Emulsion Polymerization of Tetrafluoroethylene: Effects of Reaction Conditions on the Polymerization Rate and Polymer Molecular Weight

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ABSTRACT: The emulsion polymerization of tetrafluoroethylene (TFE) was carried out in a semibatch reactor using a chemical initiator (ammonium persulfate) and a fluorinated surfactant (FC-143). The effects of the reaction condition were investigated though the polymerization rate, molecular weight of polytetrafluoroethylene (PTFE), and stability of the dispersion. The emulsion polymerization of TFE was different from conventional emulsion polymerization. The polymerization rate was suppressed when the polymer particles were significantly coagulated. The polymerization rate increased with operating temperature, surfactant concentration, and agitation speed, due to the enhanced stability of the polymer particles. However, once the parameter value was reached, the rate decreased due to the coagulation of the particles. Stable PTFE dispersion particles were obtained when the surfactant concentration was in the range between 3.48×10^{-3} and 32.48×10^{-3} mol/liter, which is below critical micelle concentration (CMC). The molecular weight of the PTFE obtained was a function of the surfactant and initiator concentrations, and the polymerization temperature. The molecular weight increased as each parameter decreased. This is against the phenomena observed in a conventional emulsion polymerization. A stable PTFE dispersion polymer having a high molecular weight was obtained by optimizing the reaction conditions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 777-793, 1999

Key words: tetrafluoroethylene; emulsion polymerization; polymerization rate; molecular weight; stability of polymer dispersion

INTRODUCTION

Polytetrafluoroethylene (PTFE) has many applications due to innate properties such as heat and cold resistance; chemical, flame, and weather resistance; electrical properties; nontackiness; soil-proofing ability, etc. $^{\rm 1-3}$

The polymerization of tetrafluoroethylene (TFE) in an aqueous medium can be carried out by two distinctly different procedures^{4,5}: suspension polymerization and emulsion polymerization. In suspension polymerization, little or no dispersing agent is employed with vigorous agitation to produce precipitated resin, commonly referred to as "granular" resin. In the emulsion

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polymerization, however, sufficient dispersing agent is employed with mild agitation, which produces small colloidal particles dispersed in the aqueous reaction medium.

There are many patented processes for TFE polymer production using bulk, solution, and emulsion polymerization techniques; however, there is little information on the kinetics of the process in the literature.

Highly fluorinated and perfluorinated dispersing agents have been used to give a stable aqueous dispersion of small polymer particles, as well as to permit a high rate of polymerization, and to decrease the contamination of the polymer product with hydrocarbon-based residues.⁶ The rate of polymerization and the shape of the polymer particles are a strongly related to the concentration of surfactant.^{7,8}

Control of coagulant formation is of importance in the emulsion polymerization process. Coagulation can be formed due to a lack of surfactant, the wrong type of surfactant, too much shear, or poor temperature control.⁹ A stabilizer (anticoagulant) can be added to prevent coagulation during the TFE polymerization.¹

The solubility of a monomer in water is dependent on the type of monomer,¹⁰ and has a significant effect on both the principal reaction loci and mechanism of particle formation.¹¹ The Smith-Ewart theory¹² of particle formation and reaction in polymer particles seems to estimated for sparingly water-soluble monomers such as styrene (0.0271%, 25°C). The homogeneous nucleation theory¹³ is the prevailing theory for highly watersoluble monomers, such as methyl methacrylate and vinyl acetate (2.4%, 20°C).¹⁴ However, TFE emulsion polymerization in connection with monomer–water solubility has not been thoroughly investigated.

PTFE is insoluble in any solvent, so that ordinary methods using solvents cannot be applied to determine the molecular weight of PTFE. Instead, it is customary to estimate the molecular weight of PTFE by measuring the specific gravity^{15,16} and the heat of crystallization.^{16,17} The effects on molecular weight of the PTFE prepared by emulsion polymerization of TFE by radiation in connection with various polymerization conditions was investigated by Suwa et al.^{18,19} However, no data for the molecular weight of the PTFE prepared by chemical initiators are available.

In this study, the emulsion polymerization of TFE was investigated using a chemical initiator

(ammonium persulfate, APS) and a fluorinated surfactant (FC-143) in a semibatch reactor with a continuous flow of TFE. The kinetic behavior of the polymerization was also examined at various process conditions. The effects of impeller type and agitation speed, concentration of chemical initiator and surfactant, reaction pressure and temperature, and the type and concentration of paraffin wax were investigated on the polymerization rate, PTFE molecular weight, and stability of the dispersion.

