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Siloxane-modified poly(acrylic acid) synthesized in supercritical CO_2

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Abstract

Copolymerization of acrylic acid and 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate (TMSPMA) in supercritical carbon dioxide was successfully carried out. The products were obtained in the form of dry white powder with diameter about 0.2 μm. Viscosities of 2% aqueous solution of the copolymers dramatically increased as the content of TMSPMA in the copolymer increased and it was much higher than that of poly(acrylic acid). In addition, the viscosity of the copolymers showed a strong dependence on pH with a maximum at pH 5.0, which is due to the cooperation of intermolecular association and electrostatic repulsion.

Keywords: Supercritical carbon dioxide; Siloxane-modified poly(acrylic acid); Hydrophobic association

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1. Introduction

Hydrophobically modified water-soluble polymers have received more and more attention in recent years [1–8]. When dissolved in water, the hydrophobic groups undergo intermolecular association that imparts unique rheological properties to the solution, such as greatly enhanced viscosity, large shear dependence of viscosity and thixotropy [9–15]. These unique properties enable the hydrophobically modified water-soluble polymers to have wide applications, for example, water treatment, enhanced oil recovery, water-borne coatings and personal care products [16–18].

As to the water-soluble main chain, both electrolytes such as poly(acrylic acid) and non-electrolytes such as polyacrylamide have been studied [19–24]. The difference between the two systems is that the viscosity of non-electrolytes solution does not show pH dependence, but the viscosity of hydrophobically modified polyelectrolytes solution shows large dependence on pH, the maximum viscosity appears around pH 5.0, this phenomenon is interpreted to be due to the balance between hydrophobic association and electrostatic repulsion [25].

As for the hydrophobic modifier, hydrocarbon groups containing 8–18 carbon atoms were fully studied at first. In recent years, it was found that fluorocarbon groups are much more effective than hydrocarbon groups [26,27]. It is clearly because the fluorocarbon groups possess much more hydrophobicity. We speculated that since polysiloxane also possesses much more hydrophobicity than hydrocarbons, siloxane-containing modifier also should be much effective. In addition, siloxane-containing monomer is much cheaper than fluorine-containing monomer; this advantage will be meaningful in industrial applications. However, we have not noticed any reported research work on siloxane-modified water-soluble polymers by now, so we focused our work on this field. We synthesized siloxane-modified poly(acrylic acid) through copolymerization of acrylic acid and 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate (TMSPMA) (Fig. 1) in supercritical CO_2.

The polymerization of acrylic acid is commonly carried out in water, but TMSPMA is not soluble in water. At the same time, utilizing organic solvents may cause another problem of pollution to the product, which can be more serious when the polymer is used in personal care products, cosmetics and even medical products. Supercritical CO_2 as an alternative to conventional organic solvents has attracted increasing attention recently, especially after DeSimone reported the homogeneous polymerization of 1,1-dihydroperfluorooctyl acrylate (FOA) in supercritical CO_2 that substitutes the Freon as commonly used solvent [28]. Using supercritical carbon dioxide as the reaction medium offers an attractive advantage that products are virtually free of contamination and obtained as dry powder easily just by

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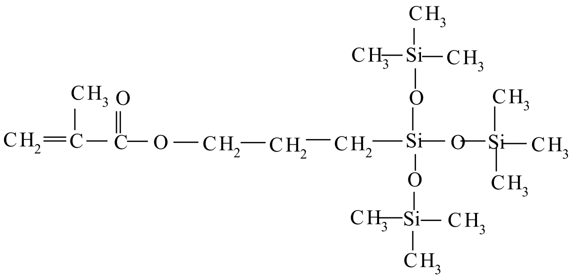

Fig. 1. The structure of the comonomer TMSPMA.

releasing the CO_2 at the end of the reaction, at the same time, no contaminant is released to our environment. DeSimone and other researchers have reported many polymerizations in supercritical CO_2 [28–36] including the homopolymerization of acrylic acid [37].

Herein we describe the successful copolymerization of acrylic acid and TMSPMA in supercritical carbon dioxide at 60 °C and 15.0 MPa utilizing 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator. Series copolymers with different composition are obtained and characterized.

2. Experimental

2.1. Materials

Acrylic acid was purified by vacuum distillation of the commercial product. The siloxane-containing comonomer TMSPMA (98%) was obtained from Aldrich Company and used as received. AIBN was recrystallized from methanol. The CO_2 with purity of 99.9% was used as received.

2.2. Polymerization

A series of copolymers of poly(acrylic acid) and varying amounts of TMSPMA were synthesized by free-radical polymerization initiated by AIBN in supercritical carbon dioxide in 20 ml high-pressure reactor with a magnetic stir bar. 2.0 g acrylic acid, 0.02 g AIBN and varying amount of TMSPMA were charged to the high-pressure reactor, then purged with carbon dioxide at 0.5 MPa and 0.1 $\mathrm{l\ min^{-1}}$ for ca. 5 min to remove O_2. The reactor was sealed and enough liquid carbon dioxide was added through 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. Open the reactor and product in form of white powder was obtained.

