Copolymers of 3,3,3-Trifluoropropene and Vinyl Acetate: Synthesis, Characterization, and Hydrolysis

Shuxiang Zhang, Anhou Xu, Bing Geng, Pandeng Xia, Shanzhuang Chu, Min Liu

College of Chemistry & Chemical Engineering, Jinan University, Jinan 250022, People's Republic of China

ABSTRACT: Copolymers based on 3,3,3-trifluoropropene (TFP) and vinyl acetate (VAc) were synthesized in supercritical carbon dioxide(sc—CO_2). The copolymers were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and differential scanning calorimetry (DSC) as the thermal analysis method. The copolymer compositions were estimated by three techniques: mass balance, NMR and electric potential analysis. The mole fraction of TFP in the copolymer increased with the feeding TFP added from 12.1% to 76.4% and almost unchanged with

a feeding TFP increase from 76.4% to 89.7%. After partial carboxyl groups turned to hydroxyl groups by hydrolysis, the P(TFP-*co*-VAc) copolymer turned into terpolymers, P(TFP-VAc-VA). Dispersed in water, the hydrolyzed copolymer obtained emulsion by self-emulsifying. The size distribution and the morphology of the latex were also investigated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 533–538, 2007

Key words: supercritical carbon dioxide; 3,3,3-trifluoropropene; self-emulsifying

INTRODUCTION

Fluoropolymers have been used in various fields such as cloth, plastic, rubber, and paint because of their heat and chemical resistance, weatherability, corrosion resistance, water and oil repellency, and oxidation resistance properties.[1–3] Since fluorine-containing polymers were insoluble in solvents, a high-temperature process was required and application was limited. To overcome this problem, various solvent-soluble fluoropolymers have recently been developed. Shoichet[4] and others[5,6] have synthesized trifluorovinyl ether (TFVE) polymers, which have a hydrocarbon oligoether pendant group and a fluorinated backbone, thereby incorporating some hydrocarbon properties into a fluorinated system. The polymers are easier to process and more soluble in organic solvents.

The chemical industry has become increasingly aware of environmental concerns over the use of volatile organic solvents and chlorofluorocarbons in the manufacture of commercial fluoropolymer products. The use of water alleviates these problems somewhat, but still results in large amounts of hazardous aqueous waste that require treatment.[7] Supercritical carbon dioxide (sc-CO_2) has been shown to be an excellent reaction medium for the synthesis of

fluoropolymers due to its inertness in free-radical polymerizations, its cost-effectiveness, and its numerous environmental advantages.[8–11]

DeSimone[12–15] and others[16,17] have reported the homopolymerization or copolymerization of the fluorocarbon monomer such as tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), vinylidene fluoride (VDF) in sc-CO_2. 3,3,3-Trifluoropropene (TFP) as a new fluorocarbon monomer, which is rarely used in polymerization,[18] is usually used as an intermediate in the manufacture of fluorosilicone, medicines, and pesticides.[19,20] Herein, TFP and VAc were copolymerized in sc-CO_2 by a free radical mechanism in order to clarify the typical properties of TFP monomer, and the TFP-VAc copolymer was hydrolyzed to yield vinyl alcohol group that can ensure the copolymer obtain emulsion dispersed in water by self-emulsifying. The hydrolysis produces a reactive functional group for further modification such as prepare a hybrid emulsion in the future.

EXPERIMENTAL

Materials

TFP was obtained from Weihai Newera Chemical Co. Ltd, Shandong China; vinyl acetate (VAc), analytical reagent, which was distilled before use, was obtained from Shanghai Chemicals; acetone, ethanol, tetrahydrofuran (THF), concentrated sulfuric acid, and sodium bicarbonate were obtained from Beijing Fine Chemicals Inc. Ltd.

Correspondence to: S. Zhang (chm_zhangsx@ujn.edu.cn).

TABLE I
Polymerization of the TFP Monomer[a]

Sample	TFP in feed (mol %)	VAc conversion (wt %)	TFP conversion (wt %)	Mn (g mol^{-1})	PDI
1	100	—	5	8063	1.41
2	89.7	91	16	23028	1.60
3	76.4	88	27	24671	1.61
4	50	79	69	45577	1.80
5	12.1	65	94	99200	2.15
6	50	90	40	78365	2.13

[a] 6-Bulk polymerization of TFP and VAc.