EXPERIMENTAL

Chemicals

The TFE monomer was supplied by 3F (China). Before using the TFE, impurities such as inhibitor *d*-limonene, octafluorocyclobutane (RC-318), difluoromethane (R-32), etc.) were removed by passing the TFE monomer through silica gel and a granular-activated carbon bed subsequently at -25° C. The purity of the TFE treated was about 99.9995%.

Water (about 18.2 M Ω), purified by Millipore Milli-Q, was used as the polymerization medium for the PTFE dispersion. *n*-Hexadecane, purchased from Aldrich, and paraffin waxes (p-wax) purchased from Wako were used as stabilizers without further purification, and their specifications are described in Table II. The initiator ammonium persulfate purchased from Sigma was purified up to 99.5% by recrystallizing. Ammonium perfluorooctanoate (Fluorad[®] Fluorochemical surfactant FC-143) from 3M was used as a surfactant without any purification. The pH value of the aqueous solution was about 5.

Apparatus and Polymerization Method

Figure 1 is a diagram of the experimental apparatus used in the emulsion polymerization. The apparatus consists of a TFE purification system and a reactor (model Buchiglauster, Swiss). The reactor is a cylindrical jacketed glass vessel with a dish-like bottom equipped with an anchor-type impeller, and an injection/sampling port that allows for the injection of initiator/water and sampling during polymerization.

The impeller was selected by a preliminary experiment in which various types of impellers were tested to determine their reaction performance. The anchor-type impeller produces a

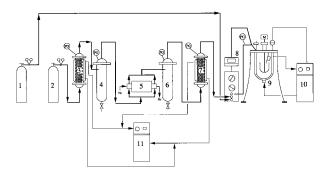


Figure 1 Schematic diagram of the experimental apparatus. 1. High purity nitrogen cylinder; 2. TFE cylinder; 3. Silica gel column; 4, 6 Buffer tank; 5. Gas booster; 7. Activated carbon column; 8. Pressure flow controller; 9. Glass reactor (1 liter); 10, 11 Thermostatic bath and circulator. PG: pressure gauge.

strong vortex around the driving shaft during agitation. A baffle was placed in the reactor to produce turbulence by breaking the flow stream induced by the impeller. A detail of the reactor is described in Figure 2.

The introduction rate of TFE into reactor during polymerization is controlled by a Buchi pressflow gas controller (model bpc 6010), which is capable of controlling flow with an accuracy of ± 0.001 liter. After charging the surfactant, stabilizer, and water, the reactor was degassed with slow stirring. The reactor was then evacuated for about 10 min and flushed out five times with nitrogen at 10 bar and three times with TFE at 3 bar. After the inhibitor contained in the TFE was removed by passing through a silicagel column at -25°C, the TFE was compressed to about 10 bar by a gas booster. Subsequently, the TFE was purified by activated carbon at -25°C and then put into the reactor.

After the stirring speed and temperature of the reaction reached the desired values, the pressure inside the reactor was turned to the desired reaction pressure. A desired amount of the initiator dissolved in water was injected into the reactor. The TFE supply line was opened, allowing the TFE to flow into the reactor, while the consumed amount (uptake, liter) of TFE and reaction time at constant pressure were recorded and controlled by the Buchi press-flow gas controller until about 26% of PTFE yield was attained (Table IV). The reaction temperature was controlled with an accuracy of $\pm 0.1^{\circ}$ C by circulating heating media (silicone oil) from a thermostatic bath and circulator (model Hakker 320).

After polymerization, a part of the resulting PTFE dispersion was coagulated forcibly by vigorous agitation, washed, and dried to analyze the molecular weight and polymer yield. The polymer yield is defined as follows:

polymer yield (wt %) = polymer/(polymer

+ water + surfactant) \times 100 (1)

But when the coagulation formed, the quantitative amounts of coagulant are difficult to measure due to the attachment of the impeller and the baffle with the reaction ingredient. The polymer yield in these cases is not included the weight of a coagulant polymer.

The polymerization conditions used in this study are given in Table I.

