslinks existed in their solutions, it would also do for

the solutions of **A1000**, **A400**, and **FA2000**. Since strong elasticity does not appear for them, the possibility for chemical crosslinks is eliminated and the prominent viscoelasticity shown by the solution of **FA1000** should be mainly attributed to the spacer-facilitated hydrophobic association of fluorocarbon groups.

Conclusion

A series of poly (acrylic acid-co-R_f-PEG macromonomer)s (EO number: 1, 9, 23, 45) and corresponding copolymers without fluorocarbon end groups were synthesized. Comparing the rheological properties of these polymer solutions, it was found that hydrophobic association of fluorocarbon groups were predominated on the solution viscosity when the hydrogen bond between grafted PEG and the acid backbone was inhibited over the pH value of 6. Especially, the effect of the PEG spacer on the rheological performance for poly(acrylic acid-co-R_f-PEG macromonomer)s was investigated. When the ethylene oxide number is 23, the polymer solution shows the best thickening effect. The length of the spacer should be suitable so that it can help the hydrophobes to get rid of the restriction from the backbone to promote the formation of intermolecular association. On the other hand, the possibility to form intramolecular association will increase when the spacer is too long, as shown by **FA2000** holding a

spacer with EO number of 45.

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References

- 1 Jenkins, R. D.; DeLong, L. M.; Bassett, D. R. In *Hydrophilic Polymers: Performance with Environmental Acceptability*, Advances in Chemistry Series 248, Ed.: Glass, J. E., American Chemical Society, Washington DC, 1996.
- 2 Tam, K. C.; Jenkins, R. D.; Winnik, M. A.; Bassett, D. R. *Macromolecules* 1998, 31, 4149.
- 3 Kjoniksen, A. L.; Nilsson, S.; Thuresson, K.; Lindman, B.; Nystrom, B. *Macromolecules* 2000, 33, 877.
- 4 Zhang, Y. X.; Da, A. H.; Hogen-Esch, T. E.; Butler, G. B. *J. Polym. Sci., part A: Polym. Chem.* 1992, 30, 1383.
- 5 Tam, K. C.; Farmer, M. L.; Jenkins, R. D.; Bassett, D. R. *J. Polym. Sci., part B: Polym. Phys.* 1998, 36, 2275.
- 6 Noda, T.; Hashidzume, A.; Morishima, Y. *Langmuir* 2001, 17, 5984.
- 7 Chen, J.; Jiang, M.; Zhang, Y. X.; Zhou, H. *Macromolecules* 1999, 32, 4861.
- 8 Ringsdorf, H.; Simon, J.; Winnik, F. M. *Macromolecules* 1992, 25, 7306.
- 9 Petit-Agnely, F.; Iliopoulos, I. *J. Phys. Chem. B* 1999, 103, 4803.
- 10 Kaestner, U.; Hoffmann, H.; Donges, R.; Ehrler, R. *Colloids Surf., A* 1994, 82, 279.
- 11 Hwang, F. S.; Hogen-Esch, T. E. *Macromolecules* 1995, 28, 3328.
- 12 Ito, K.; Kawaguchi, S. *Advanced Polymer Science* Vol. 142, Springer-Verlag Berlin Heidelberg, Berlin, 1999.
- 13 Liu, S. P.; Du, L. B.; Zhang, Y. X.; Chen, J. Y.; Jiang, M.; Wu, S. G.; Swift, G. *Chin. J. Chem.* 2001, 19, 386.
- 14 Noda, T.; Hashidzume, A.; Morishima, Y. *Macromolecules* 2001, 34, 1308.
- 15 Dai, S.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Macromolecules* 2000, 33, 7021.
- 16 Ravey, J. C.; Stebe, M. J. *Colloids Surf., A* 1994, 84, 11.
- 17 Zhang, Y.; Li, M.; Fang, Q.; Zhang, Y. X.; Jiang, M.; Wu, C. *Macromolecules* 1998, 31, 2527.
- 18 Seery, T. A. P.; Yassini, M.; Hogen-Esch, T. E.; Amis, E. J. *Macromolecules* 1992, 25, 4784.
- 19 Kujawa, P.; Goh, C. C. E.; Calvet, D.; Winnik, F. M. *Macromolecules* 2001, 34, 6387.
- 20 Bokias, G.; Staikos, G.; Iliopoulos, I.; Audebert, R. *Macromolecules* 1994, 27, 427.
- 21 *Polymer Handbook*, 4th Edn., Eds.: Brandrup, J.; Immergut, E. H.; Grulke, E. A., Wiley, 1999, Chap. 2.
- 22 Gao, B.; Wesslen, B.; Wesslen, K. B. *J. Polym. Sci., Part A: Polym. Chem.* 1992, 30, 1799.
- 23 Aubry, T.; Moan, M.; Argillier, J. F.; Audibert, A. *Macromolecules* 1998, 31, 9072.
- 24 Guo, L.; Tam, K. C.; Jenkins, R. D. *Macromol. Chem. Phys.* 1998, 199, 1175.
- 25 Chen, J.; Du, L. B.; Zhang, Y. X.; Hogen-Esch, T. E.; Jiang, M. *Polym. Int.* 2001, 50, 148.
- 26 Seng, W. P.; Tam, K. C.; Jenkins, R. D.; Bassett, D. R. *Macromolecules* 2000, 33, 1727.
- 27 Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. *Macromolecules* 1997, 30, 1426.
- 28 Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. *Macromolecules* 1997, 30, 3271.
- 29 Green, M. S.; Tobolsky, A. V. *J. Chem. Phys.* 1946, 14, 80.

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