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Synthesis of fluorocarbon-modified poly(acrylic acid) in supercritical carbon dioxide

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Abstract

Copolymerization of acrylic acid and 1*H*,1*H*,11*H*-perfluoroundecyl acrylate 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 were much higher than that of poly(acrylic acid) and it showed a strong dependence on pH, which is due to the intermolecular association. © 2002 Published by Elsevier Science Ltd.

Keywords: Supercritical carbon dioxide; Fluorocarbon-modified poly(acrylic acid); Hydrophobically association

1. Introduction

Water-soluble polymers are of great importance to both academic studies and applications, modified with hydrophobic groups, e.g. introducing a few of long alkyl chains commonly containing 8–18 carbon atoms grafted to the water-soluble main chain or attached to one or two ends of the chain will greatly influence its rheological features [1–7]. These so-called hydrophobically modified water-soluble polymers usually produced by copolymerization of water-soluble polymer monomer and hydrophobes exhibit unique rheological properties in solution compared to those of the unmodified parent polymers, such as greatly enhanced viscosity and its large shear dependence, which are due to the intermolecular hydrophobic association. In recent years, it has been reported that fluorocarbon hydrophobes are much effective than hydrocarbons [8,9]. As for the hydrophilic main chain, both electrolytes and non-electrolytes have been extensively studied [10–15]. When polyelectrolytes are used as the main chain, the hydrophobic association and then the viscosity of the solution are sensitive to the pH, which is due to conformational changes of the chain through ionization of the carboxyl groups [16]. Unique properties enable such polymers to have wide applications, for example, in water treatment, food, cosmetics and personal care products.

The polymerization of acrylic acid is commonly conducted in water, since hydrophobes are insoluble in water, the copolymerization of acrylic acid and hydrophobes such as fluorine-containing acrylates cannot undergo 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, food and even medical products. Supercritical carbon dioxide as an alternative to conventional organic solvents has attracted more and more attention in recent years, especially after DeSimone [17] reported the homogeneous polymerization of FOA in supercritical carbon dioxide which substitutes the Freon as commonly used solvent. 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 releasing the carbon dioxide at the end of the reaction. At the same time, no contaminant is released to 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 [17–25] including the homopolymerization of acrylic acid [26].

It has been found that acrylic acid and 1*H*,1*H*,11*H*-perfluoroundecyl acrylate (FUA) are soluble in supercritical

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carbon dioxide at 60 °C and pressure above 14.0 MPa. Herein we describe the successful copolymerization of acrylic acid and FUA in supercritical carbon dioxide at 60 °C and 15.0 MPa utilizing 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator. Series copolymers with different monomer ratio are obtained and characterized.

2. Experimental

2.1. Materials

Acrylic acid was purified by vacuum distillation of the commercial product. The fluorine-containing comonomer FUA (Fig. 1) was obtained from Lancaster Company and used as received. AIBN was recrystallized twice from methanol. The CO_2 with 99.9% purity is used as received.

2.2. Polymerization

A series of copolymers of poly(acrylic acid) and varying amounts of FUA 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. Acrylic acid (2 g), AIBN (0.02 g) and varying amount of FUA were charged to the high-pressure reactor, 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 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 the form of white powder was obtained.

2.3. Characterization

The products were extracted by supercritical carbon dioxide in situ at 45 °C and 20 MPa to remove the unreacted monomers. At the same time, if there is homopolymer of FUA, it can also be removed since it has been reported that highly fluorine-containing amorphous polymers such as poly(FUA) are soluble in supercritical carbon dioxide [17]. The extraction proceeded till the mass of the products did not change, then the yield of polymerization was calculated according to the mass of final products and the monomer. The contents of FUA in final products were determined by fluorine elemental analysis and then the conversion of FUA was calculated. The molecular weight of poly(acrylic acid) was determined by GPC, the intrinsic viscosity of the products was determined with Brookfield viscometer. Since the chains of the fluorocarbon-modified copolymers will associate in water solution which leads to a physical cross-linking and then affect the viscosity of the water solution, the viscosity measurement was performed in dioxane solution at 20 °C.

