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Polymerizations of Tetrafluoroethylene in Homogeneous Supercritical Fluoroform and in Detergent-Free Heterogeneous Emulsion of Supercritical Fluoroform/Water

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ABSTRACT: Homogeneous polymerizations of tetrafluoroethylene (TFE) were executed in supercritical fluoroform ($scCHF_3$), and the resulting poly(tetrafluoroethylene) (PTFE) was uniformly dispersed and twined fibers (ca. 100 nm in width and 10 μm in length). The number-average molecular weight and the conversion of PTFE can be controlled by pressures of $scCHF_3$ from $M_n = 10^4$ to 10^6 and 60−80%, respectively. Heterogeneous detergent-free or stabilizer-free emulsion polymerization could be performed in the narrow condition of the $scCHF_3$/water (5:3 in v/v) system at 17 MPa of the pressure with the 20−40% conversion, and the uniform spherical submicron particles (ca. 200 nm) of PTFE were obtained, in comparison with twined fibers from the homogeneous polymerization.

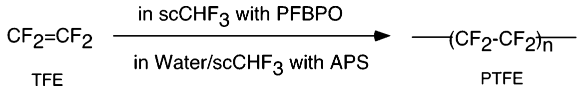
Introduction

Poly(tetrafluoroethylene) (PTFE) is a useful and being in highly demand material due to its specific hydro- and lipophobicity. It is, however, difficult to treat and manufacture PTFE as a material by the reason for its immiscibility to conventional solvents. Furthermore, tetrafluoroethylene (TFE) as a monomer is also required to handle carefully due to the explosiveness of the liquid both in the lab scale and in the industry scale.[1]

When a bulk polymerization is applied to PTFE, it is difficult to control its explosive reaction due to the extremely large heat of the reaction. The solution polymerization of PTFE is also difficult due to the very low solubility of PTFE in organic solvents, and the polymerization is frequently inhibited by the small amount of impurities. Therefore, a suspension or emulsion polymerization of TFE in water is generally accomplished in the preparation of PTFE to dilute the monomer concentration and remove the large heat of the reaction. In the case of heterogeneous emulsion polymerization, it is difficult to control the molecular weight, the dispersibility, and the crystallinity of PTFE. Therefore, it is strongly requested to develop a new polymerization method of TFE in homogeneous or emulsion systems.

Recently, supercritical carbon dioxide ($scCO_2$) has been expected as clean and moderate reaction media because CO_2 is inexpensive and safe and has the distinctive properties of supercritical fluids. Their physical properties (e.g., density, diffusiveness, and viscosity) are intermediate between those of gases and liquids. The large diffusiveness of supercritical fluids compared to liquids can be expected to increase the reaction rate. Several organic reactions in $scCO_2$ have been reported using organometallic complexes.[2] We accomplished the enzymatic esterification reactions catalyzed by a lipid-coated lipase[3] and transglycosylations catalyzed by a lipid-coated β-galatosidase[4] in supercritical fluids. Supercritical fluids are also useful to study effects of solvation on molecular recognition on nucleobases by hydrogen bonding[5] and on organic crystal cavities.[6] Applications of supercritical fluids as a medium to polymer syntheses will become a way of overcoming the difficulty of TFE polymerizations. DeSimone and co-workers applied $scCO_2$ as polymerization media for various monomers.[7−9] They also reported briefly the polymerization of TFE in the $scCO_2$/water emulsion system using surfactants.[9] Although $scCO_2$ is useful as reaction media due to the safety and a low price, the low polarity of $scCO_2$ due to the nonpermanent dipole moment (comparable to hexane as organic solvents) is a big problem as reaction media, because some additives are required to increase the solubility of monomers in homogeneous polymerization and surfactants are needed in the case of emulsion polymerization in $scCO_2$/water system.[7−9]

Scheme 1



In this study, we employ supercritical fluoroform ($scCHF_3$) as reaction media in the polymerization of TFE instead of $scCO_2$ (see Scheme 1). The reason why we chose $scCHF_3$ is the high polarity of $scCHF_3$ in comparison with $scCO_2$.[10] $scCHF_3$ has the high solubility for substances, and the dielectric constant of $scCHF_3$ can be changed from 1 to 7 (corresponding to the value of hexane to tetrahydrofuran as organic media) by manipulating either the temperature or the pressure of $scCHF_3$.[11] In addition, $scCHF_3$ is immiscible to water and can form stable emulsions without any surfactants and other additives from our observations through a sapphire glass window. Kamat et al. reported the enantioselectivity of enzymatic reactions could be controlled in $scCHF_3$.[12] We have reported the reaction rate in enzymatic transformation can be regulated by the tune of pressure or temperature of $scCHF_3$.[3,4]

