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ORIGINAL CONTRIBUTION

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# Synthesis of associating poly(acrylic acid) in supercritical carbon dioxide and its solution properties

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**Abstract** Hydrophobically associating polymers have been synthesized in supercritical carbon dioxide by copolymerization of acrylic acid with different amounts of acrylate with hydrocarbon or fluorocarbon groups. It was found that conversion of hydrocarbon comonomers was above 95% whereas that for fluorocarbon comonomers was only about 50%. In addition, large amounts of hydrophobic groups could be easily introduced to poly(acrylic acid) by reaction in supercritical carbon dioxide. The solution properties were investigated by rheology. The results indicated that intermolecular association of the copolymer was strong and viscosity was maximum under acidic conditions. In aqueous solutions fluorocarbon hydrophobes associated much more strongly than the hydrocarbon variety, but the viscosifying effect of PAAC-18 series copolymers in 2% (*w*/*w*) solution was more pronounced than that of the PAAF series, results which did not agree with the conclusions of Ravey and Stébé. It was also found that the thixotropy behavior of copolymer solution at pH 3.2 was more complex than that at pH 5.0, at which pseudoplasticity only was observed for solutions of all copolymers. Contact angles of copolymer solutions on a glass sheet were measured. The data indicated that contact angles of hydrocarbon-modified polymers were smaller than those of fluorocarbon analogues. As time passed the contact angle became smaller and smaller. Fluorocarbon analogues were better than hydrocarbon analogues, and longer hydrophobic chains were better than shorter chains, at maintaining the hydrophobic character of the surface.

**Keywords** Hydrophobic association · Supercritical carbon dioxide · Water-soluble polymer · Acrylic acid

## Introduction

Hydrophobically associating polymers consist of a water-soluble polymer containing a small number of hydrophobic groups [1, 2, 3]. In aqueous solution, above a certain polymer concentration, intermolecular hydrophobic interactions lead to the formation of polymolecular associations. As a consequence, these copolymers have thickening properties equivalent to those observed for higher molecular weight homopolymers. Under increasing shear, the physical links between chains are disrupted but reform with decreasing shear. In this way it is possible to avoid the irreversible mechanical degradation which occurs for very high molecular weight samples when subjected to high shear stresses [4, 5]. Furthermore, the reversible association/dissociation process gives rise to particular rheological behavior as a function of shear rate or shear time. Such shear thinning and thixotropic properties are of great technological importance especially in applications in water-based systems which involve viscosity control [6, 7, 8].

Most of the associating polymers are amphiphilic. They are composed of a hydrophilic main chain or backbone and hydrophobic end or side chains. Hydrocarbon chains containing from 8 to 18 carbon atoms are commonly used as hydrophobes. In recent years it has been reported that compared with hydrocarbons fluorocarbon hydrophobes associate much more strongly in aqueous solutions, because of their low cohesive energy density and surface energy [9, 10]. In fact, Ravey and Stébé reported that a $CF_2$ group was equivalent to 1.7 $CH_2$ units in terms of hydrophobicity [11]. As for the hydrophilic main chain, both electrolytes and non-electrolytes have been extensively studied [12, 13, 14, 15, 16]. Among these, different types of poly(ethylene oxide), polyacrylamide, and cellulose are the most common non-electrolytes whereas poly(acrylic acid) and poly(methacrylic acid) are widely used polyelectrolytes. When polyelectrolytes are used as the main chain the hydrophobic association, and therefore the viscosity of the solution, are sensitive to the pH, because of conformational changes of the chain as a result of ionization of the carboxylic groups [17].

Polymerization of acrylic acid is commonly conducted in water. Because hydrophobes are insoluble in water, the copolymerization of acrylic acid and hydrophobes such as fluorine-containing acrylates cannot occur in water. At the same time, utilizing organic solvents might cause another problem of pollution of the product, which would be more serious when the polymer is used in personal care products, food, and even medical products. Supercritical carbon dioxide as an alternative to conventional organic solvents has attracted increasing attention in recent years [18, 19, 20], especially after DeSimone reported the homogeneous polymerization of 1,1-dihydroperfluorooctyl acrylate in supercritical carbon dioxide which substitutes the Freon as commonly used solvent [21]. Using supercritical carbon dioxide as the reaction medium has the attractive advantage that products are virtually free from contamination and are easily obtained as dry powder just by releasing the carbon dioxide at the end of the reaction. At the same time, no contaminant is released into our environment. In addition, supercritical-fluid extraction process can be used in-situ to remove the unreacted monomer. DeSimone and other researchers have reported many polymerizations in supercritical carbon dioxide [22, 23, 24, 25, 26] including the homopolymerization of acrylic acid [27].