Synthesis of polymers: P(TFP-co-VAc)

Polymerizations were conducted in sc-CO$_2$ in a 50 mL high-pressure reactor. The head of the reactor was fitted with a magnetic drive, and the reactor was heated by a water bath connected to a temperature controller. The reactor was sealed and evacuated. Subsequently, the desired amount of chilled VAc ($T \sim 0°C$), which dissolved 2,2-azobis(isobutyronitrile) (0.5% AIBN) initiator, was transferred by cannula to the evacuated reactor. With stirring, the desired amount of TFP was added to the reactor for a total monomer weight of 20 g. Designed amounts of CO$_2$ were then located into the reactor and the system was then heated up to 65°C. Pressures were initially between 18 to 20 MPa.

Polymerizations were stopped after 24 h by cooling the reactor to room temperature. After the reactor was slowly vented, the white and tacky solid was dissolved in acetone, completely removed, and precipitated into water. The polymer was collected by vacuum filtration and washed several times with distilled water before drying.

Acid hydrolysis of P(TFP-co-VAc) to P(TFP-co-VAc-co-VA)

In a 250 mL round-bottom flask equipped with a condenser and a magnetic stir bar, 6 g of copolymer, 150 mL of ethanol, 2 mL of distilled water, and 1 mL of concentrated sulfuric acid were added. The mixture was stirred and refluxed for four days. A approximately clear polymer solution resulted, which was then cooled to room temperature and neutralized by the slow addition of sodium bicarbonate, with vigorous stirring. The polymer solution was centrifuged to remove the sodium sulfate salt. The polymer was collected after removing the ethanol by rotary evaporation and then further dried under vacuum.

Self-emulsifying emulsion

A certain amount of hydrolyzed polymer was added in 50 mL beaker and dissolved by THF and put for

24 h after full dissolution. Then THF which has dissolved polymer was slowly dropped in a certain amount of distilled water under mixing violently. Since THF has low boiling point, it can be removed easily in vacuum under the room temperature. Finally, the emulsion was prepared after decompression for 48 h to dispose of the dissolved THF in water.

Characterization

Molecular weight was characterized by a GPC (Gel Permeation Chromatography, Waters injector, 1525 pump) equipped with a refractive index detector (Waters 2414). Using a THF mobile phase at a flow rate of 1 mL·min^{-1}, molecular weight was calculated relative to polystyrene standards. The copolymer samples were prepared as thin films and mounted in transmission mode in the FTIR (PE-983). ^{1}H and ^{19}F NMR spectra (Bruker ARX-400NMR) were obtained in CDCl$_3$, using TMS as external references. The glass transition temperature T_g was measured using a differential scanning calorimeter (Pryris Diamond DSC, Perkin-Elmer), under nitrogen atmosphere, with a heating rate of 10°C/min and scanning range of 10°C to 80°C. The size distribution of the latex particles was characterized by dynamic light scattering analyzer (Zetasizer 3000, Malvern). The morphology of the latex was observed with a HITACHIH-600 transmission electron microscope (TEM).

RESULTS AND DISCUSSION

To clarify the typical properties of TFP monomer, which is rarely used in polymerization, TFP was homopolymerized and was also copolymerized with VAc in sc-CO$_2$ by a free radical mechanism.