We employed the homogeneous polymerization of TFE in $scCHF_3$ and heterogeneous emulsion polymerization in $scCHF_3$/water without any surfactants. In these systems, after evaporating $scCHF_3$, only PTFE was obtained as precipitates. It is important to obtain pure PTFE because PTFE is immiscible to any solvents and intractable as plastics. In this paper, we show that the reactivity of TFE, the shape, size, and dispersibility of PTFE can be controlled by pressure-regulation in the system.

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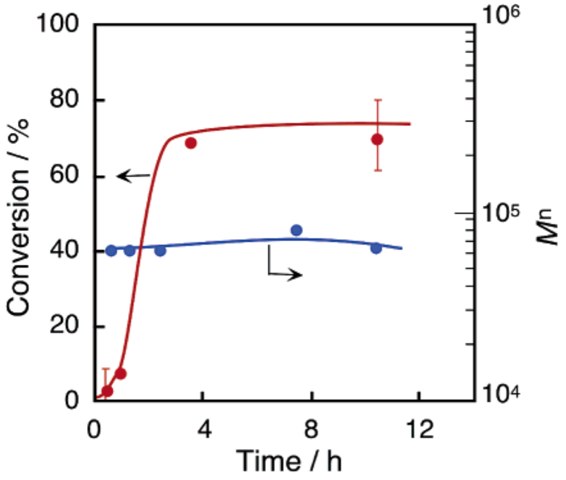

Figure 1. Typical time courses of conversions and number-average molecular weights (M_n) of the homogeneous polymerization of TFE initiated with perfluorobenzoyl peroxide (PFBPO) in $scCHF_3$ at 14 MPa and 60 °C. [TFE] = 1.0 g in 10 g of $scCHF_3$ (10 wt %), [PFBPO]/[TFE] = 1/1000.

Materials and Methods

Materials. Tetrafluoroethylene (TFE), fluoroform (purity: 99.999%), and perfluorobenzoyl peroxide (PFBPO) were kindly provided by Asahi Glass Co. (Tokyo) and were used as received. Other reagents for polymerizations were purchased from SIGMA-Aldrich Chemical Co. (Milwaukee, WI) or Tokyo Kasei Co. (Tokyo) and were used without further purification.

Equipment and Polymerization. Reaction vessels made of stainless steel were purchased from Taiatsu Glass Co. (Tokyo), and other pressure-resistant lines (tubes, bulbs, unions, and adaptors) were purchased from Swagelok Co. (Solon, OH). Polymerizations were performed in 10 mL pressure-resistant stainless vessels equipped with sapphire glass windows, which permit visual observation during the reactions. The vessel was charged with initiators such as PFBPO powders for the homogeneous polymerization or a certain amount of aqueous solution (0.2−8 mL) of ammonium persulfate (APS) for the emulsion polymerization in advance. The vessel was cooled and evacuated prior to the addition of gaseous TFE monomers.

TFE should be treated carefully. Since the liquid TFE is explosive, it was stored in a gas cylinder below the pressure of 0.3 MPa. TFE monomer transferred from the gas cylinder to a small stainless bottle (100 mL volume) in the gas state and then moved to the reaction vessel cooled at −100 °C. The amount of solidified TFE monomer was weighed (0.5−1.0 g), and then TFE was immediately diluted by the injection of liquid CHF_3 at −5 °C and 5−25 MPa from a LC pump (model: PU-980 HPLC pump, JASCO, Co., Tokyo) connected to a CHF_3 gas cylinder. The vessel was warmed with stirring magnetically above 25 °C to keep a supercritical state, under the constant pressure (±0.1 MPa) by a back-pressure regulator (model: 880-81, JASCO, Co., Tokyo). Then the temperature was kept at 40 °C for 2 h and risen to 60 °C for the thermal radical polymerization. At the certain reaction time, the solvent was evacuated from the vessel through back-pressure regulator carefully and slowly under cooling at 0 °C. A white powdery polymer was obtained. In the case of emulsion polymerization, the resulting polymer was washed with Milli-Q water and dried mildly.