Molecular Weight of PTFE

Standard Specific Gravity (SSG)

SSG is defined as the weight ratio of a PTFE sample prepared by a standard procedure to wa-

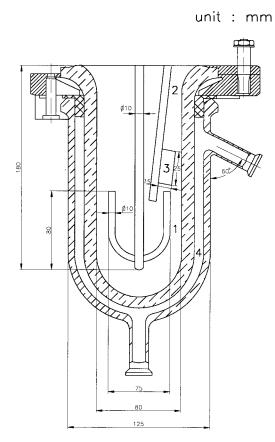


Figure 2 Details of a reaction vessel. 1. Anchor-type agitator; 2. Thermocouple; 3. Baffle plate; 4. Jacketed vessel.

Condition and Variable	Standard Recipe				
Pure water	500 mL				
Surfactant: FC-143	$3.48 imes 10^{-3}$ mol/liter (0.75 g)				
Initiator: APS	2.19×10^{-4} mol/liter (0.05 g)				
paraffin wax: p- wax(1)	40 g/liter (20 g)				
Agitation type and speed	Anchor, 500 rpm				
Reaction pressure	4 bar				
Reaction temperature	75°C				

Table I	Standard Recipe for the Emulsion
Polymer	ization of Tetrafluoroethylene

ter having the same volume as the PTFE sample at 23°C.¹⁶ The PTFE sample of 12 g, was molded up to 352 bar, and then prepared by calcination at 290°C. In general, SSG is used as an indirect measure of the average molecular weight (M_n) of unmodified PTFE polymer. The M_n of PTFE polymerized at different conditions was determined from the following relationship with SSG:

$$\log_{10} M_n = 31.83 - 11.58 \times \text{SSG}$$
(2)

DSC Measurement

DSC (differential scanning calorimeter) measurements were carried out using a 2910 DSC (TA Instruments). The operating temperature ranged from 200 to 370°C. The heating and cooling rates were $\pm 10^{\circ}$ C/min. The endothermic curve of melting and the exothermic curve of crystallization were obtained from the heating and cooling steps, respectively.

Figure 3 presents typical DSC thermograms for melting and crystallization. The heat of crystallization (ΔH_c) was calculated from an area surrounded by the curve in the endothermic curve.

From ΔH_c data, the M_n was determined by the following equation.^{18,19}

$$M_n = 2.1 \times 10^{10} \Delta H_c^{-5.16} \tag{3}$$

The molecular weights of PTFE determined by both of the methods are listed in Table IV.

CMC of FC-143 Surfactant

In the literature, $^{21-23}$ the CMC of the FC-143 surfactant (or $C_7F_{15}COONH_4$) is reported to be in

the range from 0.5 to 1.422%, depending on the experimental techniques and temperature. The Wilhelmy plate method was employed for the determination of the CMC of the FC-143 surfactant. In this method, the surface tension of the surfactant-aqueous solution determined was plotted against the surfactant concentration, as shown in Figure 4. The CMC, which is taken as the point of discontinuity of the lines, was determined to be 1.342%. The tensiometer used was the SIGMA 70 (KSV Instruments Ltd., Finland).

Solubility of TFE in Water

The only solubility data of TFE in water available are for 1 bar and 30° C.²⁴ The pressure-drop method^{25,26} was used to estimate the solubility of TFE in water as a function of pressure and temperature. The solubility measurements were made at pressures up to 9 bar and over a temperature range of 20 to 80°C. The polymerization reactor of TFE was utilized for determining the solubility. The closed vessel was charged with 0.7 liter of pure water.

S, the solubility of TFE gas dissolved in water, was calculated from the pressure changes by the following equation.

$$S = (n_o - n_g)/V_l = \{(P_o - P_s)/RT\} \times (V_g/V_l) \quad (4)$$

where S is the solubility of dissolved gas in the liquid (mol/liter); P_o , P_s are the initial and the saturation pressure (bar); T is the temperature (K); V_l , V_g is the volume of the liquid and gas phase in the cell (liter); n_o is the initial mol (the total number of mol) of the gas in the cell (mol); and n_g is the number of mol of gas in the vapor phase at saturation (mol).