In previous work we have studied the copolymerization of acrylic acid and 1*H*,1*H*,11*H*-perfluoroundecyl acrylate in supercritical carbon dioxide [28]. In this paper we present detailed results from synthesis of perfluorinated analogues, and their solution properties. Similarities and differences in the solution properties of polymers containing long alkyl side groups (dodecyl or octadecyl) and perfluorinated analogues are compared.

## Experimental

### Materials

Acrylic acid (AA) was purified by vacuum distillation of the commercial product. The comonomers 1*H*,1*H*,11*H*-perfluoroundecyl acrylate and 1,1-dihydroperfluorooctyl acrylate were obtained from Lancaster and used as received. The lauryl acrylate and octadecyl acrylate were obtained from Aldrich and used as received. The 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. $CO_2$ of purity 99.9% was used as received.

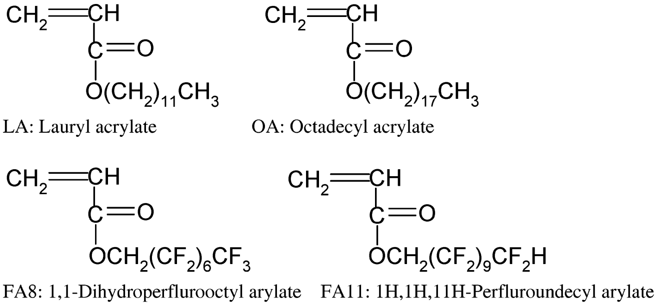
### Polymerization

A series of copolymers of acrylic acid with different amounts of comonomers were synthesized by free-radical polymerization initiated by AIBN in supercritical carbon dioxide in a 20-mL high-pressure reactor with a magnetic stir bar. The high-pressure reactor was charged with acrylic acid (2.0 g), AIBN (0.02 g), and different amounts of comonomers, then purged with $CO_2$ at 0.5 MPa and 0.1 L min$^{-1}$ for ca. 5 min to remove $O_2$. The reactor was sealed and enough liquid carbon dioxide was added through a syringe. The temperature was gradually increased to 60 °C and carbon dioxide was added to 15 MPa. All reactions proceeded for 4 h, the reactor was cooled and vented slowly. The product was obtained in the form of a white powder.

### Characterization

The products were extracted by supercritical carbon dioxide in-situ at 45 °C and 20 MPa to remove the unreacted monomers until the mass of the products did not change. The contents of AF8 or AF11 (for structures see Scheme 1) in the final products were determined by fluorine elemental analysis, then the conversion was calculated. The contents of LA or OA in the final products were determined by acid–base titration. The detailed procedures were described in Ref. [29].

The morphology of the polymer powder was detected by scanning electron microscopy (SEM, XL-30, Philips).



LA: Lauryl acrylate

OA: Octadecyl acrylate

FA8: 1,1-Dihydroperfluorooctyl arylate

FA11: 1H,1H,11H-Perfluroundecyl arylate

**Scheme 1** The structures of comonomers

The intrinsic viscosities of poly(acrylic acid) and modified poly(acrylic acid) were measured in 2 mol $L^{-1}$ NaOH at 30 °C. The molecular weights were calculated by use of Eq. (1) [30]:

$$[\eta] = 3.38 \times 10^{-3} \times M^{0.43} \quad (1)$$

Viscosity and rheological property measurement were performed with a Rheometrics Fluids spectrometer at a concentration of 2% (*w*/*w*) for each sample. To study the dependence of viscosity on pH, 10 mol $L^{-1}$ NaOH was used to adjust the pH of the solutions.

Contact angle measurement was performed with an Erma instrument. The 2% (*w*/*w*) aqueous copolymer solutions were applied to a clean glass sheet at least 72 h before measuring. The measurements were made at 20 °C, relative humidity 40% with distilled water.

## Results and discussion

### Composition and morphology of the copolymers

The structures of the LA, OA, AF8, and AF11 comonomers are shown in Scheme 1. The properties of the corresponding acrylic acid copolymers are listed in Tables 1, 2, 3, and 4. The modified polymers are denoted, for instance, PAAC-12-2 for a sample modified with AA (98% *w*/*w*) and LA (2% *w*/*w*). PAAF-8-4 means that the mass content of AF8 in the feed is 4%. A blank sample (PAA-0) is obtained by the same treatment without addition of comonomers in the reaction.