From Table I it can be seen that the conversion of TFP in sample 1 is only 5%, and its molecular weight is 8063 g·mol^{-1}, which shows that TFP monomer is difficult to homopolymerize under these reaction conditions, and TFP and VAc monomer could copolymerize well. As the mole fraction of TFP was
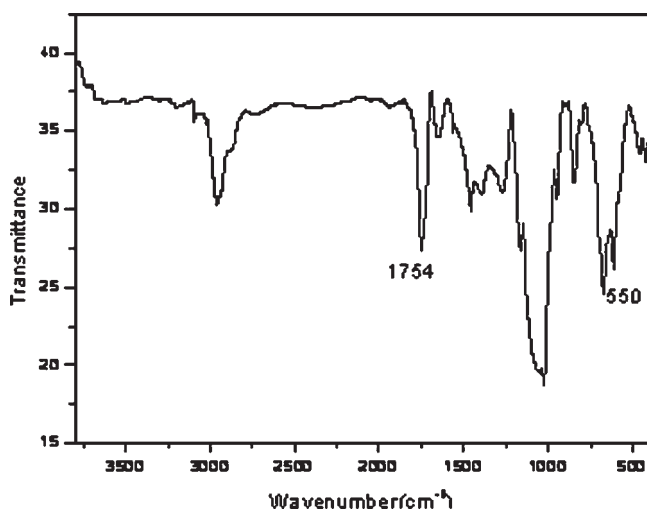
Figure 1 FTIR spectra of P(TFP-co-VAc) copolymerized in sc—CO_2.

Figure 2 DSC thermogram of P(TFP-co-VAc) copolymerized in sc—CO_2.

89.7%, as shown in sample 2, the conversion of VAc was high (up to 91%) while that of TFP was 16%. After VAc monomer was mostly consumed, the residual TFP was difficult to homopolymerize, so its conversion was low. At lower mole fraction of TFP (12.1%), as sample 5 shows, the conversion of TFP was as high as 94%, while that of VAc was 65%. After most of the TFP was copolymerized with VAc, the residual VAc monomer could homopolymerize sequentially. Because of the poor solubility of PVAc in sc-CO_2, the growing polymers precipitated and the macroradical chains were mostly trapped into the polymers as the reaction went on, so the conversion of VAc was lower.

Contrasting samples 4 and 6, the conversion of VAc in sample 4 is lower than that of sample 6, and the conversion of TFP in sample 4 is higher than that of sample 6. In sample 4, when the polymerization went on to an extent, the molecular weight of the polymers reached the point when the polymers could not be dissolved in sc-CO_2, the polymers precipitated, and the polymerization ended. While in sample 6 the polymerization took place in the absence of any solvent, the VAc monomer could not only copolymerize with TFP, but also homopolymerize without precipitation, so its conversion was higher than that of sample 4. In addition, because more TFP was kept in gas phase in sample 6, which reduces the chance for TFP and VAc to copolymerize, the conversion of TFP in sample 6 was lower than that in sample 4.

Characterization of copolymer

The TFP-VAc copolymer was characterized by FTIR, DSC, ^{1}H NMR, and ^{19}FNMR. The FT-IR spectra are shown in Figure 1, which shows the transmittance
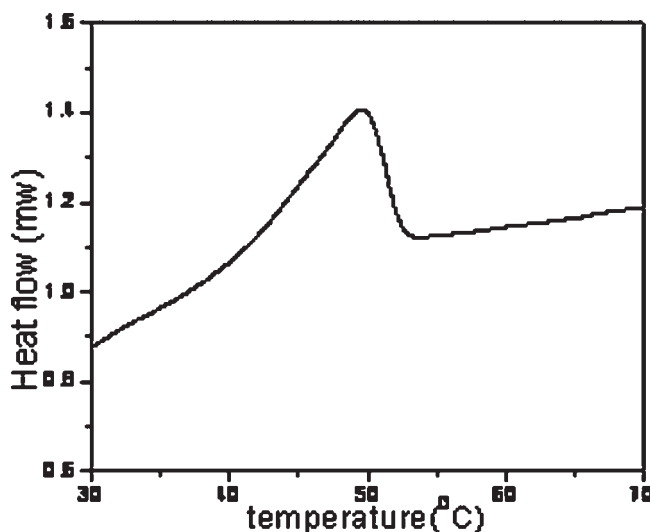
peaks at 1754 cm^{-1}, 550 cm^{-1} ascribed to v (C=O) and v (C—F), respectively. The DSC thermogram of the copolymer shows a single T_g (Fig. 2). Both FTIR and DSC indicate that TFP and VAc were well copolymerized.