2.3. Characterization

The products were washed with supercritical carbon dioxide in situ at 45 °C and 20 MPa to remove the unreacted monomers till the mass of the products did not change. The yield of these polymerizations is around 95%, which is calculated according to the mass of final products and the added monomer.

The morphology of the polymer powder was detected by SEM.

The contents of TMSPMA in final products were determined by acid–base titration described below: Dissolve the polymer sample into water with a concentration about 0.1%, add excessive NaOH aqueous solution V_{OH} (l) to neutralize the carboxylate groups. Then drop in phenolphthalein, showing red, titrate the superfluous NaOH with HCl till the solution turns achromatous, the volume of HCl used is V_{H} (l). Then the content of TMSPMA in the polymer (C_{Si}) is calculated by the following formula (note that the molecular weight of acrylic acid is 72):

$$C_{\mathrm{Si}} = \frac{m_{\mathrm{P}} - 72(C_{\mathrm{OH}}V_{\mathrm{OH}} - C_{\mathrm{H}}V_{\mathrm{H}})}{m_{\mathrm{P}}} \times 100\%$$

In the formula, C_{OH} is the concentration of NaOH aqueous solution ($\mathrm{mol\ l^{-1}}$), C_{H} is the concentration of HCl aqueous solution ($\mathrm{mol\ l^{-1}}$), m_{P} is the quantity of the polymer sample (g).

The intrinsic viscosities of PAA and modified PAAs were measured in 2 M NaOH aq. at 30 °C. The molecular weights were calculated using the equation [38] $[\eta] = 3.38 \times 10^{-3} M^{0.43}$.

Viscosity and rheological property measurement were performed with Rheometrics Fluids Spectrometer at concentration of 2% for each sample. To study the viscosity dependence on pH, 10 $\mathrm{mol\ l^{-1}}$ NaOH aq. was used to adjust the pH value of the solutions.

3. Results and discussion

3.1. Morphology

The polymers obtained here were in form of dry white powder, their morphologies and particle size were determined by SEM. It shows that the diameter of the primary particle is around 0.2 μm. There is no remarkable difference among homopolymer PAA and the copolymers with different TMSPMA content. Figs. 2 and 3 show the SEM photographs of sample No. 3 and 5.

3.2. Composition of the copolymers

The copolymerization of 2.0 g acrylic acid with different amount of TMSPMA produced a series of copolymers with different composition, the results are shown in Table 1 that also shows the molecular weights. It is evident that high siloxane-containing monomer feed ratio leads to high siloxane-containing monomer content in the copolymer. An interesting phenomenon is that the content of TMSPMA in copolymers is higher than in feed, which indicates that TMSPMA is more active than acrylic acid in such a copolymerization.

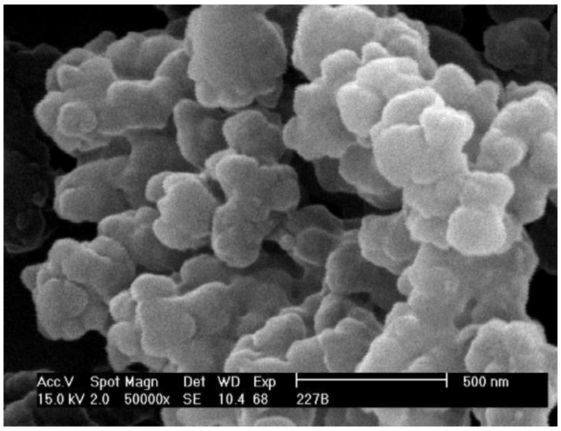

Fig. 2. SEM photograph of sample No. 3.

3.3. Viscosity study

3.3.1. Viscosity dependence on pH and composition

The viscosity of the aqueous solution of poly(acrylic acid) increases gradually with the increase of pH value, and then levels off (Fig. 4). It is because that the carboxylate groups get ionized with the increase of pH value, and then the electrostatic repulsion between the anions along the polymer chains leads to an extension of the chains, so the viscosity increases till levels off when almost all the carboxylic groups are ionized.