The homopolymer of acrylic acid and copolymers obtained at 60 °C and 15 MPa are fluffy, white, free-flowing powders. Electron micrographs of products PAAC-12-2 and PAAF-11-20 are shown in Fig. 1 (top and bottom, respectively). The micrographs show large aggregates of primary particles <200 nm in size which is similar to some results reported by DeSimone et al. [27] and Hongqi Hu [29].

Tables 1, 2, 3, and 4 show the conversions of LA and OA are quite high, above 95%, while the conversions of AF8 and AF11 are relatively low, only about 50% of comonomers can be polymerized into the copolymer. The clear reason is unknown; maybe hydrocarbon analogues are more active than fluorocarbon analogues in supercritical carbon dioxide. Therefore, the fraction of fluorocarbon analogues forming the intended polymer is

**Table 1** Properties of LA-containing copolymers

| | $M\eta\times10^{-6}$ | Comonomer in feed | | Comonomer in polymer | | LA conversion (%) |
|---|---|---|---|---|---|---|
| | | % (*w*/*w*) | mol% | % (*w*/*w*) | mol% | |
| PAA-0 | 0.56 | 0 | 0 | 0 | 0 | 98 |
| PAAC-12-2 | 0.62 | 2.0 | 0.61 | 1.92 | 0.59 | 96 |
| PAAC-12-4 | 0.73 | 4.0 | 1.23 | 3.87 | 1.19 | 96.7 |
| PAAC-12-6 | 0.86 | 6.0 | 1.88 | 5.72 | 1.79 | 95.3 |
| PAAC-12-8 | 1.14 | 8.0 | 2.53 | 7.64 | 2.42 | 95.5 |
| PAAC-12-10 | 1.52 | 10.0 | 3.22 | 9.56 | 3.08 | 95.6 |
| PAAC-12-20 | 2.53 | 20.0 | 6.98 | 19.26 | 6.72 | 96.3 |

**Table 2** Properties of OA-containing copolymers

| | $M\eta\times10^{-6}$ | Comonomer in feed | | Comonomer in polymer | | OA conversion (%) |
|---|---|---|---|---|---|---|
| | | % (*w*/*w*) | mol% | % (*w*/*w*) | mol% | |
| PAAC-18-2 | 0.65 | 2.0 | 0.45 | 1.92 | 0.43 | 96.1 |
| PAAC-18-4 | 0.87 | 4.0 | 0.91 | 3.85 | 0.88 | 96.3 |
| PAAC-18-6 | 1.02 | 6.0 | 1.40 | 5.77 | 1.35 | 96.2 |
| PAAC-18-8 | 1.22 | 8.0 | 1.90 | 7.71 | 1.83 | 96.4 |
| PAAC-18-10 | 1.73 | 10.0 | 2.41 | 9.58 | 2.31 | 95.8 |
| PAAC-18-20 | –[a] | 20.0 | 5.26 | 19.12 | 5.03 | 95.6 |

[a] Insoluble in 2 mol $L^{-1}$ NaOH solution

**Table 3** Properties of FA8-containing copolymers

| | $M\eta\times10^{-6}$ | Comonomer in feed | | Comonomer in polymer | | FA8 conversion (%) |
|---|---|---|---|---|---|---|
| | | % (*w*/*w*) | mol% | % (*w*/*w*) | mol% | |
| PAAF-8-4 | 0.58 | 4.0 | 0.66 | 2.25 | 0.37 | 56.3 |
| PAAF-8-7 | 0.66 | 7.0 | 1.18 | 4.30 | 0.72 | 61.4 |
| PAAF-8-12 | 0.78 | 12.0 | 2.11 | 7.08 | 1.24 | 59.0 |
| PAAF-8-14 | 0.85 | 14.0 | 2.51 | 7.50 | 1.35 | 53.6 |
| PAAF-8-18 | 1.10 | 18.0 | 3.36 | 10.3 | 1.92 | 57.2 |