Determination of Polymerization Rate and Molecular Weight

Polymerization Rate

The polymerization rate is expressed by the TFE uptake amount (mol) per unit reaction time

Table II	Types of	Stabilizers	Used
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Types of Stabilizer	Melting Point (°C)	Manufacturing Company		
p-wax(1)	44–46°C	Wako (Japan)		
p-wax(2)	$56-58^{\circ}C$	Wako (Japan)		
p-wax(3)	$64-66^{\circ}C$	Wako (Japan)		
<i>n</i> -hexadecane	18°C	Aldrich (USA)		

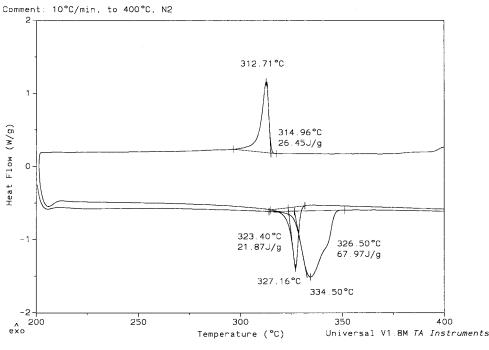


Figure 3 Typical DSC thermograms of PTFE for melting and crystallization.

(hour) in the aqueous phase. As the patterns of the polymerization curve appear different according to reaction conditions, R_p must be determined in different ways. First, when the polymerization rate increases sharply with reaction time and levels off at any time at an agitation speed less than 750 rpm as shown in Figure 7(b), R_p (mol/liter \cdot h) is regarded as the polymerization rate remaining constant with the reaction time, t_p (minute) is the time as soon as R_p is constant. Second, when the polymerization rate decreases rapidly after reaching its maximum, as shown at 750 rpm of Figure 7(b) and at high surfactant concentration of Figures 9 and 10, R_p and t_p are regarded as the polymerization rate and the time attained at the maximum value, respectively. Finally, when the polymerization rate increases steadily with the reaction time in any range of the surfactant concentration as shown in Figures 9 and 10, R_p and t_p are the polymerization rate and the time when coagulation starts, respectively.

Molecular Weight

The molecular weights of PTFE obtained are summarized in Table IV. Here, the M_n of columns 10 and 12 were calculated by eq. (2) using SSG, and eq. (3) using ΔH_c , respectively. Generally, SSG has been used to estimate the molecular weight of PTFE. The second row (ep-272 to ep261) in Table IV shows a low concentration of the initiator and surfactant, and the M_n values from the SSG data are reasonable. But, when the concentration of initiator and surfactant are extremely high (third row, ep-289 to ep-290), the determination of the corrected SSG value was almost impossible because cracks formed on the particle surface during calcination at a high tem-

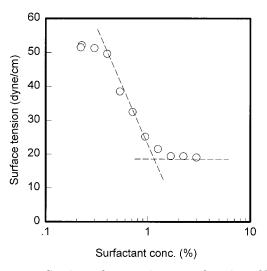


Figure 4 Static surface tensions as a function of FC-143 concentration (the values were obtained by the Wilhelmy plate method at 23°C. The CMC estimated was 1.342%).

Experiment No.	Impeller Types	Comments		
ep-101	Pitched-blade impeller, 1ea Four blade	Center of reaction vessel		
ep-102	Pitched-blade impeller, 45° angles, 1ea (upper) Flat-blade impeller, 1ea (bottom)	Distance of 4 and 9 cm from the bottom		
ep-103	Anchor impeller, 1ea Without baffle	See Figure 2		
ep-104	Anchor impeller, 1ea With baffle	See Figure 2		

Table III Impeller Features

Other reaction conditions are given in Table I.

perature in the preparation of the PTFE sample. ΔH_c levels off after a rapid increase with reaction time, the same as SSG (second row), and presented a simple and reliable method with a range of error of ± 0.3 cal/g throughout the experiment. However, the M_n from ΔH_c has a higher value than those from SSG (second row), implying some errors factor in the application of eq. (3). This equation was correlated from data by radiation polymerization of TFE, and is dissimilar to our experimental conditions, so it is not adequate to estimate the M_n value with our results. The new correlated equation from our results will be described in detail in subsequent articles.

We investigated the effects on the molecular weights in connection with polymerization conditions using ΔH_c as an indirect expression of M_n . Effects of reaction conditions on ΔH_c were investigated as the heat of crystallization at same reaction time with R_n .

RESULTS AND DISCUSSION

Influences of the Reaction Conditions on Polymerization Rate

Effects of Impeller Types

Table III summarizes the impeller features used for four runs of experiments. There are two classes of impellers considered in this work, namely, radial-flow (flat-blade turbine) and axialflow impellers (pitched-blade turbine or anchor impeller).