Ownership of each hydrogen of ^{1}HNMR spectra is shown in Figure 3. ^{19}FNMR spectra show clearly that TFP has been copolymerized with VAc. To gain a better understanding of the molecular composition of our fluorocopolymers, ^{19}FNMR was used to determine the sequence distribution of the TFP and VAc units in the main copolymer chain. The relationship of different groups on the carbon chain at different positions that brings the chemical shift of CF$_3$ can be described as follows [21]:

$$\delta_{CF} = -(81 + \Delta\delta_\alpha + \Delta\delta_\beta) \tag{1}$$

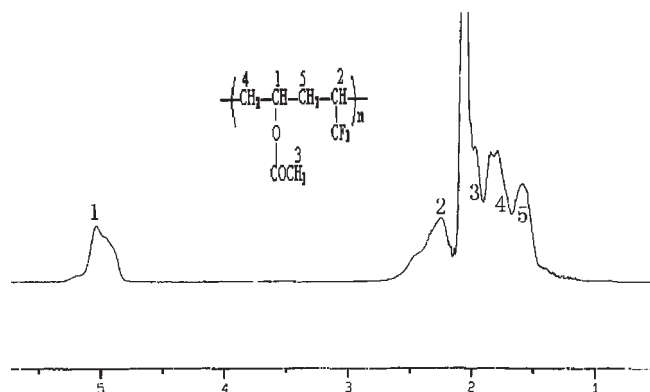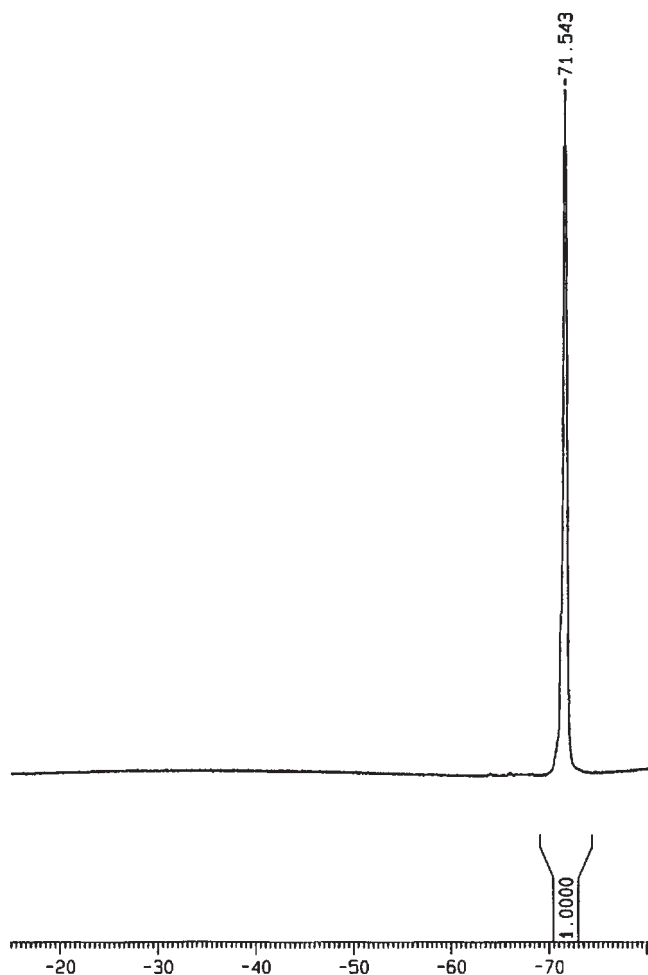**Figure 3** ^{1}H NMR spectra of P(TFP-co-VAc) copolymerized in sc—CO_2.

Figure 4 ^{19}FNMR spectra of P(TFP-*co*-VAc) copolymerized in sc—CO$_2$.

where $\Delta\delta_\alpha$ and $\Delta\delta_\beta$ are the α and β positions' chemical shifts of CF$_3$ of the carbon chain. In ^{19}FNMR spectra (Fig. 4), there is only one sharp peak at −71.5 ppm and this elucidates that the connection mode of TFP and VAc units in the main chain of copolymer is head to tail, not head to head nor tail to tail. This structure of head to tail is also in accord with the steric effect.

Copolymerization of TFP and VAC

A series of TFP-VAc copolymers were synthesized in sc-CO$_2$ and characterized for bulk composition and T_g, and the results are summarized in Table II.