**Table 4** Properties of FA11-containing copolymers

| | $M\eta\times10^{-6}$ | Comonomer in feed | | Comonomer in polymer | | FA11 conversion (%) |
|---|---|---|---|---|---|---|
| | | % (*w*/*w*) | mol% | % (*w*/*w*) | mol% | |
| PAAF-11-5 | 0.60 | 5.0 | 0.64 | 2.51 | 0.32 | 50.2 |
| PAAF-11-10 | 0.74 | 10.0 | 1.35 | 5.32 | 0.72 | 53.2 |
| PAAF-11-14 | 0.92 | 14.0 | 1.96 | 7.20 | 1.01 | 51.4 |
| PAAF-11-18 | 1.21 | 18.0 | 2.62 | 9.09 | 1.32 | 50.5 |
| PAAF-11-20 | 1.45 | 20.0 | 2.98 | 12.67 | 1.57 | 52.8 |

low, and half of those are extracted by $CO_2$ resulting in waste.

The molar content of long alkyl side group (dodecyl or octadecyl) in the molecules is also shown in Tables 1, 2, 3, and 4. The conventional synthesis and preparation of hydrophobically modified water-soluble polymers and the ‘‘micellar’’ process were shown to be well suited for copolymers with a low content of hydrophobic units ( $\leq$ 3 mol%) [31, 32]. High hydrophobic group content can easily obtained by use of supercritical carbon dioxide. This is because supercritical carbon dioxide is a good solvent for most nonpolar and some polar molecules of low molar mass [33], so monomer and initiator could be dissolved in $CO_2$ and the polymerization begun as a homogeneous phase. The onset of polymerization could be observed, because the reaction turned yellow, then orange (the growing first particles were just large enough to scatter visible light) and then white and cloudy [34]. Within minutes white particles could be observed settled on the reactor bottom and wall. After the polymerization, the reactor was filled with dry, free-flowing powder.

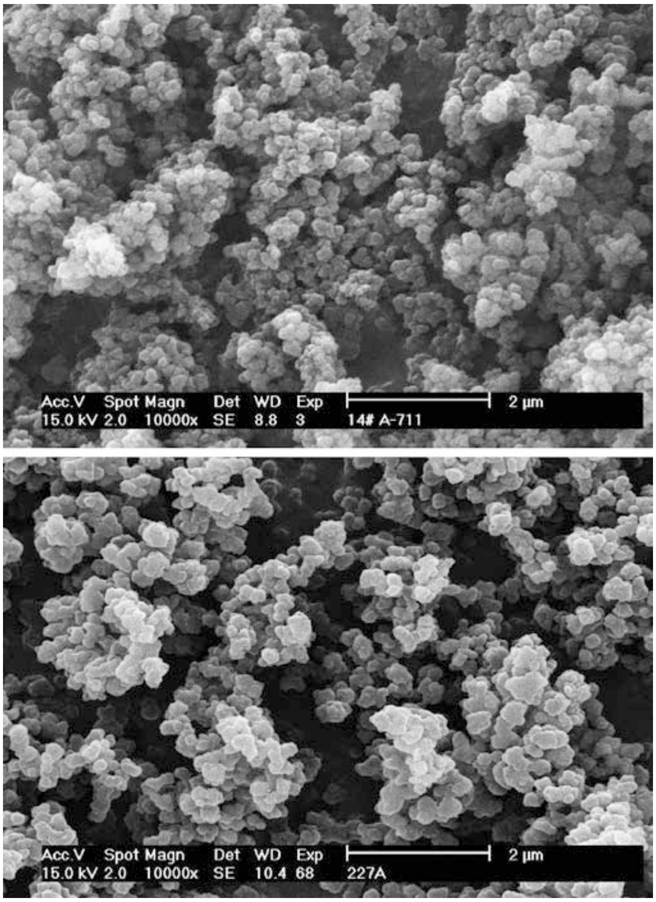


**Fig. 1** Scanning electron micrographs of PAAC-12-2 and PAAF-11-20 prepared by polymerization in supercritical $CO_2$: *top*, PAAC-12-2; *bottom*, PAAF-11-20

## Dependence of viscosity on pH and composition

The viscosity of an aqueous solution of poly(acrylic acid) increases gradually with increasing pH, and then levels off (Fig. 2). This is because that the carboxyl groups become ionized with increasing pH, and then electrostatic repulsion between the anions along the polymer chains leads to extension of the chains, so the viscosity increases then levels off when almost all the carboxyl groups are ionized.