The siloxane-modified copolymers show quite different behavior. Firstly, there is a maximum on the viscosity curve of copolymers versus pH, which is at about pH 5.0, as is shown in Fig. 4 that demonstrates the viscosity of 2% aqueous solution of poly(acrylic acid) and copolymer No. 3 as a function of pH value. Secondly, the viscosity of 2% aqueous solution of the copolymers is much higher than that of poly(acrylic acid) at the same concentration and pH value, and it increases dramatically with the increase of the content of TMSPMA. Fig. 5 shows the viscosity of 2% aqueous solution of the copolymers at pH 5.0 as a function of the content of TMSPMA. These phenomena can be explained as a consequence of hydrophobic association among copolymer chains. It has been reported that in aqueous solution of hydrophobically modified polyelectrolytes, these phenomena are always observed. As Ming Jiang and coworkers clarified [25], the increase of pH value has two effects: (1) neutralization of carboxylic groups leads to intramolecular electrostatic repulsion and then the extension of 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. Effect (1) dominates when pH value is lower than 5.0, while effect (2) dominates at pH above 5.0. So the viscosity of copolymers is much higher than that of poly(acrylic acid) and it shows a maximum at pH 5.0.

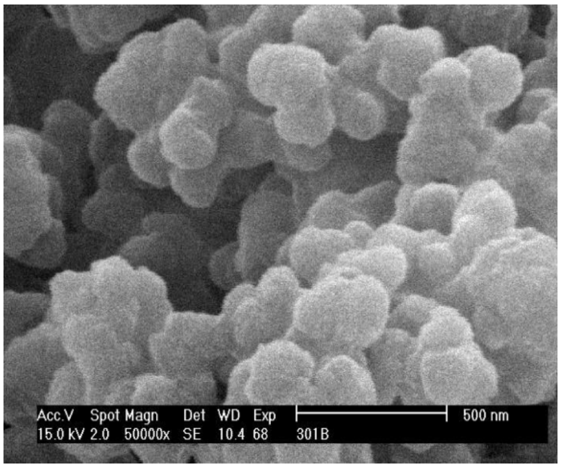

Fig. 3. SEM photograph of sample No. 5.

Table 1
Feed ratio and copolymer composition

Sample No.	$M_\eta \times 10^{-6}$	TMSPMA in feed		TMSPMA in polymer	
		wt%	mol%	wt%	mol%
1	0.56	0	0	0	0
2	0.64	2.27	0.40	8.74	1.61
3	1.23	4.43	0.78	12.51	2.38
4	1.89	6.51	1.17	14.50	2.80
5	2.43	8.49	1.55	18.85	3.80

Now we compare the siloxane-modified poly(acrylic acid) with fluorocarbon-modified poly(acrylic acid). Fluorocarbon-modified water-soluble polymers have been reported: Ming Jiang and coworkers reported the copolymerization of acrylic acid and fluoro-containing monomers in dioxane [25]. Zhang and coworkers reported the copolymerization of acrylamide and fluoro-containing monomers in water-acetone mixed solvent [26]. We reported the copolymerization of acrylic acid and 1H,1H,11H-perfluorodecyl acrylate in supercritical CO_2 [39]. Comparing the siloxane-modified poly(acrylic acid)

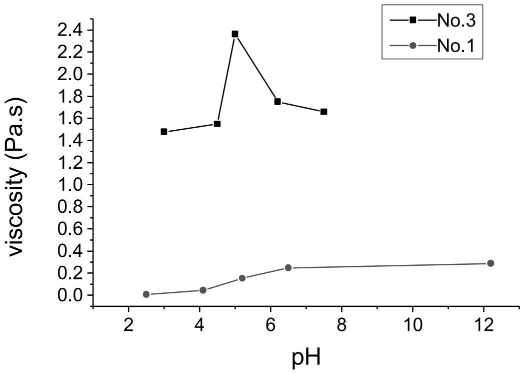

Fig. 4. Viscosity of sample No. 1 and 3 versus pH. ($C = 2\%$, $T = 25$ °C, shear rate $= 10\ \mathrm{s}^{-1}$).

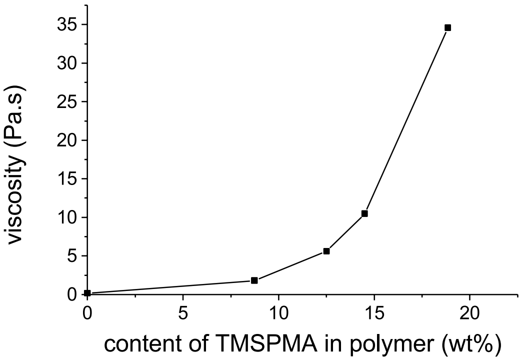

Fig. 5. Viscosity versus content of TMSPMA in copolymer ($C = 2\%$, pH = 5.0, $T = 25$ °C, shear rate = 1 s^{-1}).