The copolymer compositions were estimated by three techniques: mass balance, NMR, and electric potential analysis.[22] Mass balance was used to estimate the amount of TFP incorporated into the TFP-VAc copolymer by the difference between the feeding and the venting of TFP. NMR was used to estimate the copolymer composition by the peak area ratio of the VAc and TFP methine hydrogen in ^{1}HNMR spectra. Electric potential analysis, by selective fluorinion electrode, was based on the fact that the electrode potential moves with the concentration of fluorinion and the mole fraction of TFP in the copolymerization can be determined.

Table II shows that in sc-CO$_2$, firstly, when the TFP feed ratio increases from 12.1% to 76.4%, the mole fraction of TFP in the copolymer is increased. Then, with the feeding TFP increases from 76.4% to 89.7%, the mole fraction of TFP in copolymer was almost unchanged. From the test results, the fraction of TFP in copolymer is an upper limit of about 50%. The reactivity ratios of copolymerization of TFP and VAc in sc-CO$_2$ were calculated such that *rTFP* = 0.019 and *rVAc* = 0.40, indicating that the radical on TFP primarily cross-propagates with VAc. Since the TFP reactivity ratios approach zero, they tend to cross-propagate with VAc, yielding a largely alternating copolymer when feeding excessive TFP monomer. From Table II, it can be seen that the T_g values of P(TFP-*co*-VAc) copolymers, which are higher than that of PVAc (32.2°C), increased from 35.8°C to 42.2°C when the TFP mole fraction in feed was

TABLE II
Copolymers of TFP and VAc

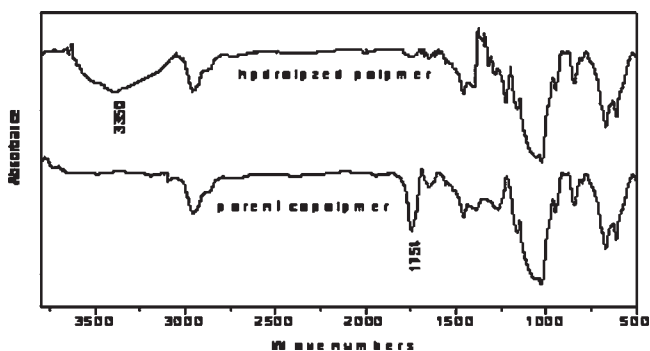| Sample | TFP in Feed (mol %) | VAc conversion (wt %) | TFP in copolymer (mol %) | | | T_g |
			Mass balance	NMR	Electric potential	
1	0	55	—	—	—	32.2
2	12.1	65	15.5	16.7	13.5	35.8
3	38.6	75	38.8	39.2	37.9	41.4
4	50.0	79	43.5	45.1	44.5	41.8
5	69.4	85	48.6	49.3	48.9	42.1
6	76.4	88	49.2	51.0	49.8	42.2
7	83.6	89	49.3	51.0	49.8	42.2
8	89.7	91	49.3	51.1	49.9	42.2
9	100	—	—	—	—	—

Figure 5 FTIR spectra of P(TFP-*co*-VAc), sample 5 in Table II, before and after hydrolysis.

added from 12.1% to 76.4%. However, the tendency of increasing stopped when the mole fraction of TFP in feed reached 76.4%.

Hydrolysis of P(TFP-co-VAc)

In the Figure 5 the obvious hydroxyl absorption (3330 cm^{-1}) can be found in the FTIR spectra of P(TFP-*co*-VAc-*co*-VA) compared with that of P(TFP-*co*-VAc). As indicated in Figure 5, most of the VAc groups were hydrolyzed to VA groups. In the case where the mole content of TFP in the copolymer is known, the hydrolysis degree of polymer can be calculated by the change of the fluorine mass content before and after hydrolysis. By calculation, the hydrolysis degree of polymer is 98%.