The tendency of R_p is found to be in the order: ep-101 (turbine impeller, 1ea) < ep-102 (turbine impeller, 2ea) \ll ep-103 (anchor impeller only) < ep-104 (anchor impeller including baffle) at standard conditions, as shown in Table I. R_p is in the range between 0.025 mol/liter \cdot h at ep-101 and 1.55 mol/liter \cdot h at ep-104. These results support that an anchor impeller produces a strong vortex around the driving shaft, rather than the turbine impeller at the same agitation speed, which increases the interfacial areas for reaction. Therefore, an increase in the interfacial area gives an increase in the polymerization rate. It was also found that coagulation could be prevented by using the anchor impeller, as shown in Figure 5.

Here, in subsequent tests, the anchor impeller with a baffle (see Fig. 2) was used.

Effects of Agitation Speed

Figure 6 shows the solubility of TFE in water at temperatures ranging from 10 to 80°C, and gas pressures up to 10 bar. As shown in Figure 6, the solubility of TFE in water increases linearly with increasing pressure, and decreases linearly with increasing temperature. The previous published data (0.01 kg of TFE/100 kg of water at 1 bar and $30^{\circ}C^{24}$) coincide with the data obtained by our experiment.

Figure 7(a) and 7(b) shows TFE uptake and the polymerization rate, respectively, against the reaction time at various agitation speeds. In Figure 7(a), no induction reaction is observed in the polymerization of TFE because nucleation or particle generation is completed in a few minutes due to the hydrophobic property observed in our previous article.²⁷ The TFE uptake (mol) increases linearly with reaction times when the agitation speed is less than 750 rpm. In Figure 7(b), the polymerization rate increases sharply with the agitation speed, but when the speed is greater than 500 rpm, the opposite trend prevails. The higher speed agitation seems to bring the stron-

	Reaction Conditions						Results				
Run No.	Reaction Time (min.)	PTFE Yield ^a (wt %)	Reaction Temp. (°C)	Reaction Pressure (bar)	Agitation Speed (rpm)	$\begin{array}{c} \text{Initiator} \\ \text{(mol/liter)} \\ \times 10^4 \end{array}$	$\begin{array}{c} \text{Surfactant} \\ \text{(mol/liter)} \\ \times 10^3 \end{array}$	ΔH_c (cal/g)	$M_n imes 10^{-4 ext{ b}}$	Standard Specific Gravity	${M_n} imes 10^{-6}$ c
ep-272	34	8.1	75	4	500	4.38	3.48	12.66	4.3	2.2493	1.8
ep-258	53	10.0	75	4	500	4.38	3.48	11.00	8.9	2.2357	3.09
ep-219	70	13.6	75	4	500	4.38	3.48	10.17	13.3	2.2096	8.7
ep-259	101	18.8	75	4	500	4.38	3.48	10.14	13.5	2.2097	7.84
ep-260	132	23.0	75	4	500	4.38	3.48	10.09	13.9	2.2085	9.11
ep-261	162	26.4	75	4	500	4.38	3.48	10.15	13.4	2.2158	6.8
ep-289	76	22.2	75	4	500	39.43	3.48	11.36	7.5	2.1602	62.16
ep-253	53	22.2	75	4	500	4.38	32.48	11.16	8.2	2.2090	8.73
ep-240	82	22.2	75	4	500	4.38	13.92	11.64	6.6	2.1857	22.5
ep-274	96	22.2	75	4	350	4.38	32.48	12.55	4.5	2.1663	48.7
ep-290	84	22.2	75	4	350	4.38	60.32	12.43	4.7	2.0630	2968.64
ep-296	67	22.2	65	8	500	0.88	3.48	6.30	157.6	2.1871	21.28
ep-281	174	22.2	75	4	500	0.53	3.48	7.86	50.3	2.2000	12.78
CD-1								7.27	75.3	2.1926	17.14
M-12								3.85	2,000	2.1466	106.84

Table IV Typical Experimental Results for M_n Measurement by Heat of Crystallization and Standard Specific Gravity at Various Reaction Conditions

^a PTFE yield (wt %) = polymer/(polymer + water + surfactant) \times 100.

^b Determination from ΔH_c .²²

^c Determination from standard specific gravity (SSG).¹⁸

CD-1; Commercial PTFE of ICI Fluoropolymers (UK) by emulsion polymerization of TFE.