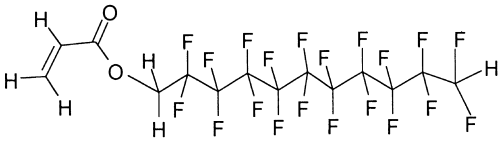


Fig. 1. The structure of comonomer.

The purification by extraction with supercritical carbon dioxide can remove monomers and poly(FUA), but it cannot separate poly(acrylic acid) from the copolymer, so the final products may be composed of the two components—poly(acrylic acid) and the fluorocarbon-modified copolymer. To clarify this, the cloudiness titration was used. The procedure is described here: the polymer was dissolved in ethanol at concentration 0.4%, add 1.0 ml of the ethanol solution into a beaker, 6.0 ml acetone was dropped in with stirring, the system kept homogeneous at this time. Then petroleum ether (boiling range 90–120 °C) was dropped in with stirring, the change of the light transmittance as a function of the amount of petroleum ether added was recorded. In the case of poly(acrylic acid) and the fluorocarbon-modified copolymer with the same intrinsic viscosity determined in dioxane, the solubility of them in ethanol–acetone–petroleum ether should be different, so the change of the light transmittance versus the amount of acetone should show difference. If the final products were composed of two components—poly(acrylic acid) and the fluorocarbon-modified copolymer, the curve of light transmittance versus the amount of petroleum ether should show two peaks. If every curve shows one peak, it can indicate that every final product is of one component.

The morphology of the polymer powder was detected by SEM.

Viscosity and rheological property measurement were performed with rheometrics fluids spectrometer (RFS II).

3. Results and discussion

3.1. Composition and morphology of the copolymers

A series of copolymers are synthesized by copolymerization of 2.0 g acrylic acid with varying amount of FUA, including 0.10, 0.20, 0.30, 0.40 and 0.60 g FUA. The overall conversion and the conversion of FUA are shown in Table 1.

It indicates that under the experimental conditions studied here, the conversion of acrylic acid is quite high while the conversion of FUA is relatively low, only about 50% of FUA can be polymerized into the copolymer. However, it also shows a trend that as the FUA feed ratio increases, the conversion of FUA increases while acrylic acid decreases.

The homopolymer of acrylic acid and all the copolymers obtained are in the form of dry white powder. Their morphology and particle size are determined by SEM. It shows that all the homopolymer and copolymer powders are particles with diameter about 0.2 μm, no remarkable difference are detected between homopolymer and

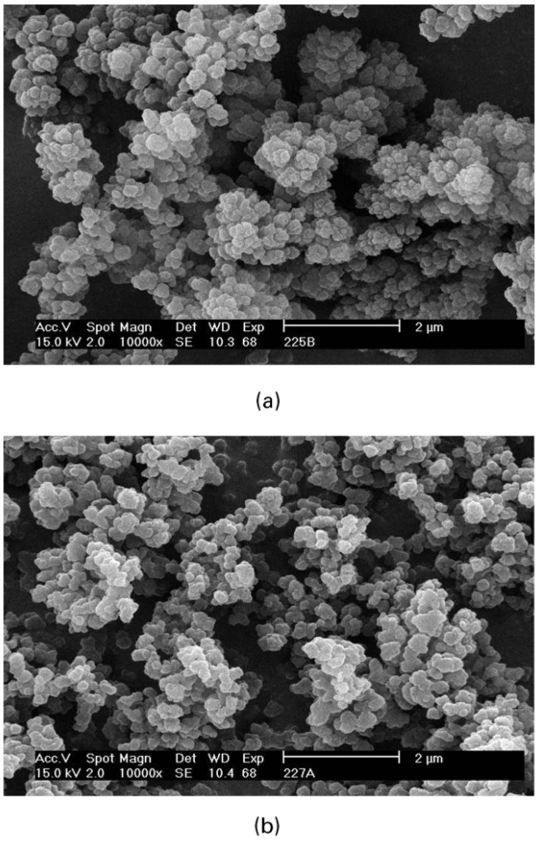
Table 1
The conversion of polymerization

Sample	FUA feed ratio (wt%)	Overall conversion (%)	FUA in polymer (wt%)	FUA conversion (%)
1	0	93	0	–
2	4.76	90	2.62	49.5
3	9.09	88	5.24	50.5
4	13.0	85	7.71	50.2
5	16.7	83	11.10	55.2
6	23.1	80	16.35	56.7

copolymers with different FUA content. Fig. 2 shows the SEM photographs of poly(acrylic acid) (sample No. 1) and copolymer No. 3.