When the polymers with many $-CF_3$ groups and $-OH$ groups, are dispersed in water, the hydrophobic group of $-CF_3$ preferentially condenses together while the hydrophilic group extends $-OH$ into the continuous phase, providing a surface anchor for the hydrophilic $-OH$ stabilizing moieties. So the colloidal particles were formed by self-emulsifying. As shown in Figure 6, the size distribution of latex particles is characterized and the average diameter of the particles is 151 nm. The TEM (Fig. 7) showed the morphology of latex.

The morphology of latex is spherical and most of the particles range in size from about 80 to 200 nm.
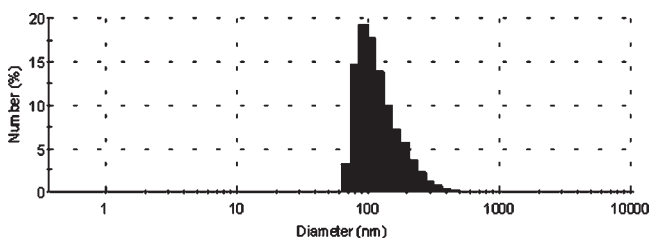

Figure 6 Distribution of the particle-size prepared hydrolyzed P(TFP-VAc), sample 5 in Table II, dispersed in water.
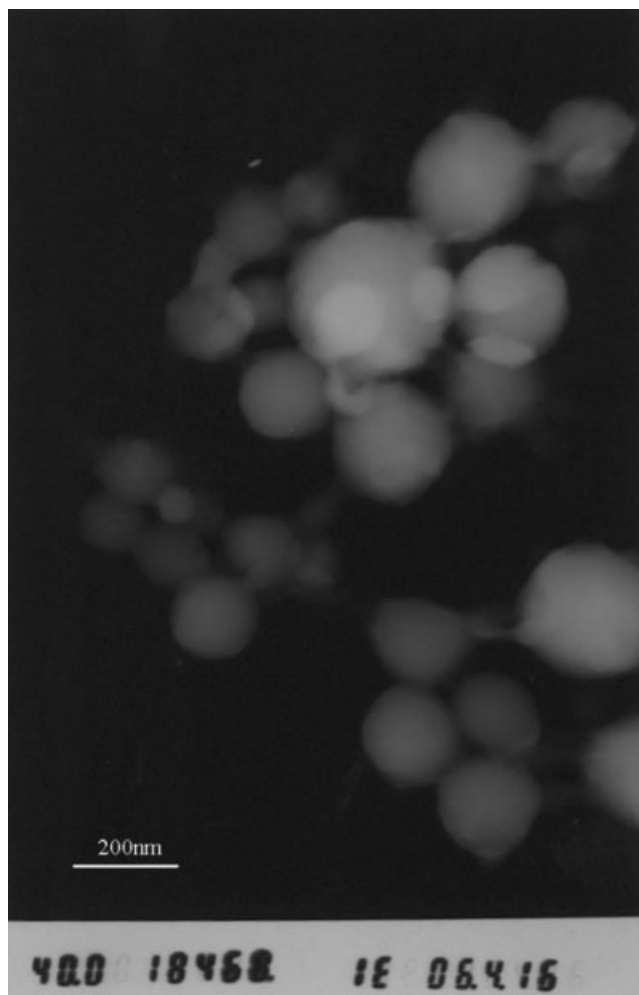

Figure 7 TEM of hydrolyzed P(TFP-*co*-VAc), sample 5 in Table II, dispersed in water (enlarged 40,000 times).

CONCLUSIONS

Based on the results obtained in this article, the following conclusions can be drawn:

1. TFP is difficult to be homopolymerized and is well copolymerized with VAc by a free radical mechanism. TFP monomer conversion is only 5% in homopolymerization while it is 69% in copolymerization with VAc in sc-CO_2.
2. Copolymers of TFP and VAc are approximately alternate with feeding-excessive TFP in sc-CO_2. The test result have shown that the mole fraction of TFP in TFP-VAc copolymer increased with the feeding TFP increase first, while the fraction was an upper limit of about 50% with the feeding TFP increase last.
3. With the hydrophobic group of $-CF_3$ and the hydrophilic group of $-OH$, the hydrolyzed polymer formed emulsion by self-emulsifying, the particles are spherical, and the average diameter is 151 nm with some particles inevitably conglutinated together.

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