Scanning Electron Microscopy (SEM). The morphology of PTFE, such as the size, shape, and uniformity, was observed by scanning electron microscopy (SEM, model: Superscan LaB6-DP, Shimadzu, Co., Kyoto). PTFE powders were immobilized on the electroconductive adhesive film, and then samples were coated with Pt/Pd by ion sputtering.

Differential Scanning Calorimetry (DSC). Differential scanning calorimetry (model: Pyris-1 DSC, Perkin-Elmer, Co., Tokyo) was employed to obtain the number-average molecular weight (M_n) of PTFE. Samples of 10 mg were heated by the scanning rate of 10 °C min^{-1}. It is difficult to measure molecular weights of PTFE from the conventional methods as well as the melting transition method using viscosity changes due to the high viscosity of PTFE ($>10^{11}$ P at 380 °C). Therefore, M_n was determined by substituting measured enthalpy of crystallization (ΔH_c: cal g^{-1}) for an empirical equation (1) according to the previously reported method by Suwa et al.[13]

$$M_n = 2.1 \times 10^{10} \Delta H_c^{-5.16} \tag{1}$$

Results and Discussion

Homogeneous Polymerization of TFE in $scCHF_3$. Figure 1 shows typical time courses of the precipitation polymerization of TFE (1.0 g) initiated with PFBPO (1.0 mg) in homogeneous $scCHF_3$ (10 g, ca. 10 mL) at 14 MPa and 60 °C. PTFE was formed in ca. 80% yield after 4 h, although the induction period of 2 h existed due to a time lag of rising temperature from $scCHF_3$ filling at 40 °C to the polymerization temperature at 60 °C. The number-average molecular weight (M_n) was 7 × 10^4, independent of the reaction time. This is due to the precipitation polymerization of TFE. M_n was relatively low compared to the conventional dispersion polymerization of TFE in water with stabilizers ($M_n > 10^6$). Figure 2a shows a SEM image of PTFE prepared by the homogeneous polymerization in $scCHF_3$ at 14 MPa and 60 °C. The twined fibrous shapes of ca. 100 nm in width and 10 μm in length were dispersed. In the polymerization in organic solvents or the dispersion polymerization without detergents or stabilizers, clumpy and nondescript shapes of PTFE have been observed for their precipitated particles. Fiber shapes were only observed in the restricted condition such as in the presence of surfactants in the concentration over their cmcs[14] and the mechanical pulling of PTFE pieces.[15] Uniformly fibrous shapes with porous cavity

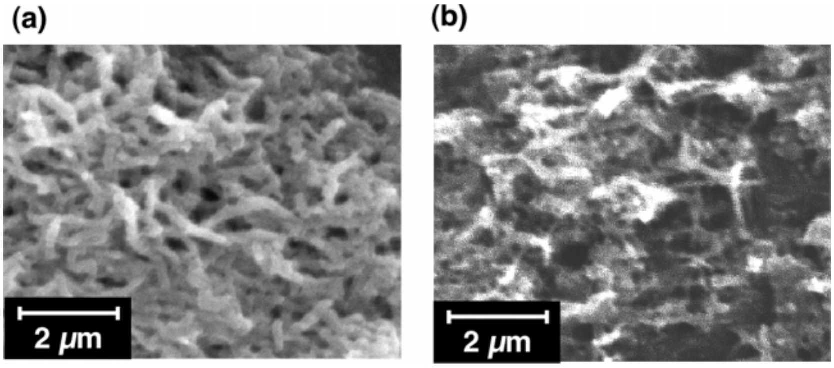

Figure 2. Scanning electron micrographs (SEM) of PTFE prepared in the homogeneous polymerization initiated with PFBPO in $scCHF_3$ at (a) 14 MPa and 60 °C and at (b) 5 MPa and 60 °C. [TFE] = 1.0 g in 10 g of $scCHF_3$ (10 wt %), [PFBPO]/[TFE] = 1/1000.