3.2. Intrinsic viscosity and cloudiness titration

The molecular weight of poly(acrylic acid) was determined by GPC (Waters 515-410, 500 column, solvent is 0.1 M NaCl, flow rate 0.6 ml min^{-1}), it shows $M_n = 2.0 \times 10^5$, $M_w = 2.8 \times 10^5$. The molecular weight distribution is very narrow, it is because of the property of supercritical CO_2 and the low monomer concentration. Supercritical CO_2 is a gas-like fluid with very low viscosity and high diffusivity, it causes almost no cage-effect during polymerizations. In this series of polymerizations with low monomer concentration of 10 w/v%, the growing polymer chain separates out from supercritical CO_2 and monomers when it gets to a certain length and dies immediately, so the MWD is very low. However, in the case of high monomer concentration of 30 w/v%, for example, the growing polymer chains absorb much amount of monomer, the post polymerization can lead to a wide molecular weight distribution of 3.8.



(a)

(b)

Fig. 2. SEMs of sample Nos 1 and 3.

Intrinsic viscosities of the products in dioxane at 20 °C are shown in Table 2. It indicates that the intrinsic viscosities of poly(acrylic acid) and its fluorocarbon-modified copolymers synthesized here are similar. However, poly(acrylic acid) and these fluorocarbon-modified copolymers exhibit quite different behavior in the cloudiness titration. In the case of sample Nos 1 and 6 with exactly the same intrinsic viscosity, homopolymer No. 1 precipitates more easily from the ethanol–acetone solution when added into petroleum ether. Fig. 3 shows that sample No. 1 begin to precipitate from the solution when 1.8 ml petroleum ether was added while sample No. 6 begin to precipitate when 2.8 ml petroleum ether was added. Furthermore, the light transmittance detected for the solution of sample No. 1 shows a minimum of 55%, while sample No. 6 shows a minimum of 75%, i.e. the fluorocarbon-modified copolymers are more compatible with ethanol–acetone–petroleum ether. The copolymer with lower specific viscosity shows more compatibility with ethanol–acetone–petroleum ether, as shown in Fig. 3. The titration curve of sample Nos 2, 3 and 5 are very close to Nos 4 and 6, they are not shown here. All these titration curves show one peak, respectively, which indicates that every sample synthesized here is composed of copolymers, i.e. there is no detectable homopolymer in the final copolymer products.

3.3. Solubility of the products

From sample Nos 1 to 6, the solubility of them in water

Table 2
Intrinsic viscosity of the products in dioxane at 20 °C

Sample	[η]
1	120
2	115
3	124
4	110
5	121
6	120

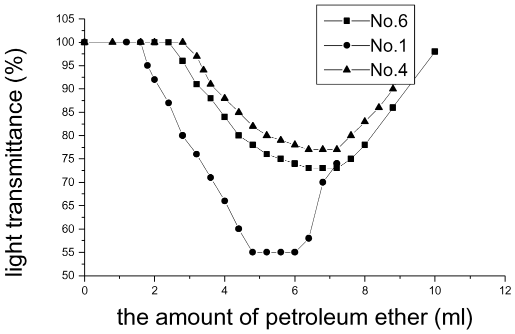


Fig. 3. Cloudiness titration plot.

decreases with the increase of FUA content in the copolymers. To dissolve the copolymer into water, it is necessary to add alkali to ionize the main chain to enhance the solubility of the copolymer. Table 3 shows the demanding pH value for each copolymer to be dissolved.

In the case of the homopolymer of acrylic acid, there is no need to add alkali to dissolve it into water, the pH value of 2% solution is 2.5. As for the copolymers, varying amount of alkali such as NaOH is needed to increase the pH value and then ionize the carboxyl group to increase the solubility of the copolymers.