The hydrophobically modified copolymers show quite different behavior. First, there is a maximum on the viscosity plot of copolymer viscosity versus pH, which is at about pH 5.0 for PAAF and about pH 6.0 for PAAC, as is shown in Figs. 3 and 4; this demonstrates

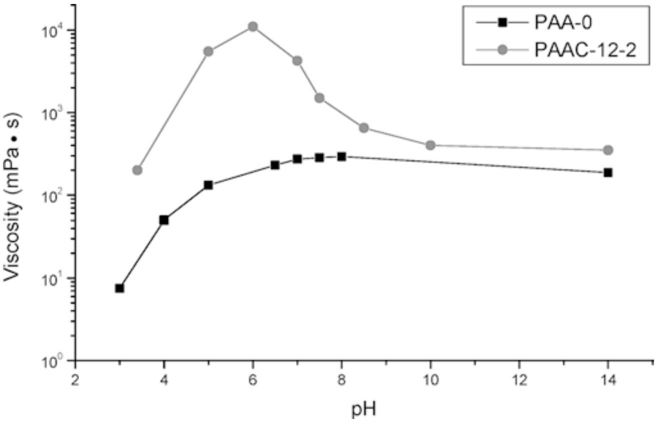


**Fig. 2** Effect of pH on the viscosity of samples PAA-0 and PAAC-12-2 ($C$ = 2% (*w*/*w*), $t$ = 25 °C, shear rate = 1 $s^{-1}$)

that the viscosity of a 2% aqueous solution of poly (acrylic acid) and copolymer as a function of pH. Second, the viscosity of a semi-diluted aqueous solution of the copolymers is much higher than that of poly(acrylic acid) at the same concentration and pH; it also increases dramatically with increasing content of the hydrophobic group. These phenomena can be explained as a consequence of hydrophobic association among copolymer chains. It has reported that in semi-diluted aqueous solution of hydrophobically modified polyelectrolytes these phenomena are always observed. As Ming Jiang and coworkers clarified [17], the increase of pH has two effects.

1. Neutralization of carboxyl groups leads to intramolecular electrostatic repulsion and then extension of the polymer chains. In the copolymers, the chain extension exposes the hydrophobic groups embedded in polymer chains, then intermolecular hydrophobic association occurs, so the viscosity increases sharply.
2. Neutralization also leads to intermolecular electrostatic repulsion, which destroys the intermolecular association and then reduces the viscosity.

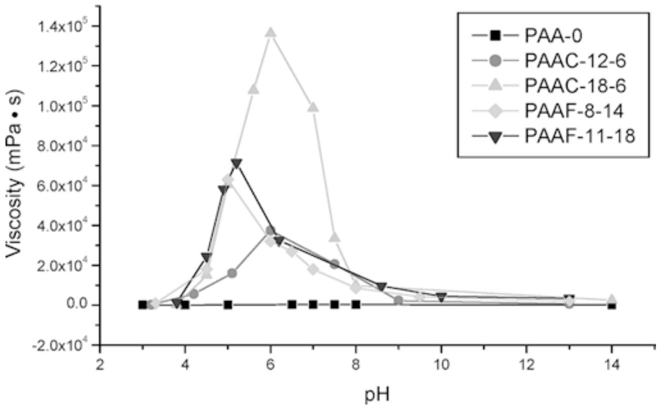


**Fig. 3** Effect of pH on the solution viscosity of several acrylic acid

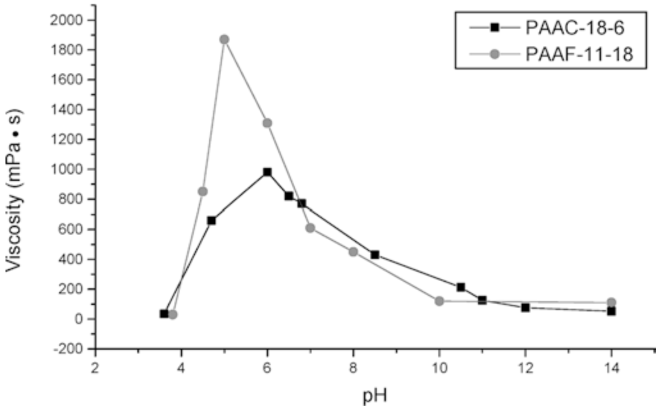


**Fig. 4** Effect of pH on the viscosity of samples PAAC-18-6 and PAAF-11-18 ($C = 0.5\%$ (*w*/*w*), $t = 25$ °C, shear rate $= 1\ \mathrm{s}^{-1}$)

Effect 1 dominates when the pH is below 5.0 for PAAF or 6.0 for PAAC, whereas effect 2 dominates at pH above 5.0 for PAAF or 6.0 for PAAC. So the viscosity of copolymers is much higher than that of poly(acrylic acid) and has a maximum at a certain pH.