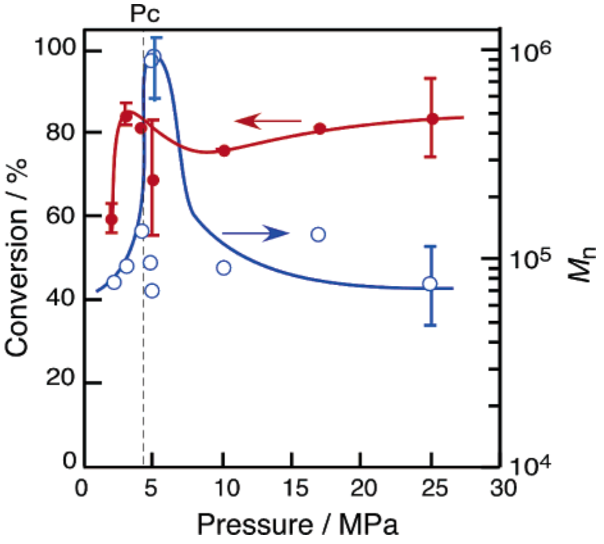

Figure 3. Effect of pressures on conversions and number-average molecular weight (M_n) in the homogeneous polymerization of TFE initiated with PFBPO in $scCHF_3$ at 60 °C. [TFE] = 1.0 g in 10 g of $scCHF_3$ (10 wt %), [PFBPO]/[TFE] = 1/1000, reaction time 12 h. P_c indicates the critical pressure at 60 °C.

of PTFE were caused by the high diffusion of $scCHF_3$, which affected to the precipitation of PTFE during polymerization.

Effect of Pressure on Homogeneous Polymerization in $scCHF_3$. One of features of supercritical fluids as a reaction medium is that their physicochemical properties such as the density and the dielectric constant (ϵ) can be manipulated by continuous changes of temperatures and/or pressures of the supercritical state.[10,16−20] Figure 3 shows the effect of pressure on the conversion and the number-average molecular weight (M_n) of PTFE in the homogeneous polymerization in $scCHF_3$. Conversions and M_n were low below the critical pressure (P_c = 4.8 MPa), where the medium exists as gaseous CHF_3. The observation through the sapphire glass window shows that TFE and gaseous CHF_3 were immiscible and separated from each other in the vessel. Molecular weight was drastically increased above 4.8 MPa and then decreased drastically above 10 MPa, where the both reactants are homogeneously solubilized in CHF_3. On the other hand, conversions were constant to be 80% in the range of 4.8−25 MPa, except at 5 MPa. This sudden increase of the reactivity near P_c has been also observed in the enzyme reaction and host−guest interactions in supercritical fluids.[3−6]

Below P_c = 4.8 MPa, the reactants were not solved in gaseous CHF_3; that is, bulk polymerization would proceed. As the reactants were moderately solved in supercritical CHF_3 over P_c, polymerizations effectively proceeded and M_n was improved. When the pressure was further raised, the density in the system increased and the degree of solvation grew and M_n decreased. The pressure in the system, which gave PTFE of the highest molecular weight, was around the gas supercritical state critical point. In this point, the fluid structure was considered to consist of density inhomogeneity.[21] The structure of the supercritical fluid has been involved in the efficiencies of chemical reactions.

Figure 2b shows the SEM of PTFE formed at 5 MPa near P_c. The each shape of PTFE was similar to that formed at 14 MPa, but their density was low in comparison with that formed at 14 MPa. This result would be related to the solvation with the substrate during the polymerization.

Heterogeneous Polymerization of TFE in Water/$scCHF_3$ Emulsion. Figure 4A indicates the density change of CHF_3