studied here with fluorocarbon-modified water soluble polymers reported in references, it can be found that the two series of copolymers similarly show a great viscosity enhancement with the increase of hydrophobe contents. Both of them are much more effective on viscosity enhancement than hydrocarbon-modified water-soluble polymers, which is obviously due to the higher hydrophobicity of siloxane and fluorocarbon groups than that of hydrocarbon groups. However, there is a difference between these two series of copolymers: in the case of fluorocarbon-modified poly(acrylic acid), as pH increases from 3.0 to 5.0, the viscosity increases greatly, for example, the viscosity of copolymers of acrylic acid and 1,1-dihydroperfluorooctyl acrylate increase by 1–2 orders of magnitude with pH increasing from 3.0 to 5.0. But in the copolymers studied here, the increase of the viscosity during the same pH range is much less, sample No. 3 reflects the common property of this series of copolymers. It is shown in Fig. 4 that the viscosity only increase by about 1.5 times as pH increases from 3.0 to 5.0. Obviously, this is due to the difference of the structure between these siloxane-containing copolymers and those fluorine-containing copolymers. In the fluorine-containing copolymers the hydrophobes are in the form of linear chain, while in the copolymers studied here, the hydrophobes are in form of branched chain. To be more important, the Si atom is much bigger than F atom, so the hydrophobic side chains in the siloxane-containing copolymers studied here are much bigger than that in fluorocarbon modified copolymers. According to the association mechanism discussed above, at low pH, the siloxane-containing side chains are exposed due to their large volume, and the intermolecular association has already existed quite strongly. As the pH increases, the molecule extends, but no remarkable amount of new side chains is exposed out, so the viscosity increase is not so large.

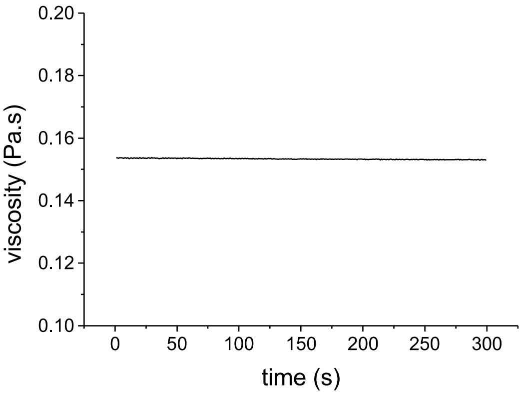

Fig. 6. Viscosity of sample No. 1 versus shear time ($C = 2\%$, pH = 5.0, $T = 25$ °C, shear rate = 10 s^{-1}).

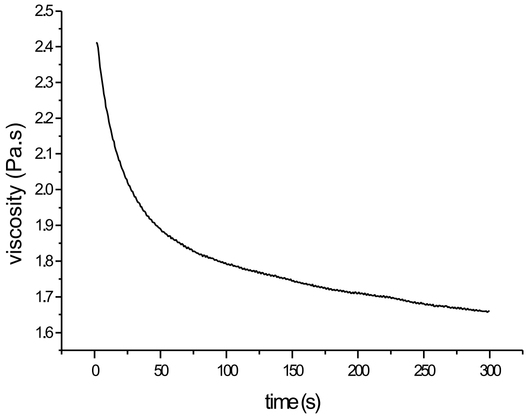

Fig. 7. Viscosity of sample No. 3 versus shear time ($C = 2\%$, pH = 5.0, $T = 25$ °C, shear rate = 10 s^{-1}).

3.3.2. *Thixotropy*

It is found that siloxane-containing copolymer solution exhibits thixotropy, i.e. at a constant shear rate, the viscosities of the copolymers—sample No. 2–5 decrease with time. The homopolymer sample No. 1 does not show this phenomenon. Figs. 6 and 7 show the results of sample No. 1 and 3 at shear rate 10 s^{-1}.

The thixotropy is evidently due to the intermolecular association: the association is a kind of physical cross link that can be destroyed by shear stress, so at a constant shear rate the viscosity will decrease with shear time. According to this explanation, given a break of shear, the association will be formed again to some extent, i.e. the viscosity will increase during the break. Fig. 8 shows the results of

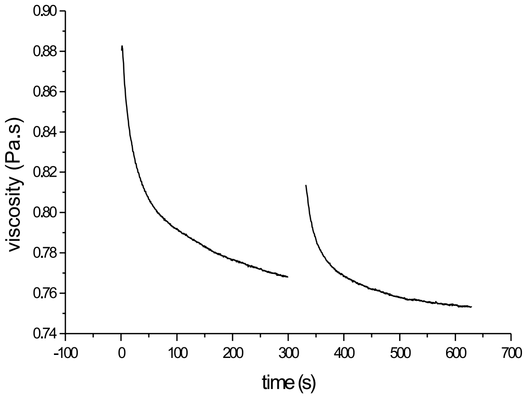

Fig. 8. Viscosity of sample No. 3 versus shear time ($C = 2\%$, pH = 5.0, $T = 25$ °C, shear rate = 100 s^{-1}, with a 30 s break).

viscosity versus time at shear rate 100 s^{-1} with a break of 30 s.

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