3.4. Viscosity study

The viscosity of the semi-diluted aqueous solution of poly(acrylic acid) increases gradually with the increase of pH value, and then levels off. It is because that the carboxylic groups get ionized with the increase in 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 fluorocarbon-modified copolymers show quite different behavior. Firstly, the viscosity of semi-diluted aqueous solution of the copolymers increase steeply with the increase in pH value at the beginning of neutralization, while that of poly(acrylic acid) is much smooth. Secondly, there is a maximum on the viscosity curve of copolymers, 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. 2 as a function of pH value. Fig. 5 shows the behavior of copolymer Nos. 3–5. In the case of copolymer No. 6, it cannot be dissolved below pH 6.5, which exceeds pH 5.0, so no maximum of the viscosity was observed, and it is not shown here. Thirdly, the viscosity of semi-diluted 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 in the content of FUA. Fig. 6 shows the viscosity of 2% aqueous solution of the copolymers at pH 5.0 as a function of the content of FUA. All the phenomena described above can be explained as a consequence of hydrophobic association among copolymer chains. It has been reported that in semi-diluted aqueous solution of hydrophobically modified polyelectrolytes, these phenomena are always observed. As Ming Jiang and coworkers clarified [16], the increase in 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 fluorocarbon groups embedded in polymer chains at low pH value, 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.

Table 3
Demanding pH values for polymers to be dissolved in water

Sample	pH
1	2.5
2	2.6
3	2.8
4	3.2
5	3.8
6	6.5

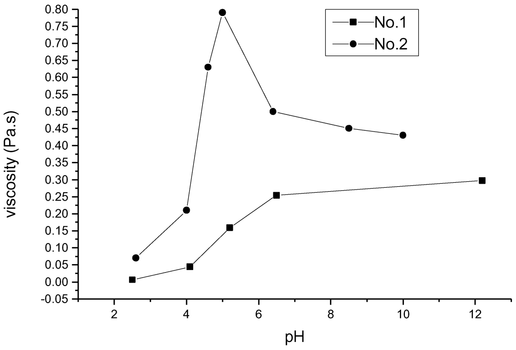


Fig. 4. Viscosity of sample Nos 1 and 2 versus pH ($C = 2\%$, $T = 25$ °C, shear rate $= 1\ \mathrm{s}^{-1}$).

From the results discussed above, we can draw a

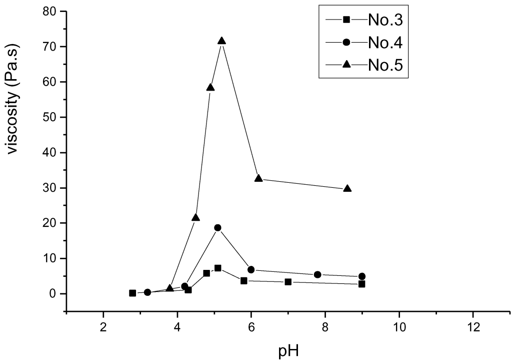


Fig. 5. Viscosity of sample Nos 3–5 versus pH ($C = 2\%$, $T = 25$ °C, shear rate $= 1\ \mathrm{s}^{-1}$).

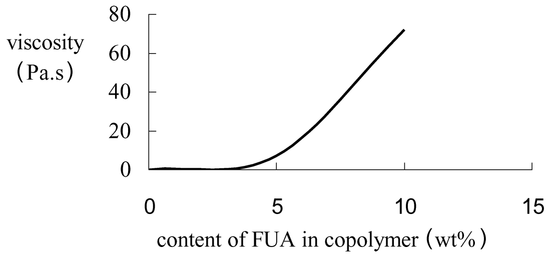


Fig. 6. Viscosity versus content of FUA in copolymer ($C = 2\%$, pH = 5.0, $T = 25$ °C, shear rate = 1 s^{-1}).

conclusion that the copolymerization of acrylic acid and FUA in supercritical CO_2 has been successfully carried out, the fluorocarbon-modified poly(acrylic acid) shows typical intermolecular hydrophobic association proved by the viscosity study, in return, the viscosity behavior testifies that the products were really fluorocarbon-modified copolymers.

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