Now we compare the solution viscosity of the hydrocarbon-modified polymers with fluorocarbon-modified ones. The Brookfield viscosities of the AF8 and AF11 series are greater than those of the LA copolymers, although hydrocarbon chain (12C) is 4 or 1 carbon atoms longer than the fluorocarbon groups (8C, 11C, respectively). That illuminates the greater apparent hydrophobic character of the perfluorocarbon compared with the hydrocarbon group. However, the viscosities of these are much less than those of the OA copolymers. Ravey and Stébé reported that a $CF_2$ group was equivalent to 1.7 $CH_2$ units in terms of hydrophobicity [11]. So the hydrophobicity of AF11 is equivalent to 18 $CH_2$ units. But the viscosity of PAAF-11-18 (actually the AF11 content of the polymer is 1.32 mol%) is only half that of PAAC-18-6 (the OA content of the polymer is 1.35 mol%). We think that for the PAAC-18 series:

1. the chain is longer, so a larger network is formed; and
2. molecular chain entanglement occurs in the areas of association and the network is stronger.

These two effects make the viscosity of PAAC-18 series greater than that of other copolymers. So we believe that hydrophobicity favors association and increasing viscosity, and that the viscosity of the solution also depends on hydrocarbon chain length and distribution of hydrophobic groups. The viscosity behavior of PAAC-18-6 and PAAF-11-18 measured at a polymer concentration of 0.5% (*w*/*w*) and a shear rate of 1 $\mathrm{s}^{-1}$ is shown in Fig. 4. The results for PAAC-18 are lower than those for PAAF-11. That means that for dilute solutions hydrophobicity plays a greater role than chain length, whereas in semi-dilute solution chain length contributes more to the increasing viscosity.

The dependence of viscosity on comonomer content of the monomer feed for 2% (*w*/*w*) aqueous solution is shown in Fig. 5. The data indicate that the viscosity of copolymers at pH 4 increases with increasing comonomer content. In the solution of the hydrophobic associating polymer, intramolecular association and intermolecular association exist at the same time. Intramolecular association causes hypercoiling of the chain and a decrease in viscosity, whereas intermolecular association causes the formation of a three-dimensional network of polymer chains and a dramatic viscosity increment. As the hydrophobic group content increases, more and more networks are formed and the viscosity of the solution increases correspondingly.

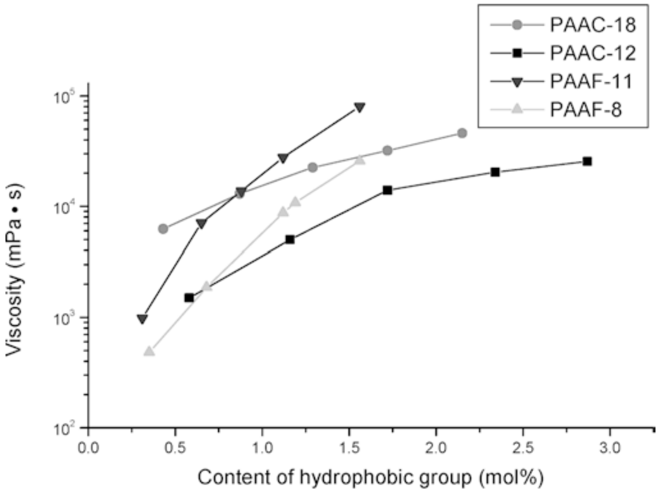


**Fig. 5** Effect of the molar content of the hydrophobic group on the solution viscosity of several acrylic acid copolymers ($C = 2\%$ (*w*/*w*), $t = 25$ °C, pH 4, shear rate = 1 $s^{-1}$)