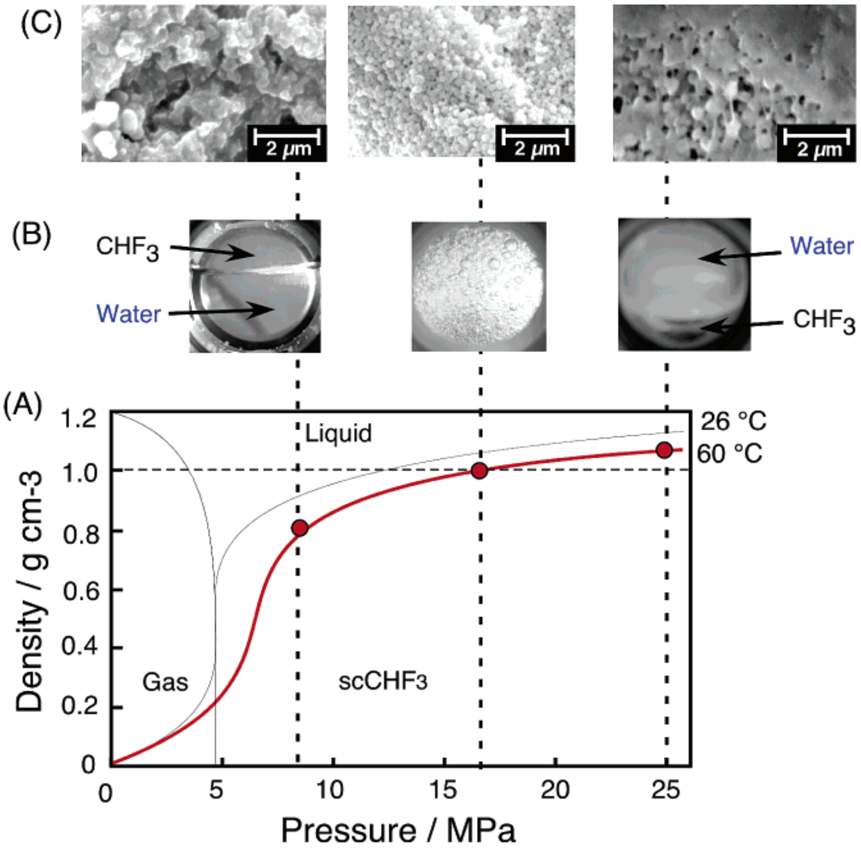

Figure 4. (A) A density and pressure curve of CHF_3 at 60 °C, (B) photos of reaction media (CHF_3: 5.0 g; water: 3.0 g) through the sapphire glass window, and (C) SEM images of the produced PTFE in the heterogeneous polymerization of TFE (0.5 g, 10 wt % of TFE) initiated with APS (1/100 of TFE) in CHF_3 (5.0 g) and water (3.0 g) at 60 °C.

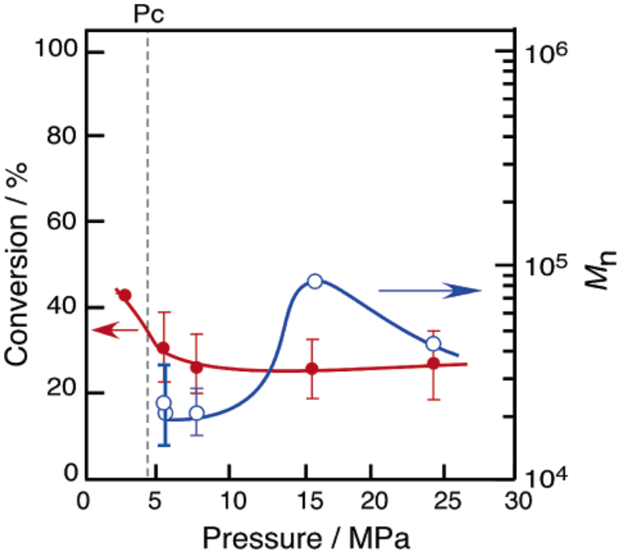

Figure 5. Effect of pressures on conversions and number-average molecular weight of heterogeneous polymerization of TFE initiated with APS in $scCHF_3$ (5.0 g) and water (3.0 g) at 17 MPa and 60 °C. [TFE] = 0.5 g, 10 wt % of TFE, [APS]/[TFE] = 1/100, reaction time 12 h.

depending on pressure, and Figure 4B shows photos of emulsions containing of CHF_3 (5.0 g) and water (3.0 g) observed through the sapphire glass window of the reaction vessel. At each pressure, TFE monomers and APS initiators were solved in $scCHF_3$ and water, respectively. The density of $scCHF_3$ was drastically changed to 0.2−1.2 in the range of 5−25 MPa at 60 °C.[21] Both $scCHF_3$ and water phases were observed to form emulsion with stirring under pressures of 8, 17, and 25 MPa. When the stirring was stopped, they were phase separated to form the CHF_3 layer above and the water layer below at 8 MPa, and the water layer above and the CHF_3 layer below at 25 MPa. This is probably due to the density of CHF_3 (0.8 at 8 MPa and 1.05 at 25 MPa; see Figure 4A). On the contrary, at 17 MPa, where the density of CHF_3 is close to 1.0 (Figure 4A), the emulsion was stable at least for 24 h even when the stirring was stopped, although the stilliform was observed on the hydrophilic window surface (middle of Figure 4B). About the stability or turbidity of the emulsion, however, we should study more by using the light scattering method.