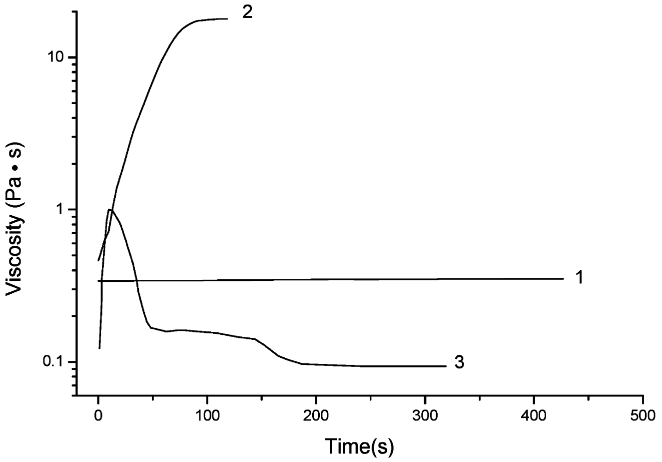


**Fig. 6** Change of viscosity of PAAF-11-14 with shear time at different shear rates ($C = 2\%$ (*w*/*w*), pH 3.2; *curve 1*, shear rate = 1 $s^{-1}$; *curve 2*, shear rate = 10 $s^{-1}$; *curve 3*, shear rate = 300 $s^{-1}$)

## Thixotropy study

Solutions of most hydrophobically associating polymers are pseudoplastic [35, 36]. The very sharp decrease in viscosity with shear rate is again consistent with the existence of network-like loose structures held together by the relatively weak hydrophobic interactions that would be expected to be disrupted readily upon application of shear. However, we found that the solutions of copolymers had quite different behavior at different pH and different shear rate (Figs. 6 and 7). When the pH is 3.2:

1. at low shear rate (1 $s^{-1}$), the viscosity does not change with time;

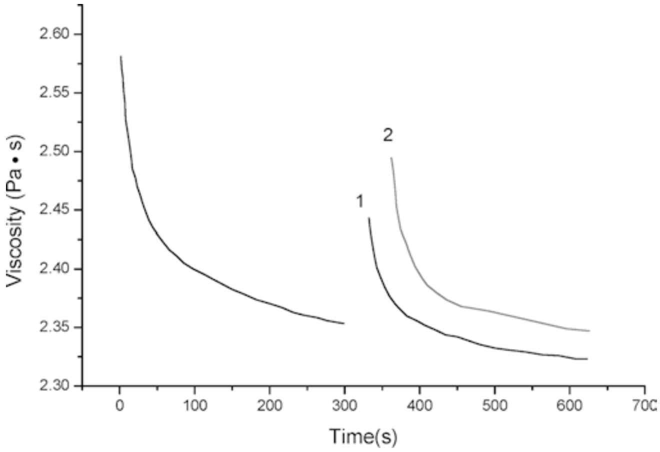


**Fig. 7** Change of viscosity of PAAF-11-14 with shear time ($C = 2\%$ (*w*/*w*), pH 5.0, shear rate = 100 $s^{-1}$; *curve 1*, with a 30 s break; *curve 2*, with a 60 s break)

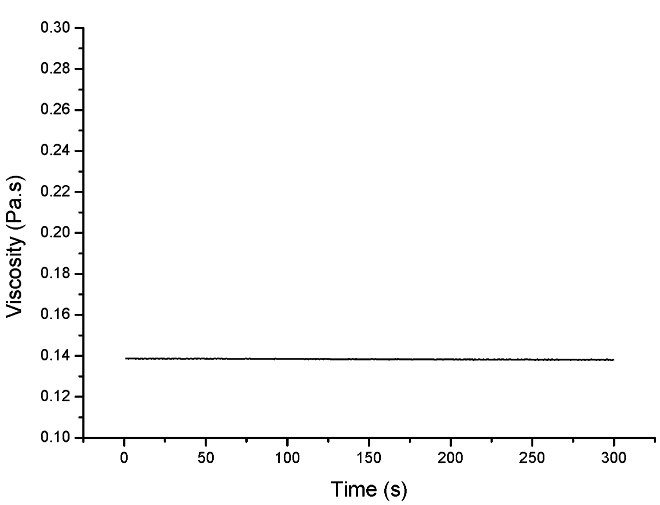


**Fig. 8** Change of viscosity of PAA with shear time ($C = 2\%$ (*w*/*w*), pH 5.0, shear rate = 100 $s^{-1}$)

2. at moderate shear rate (10 $s^{-1}$), the viscosity increases with time; and
3. at high shear rate(300 $s^{-1}$), the viscosity increases briefly then falls quickly.