At 17 MPa, CHF_3 forms a stable emulsion with water (middle of Figure 4B) and PTFE was obtained homogeneous particles in a submicron size (ca. 200 nm) (middle of Figure 4C). On the other hand, at 8 MPa, the CHF_3 phase was separated above the water phase. PTFE polymerized at 8 MPa showed colloidal form in the aqueous phase, and they were the similar size particles with cavity, due to specific solvation to reactants at near the critical point. At 25 MPa, the CHF_3 phase was separated below the water phase. The resulting polymer was taken as a granulated powder in macroscopic, but a nondescript morphology was observed for these precipitated conglomerations.

Figure 5 shows the effect of pressure on the conversion and M_n of PTFE. The conversion of the emulsion polymerization was low independent of pressures, compared with those of homogeneous polymerization shown in Figure 3. The M_n of PTFE increased near 17 MPa compared with 8 or 25 MPa, as expected. This is due to the stable emulsion formation and the uniform particle formation of PTFE at 17 MPa.

Effect of Water Content on Emulsion Polymerization. Figure 6 shows effects of the water content on the emulsion polymerization at 17 MPa and 60 °C. At the low water content (10 wt %), the polymerization did not successfully proceeded. It was consequent that the initiation of APS in the aqueous phase did not act effectively due to the less efficient interfacial area between the water and the CHF_3 phases. Increasing the water content, the conversion gradually improved up to the water content of 70% v/v. In the range of 60−70 wt % of the water content, PTFE was obtained as powders, and each powder consists of homogeneous particles in submicron size (ca. 200 nm), as shown in the middle of Figure 4C. At 80 wt % of the water content, PTFE was obtained as a nondescript morphology, that is, conglomerations. This is due to the unstable emulsion formation in this condition. Thus, the heterogeneous emulsion polymerization of TFE was succeeded at the narrow condition of the water content of 60 wt % at 17 MPa, where the emulsion was stable.

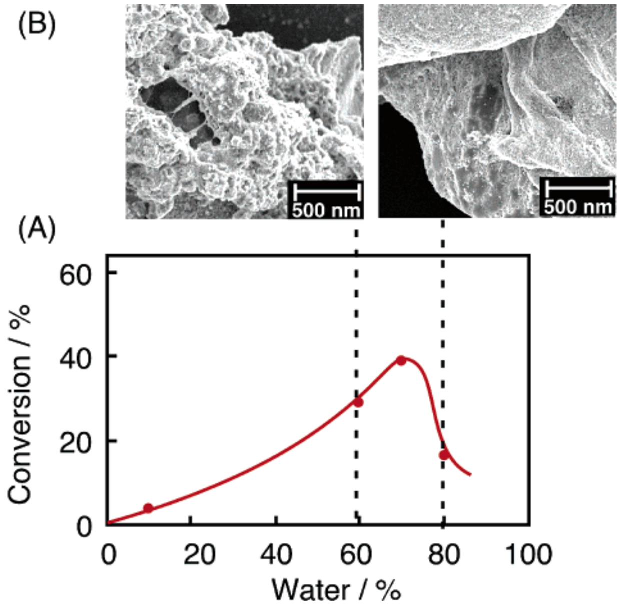

Figure 6. (A) Effect of the water content on conversions and morphologies of PTFE in the emulsion polymerization of TFE initiated with APS in $scCHF_3$ and water (total volume is 10 mL) at 17 MPa and 60 °C. (B) SEM images of PTFE at the 60 and 80 wt % water content. [TFE] = 0.5 g, 10 wt % of TFE, [APS]/[TFE] = 1/100, reaction time 12 h.

Conclusion

Polymerizations of TFE were performed in $scCHF_3$ both homogeneous and heterogeneous emulsion systems. The homogeneous polymerization gave the uniformly twined fibrous PTFE (ca. 100 nm in width and 10 mm in length) in high yields. The number-average molecular weight and the conversion of PTFE can be controlled by pressure and temperature from $M_n = 10^4$ to 10^6 and 60−80%, respectively. The emulsion polymerization gave the spherical particles (ca. 200 nm diameter) of PTFE, only when the emulsion was stably formed. Although the conversion was relatively low (20−40%), the particles were purely made of PTFE, not including any additives such as detergents. We believe that supercritical CHF_3 would become a new medium for the polymerization of TFE in the mild conditions.

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