When the pH is 5.0, only pseudoplasticity is observed for solutions of all copolymers. The solution of homopolymer PAA has no such phenomenon (Fig. 8). We believe that these phenomena are due to shear-induced conformational changes of the molecules. At pH 3.2 most of the molecular chains are coils are entangled, the hydrophobic groups are embedded in the molecular chain. The viscosity of solution is low at that time. Shear stress has two actions:

1. pulling the coil and entangled molecular chain, exposing the hydrophobic group, so association occurs and the viscosity increases; and

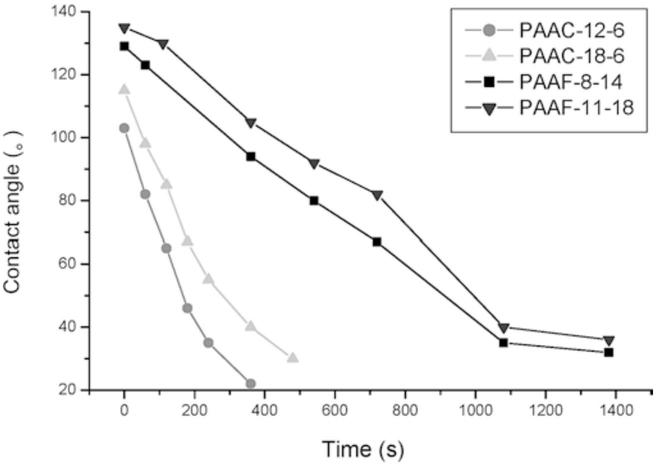


**Fig. 9** Dependence on time of the contact angles of several acrylic acid copolymers

2. making the expanded molecular chain slip, destroying the formed association areas, and making viscosity decrease.

When the shear rate is 1 $s^{-1}$, both effects 1 and 2 are weak and do not affect the structure of the molecular chain, and the viscosity of the solution is constant. When the shear rate is 10 $s^{-1}$, effect 1 plays a major role, intermolecular association occurs formed and the viscosity increases substantially. At 300 $s^{-1}$, effect 2 dominates, the viscosity of the solution decreases sharply after a brief increase. At pH 5.0 intermolecular association already exists and only effect 2 can work. A very sharp decrease of the viscosity of the solution with time is observed. The intermolecular association is a kind of physical crosslinking network. It can be destroyed by the shear stress and can also be reformed when the shear stress is removed. The longer the break time, the higher the viscosity of solution (Fig. 7).

## Contact angle study

Variation of contact angles with time of 2% (*w*/*w*) solutions of copolymers are shown in Fig. 9. As expected, PAAF series copolymers have extremely low surface free energy, the water-drops can hardly spread on their surfaces and the contact angles are large. Figure 9 also shows that the contact angles decrease with time. The weaker the hydrophobicity, the faster the decrease in the contact angle. This is because as time passes the water is absorbed by the hydrophilic group and character of surface changes.

## Conclusion

Hydrophobically associating polymers have been synthesized in supercritical carbon dioxide by copolymerization, at 60 °C and 15 MPa, of acrylic acid and different amounts of acrylate containing hydrocarbon or fluorocarbon groups. It was found that the conversion of hydrocarbon comonomers was above 95% whereas that of fluorocarbon comonomers was only about 50%. In addition, large amounts of hydrophobic groups could be easily introduced to poly(acrylic acid) by reaction in supercritical carbon dioxide.

Intermolecular association of these copolymers was strong; their viscosity was maximum under acidic conditions. Association of fluorocarbon hydrophobes in aqueous solutions was much stronger than that of hydrocarbon hydrophobes, but the viscosifying effect was more pronounced for PAAC-18 series copolymers than for PAAF copolymers in 2% (*w*/*w*) solution. We believe hydrophobicity favors association and increasing viscosity, and that the viscosity of solutions also depended on hydrophobic chain length and the distribution of hydrophobic groups.

The thixotropy of copolymer solutions was very different at different pH and different shear rate. At pH 3.2 the viscosity did not change with time at low shear rate (1 $s^{-1}$); at moderate shear rate (10 $s^{-1}$) the viscosity increased with time; at high shear rate (300 $s^{-1}$) the viscosity increased briefly and then fell quickly. At pH 5.0 pseudoplasticity only was observed for solutions of all copolymers.

The data for contact angles of copolymer solutions on a glass sheet indicated that fluorocarbon analogues were better than hydrocarbon analogues at maintaining the hydrophobic characteristic of the surface and that long hydrophobic chains were better than short ones.

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