M-12; Commercial PTFE of Daikin Ind. (Japan) by suspension polymerization of TFE.

ger shearing force, which breaks the PTFE dispersion, forming the coagulated polymer (Fig. 5). The coagulation retards the polymerization rate

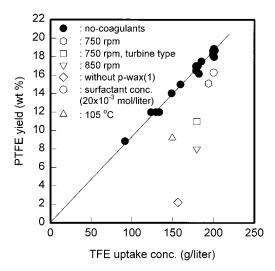


Figure 5 Relationship between PTFE yield and TFE uptake at various reaction conditions that are associated to the particle coagulation: closed symbols indicate stable PTFE dispersions and open symbols, less stable PTFE dispersions that coagulate in a few hours after polymerization. Other reaction conditions are given in Table I.

by decreasing the total surface area of the particles when the surface reaction controls the reaction.²⁷ It was observed in this study that the crystallinity of as-polymerized PTFE in this polymerization is as high as 90%; the polymer particles were rigid, so the monomer hardly diffused to the inside of the particles. These facts support the

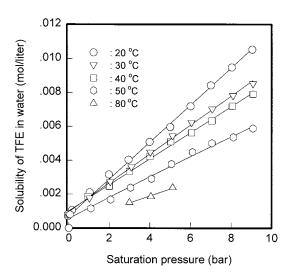


Figure 6 TFE solubility in water as a function of pressure at various temperatures.

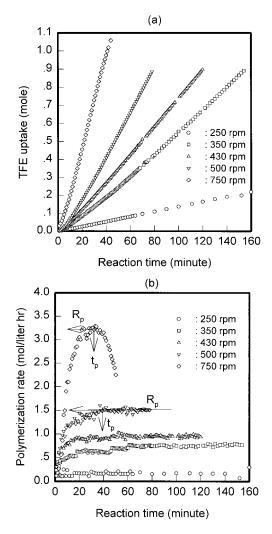


Figure 7 Variation of (a) TFE uptake and (b) polymerization rate according to reaction time at various agitation speeds. Other reaction conditions are given in Table I.

hypothesis that polymerization after particle generation proceeds dominantly on the surface of the particle.

Figure 8 shows the effects of agitation speed on R_p and t_p . As agitation speed increases, R_p increases and t_p decreases, linearly. These results support the fact that the diffusion or dissolution of the TFE into the aqueous phase is the rate-determining process under the entire agitation range.

Generally, the polymerization in gas-liquidsolid phases occurs by contact of colloid particles with the gas dissolved in the aqueous phase. However, the polymerization of TFE in an emulsion can be considered as a direct contact reaction between the dispersed phase of bubbles of TFE in the aqueous phase and the colloid phase, because the TFE solubility in the aqueous phase is much lower than other monomers. The reaction in the emulsion can propagate faster than that in the aqueous media, in which the TFE gas must diffuse to react.

The reactor configuration-like type of impeller and baffle and agitation speed are very important variables in the polymerization by the contact of TFE gas and the polymer colloid, and hence, in the stability of the PTFE dispersion.

Effects of Surfactant Concentrations

Figure 9 presents the relationship between the polymerization rate and the reaction time at various surfactant concentrations ranging from 0 to 60.32×10^{-3} mol/liter. As the surfactant concentration increases, the polymerization rate increases. The curves of the polymerization rate are classified into four types by the amount of surfactant added.

The first type, at above CMC, has the change of polymerization rate divided into three stages. In the first stage, the polymerization rate decreases sharply with reaction time. This stage lasted for 10 min at a surfactant concentration of 46.40 $\times 10^{-3}$ mol/liter, and for 15 min at 60.32 $\times 10^{-3}$ mol/liter corresponding in the PTFE dispersion concentration of 2.0%. In the second stage, the polymerization rate increases sharply with the reaction time. In the third stage, the polymerization rate decreases steeply with the reaction time and the coagulation of particles occurred.²⁷ The

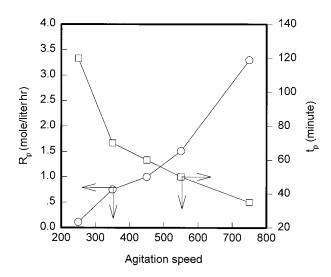


Figure 8 Effects of agitation speeds on R_p and t_p . Other reaction conditions are given in Table I.

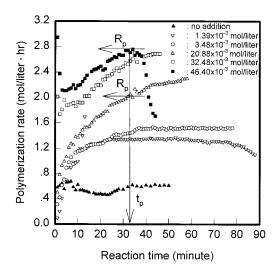


Figure 9 Polymerization rate vs. reaction time at various surfactant concentrations. Other reaction conditions are given in Table I.

coagulation can be accelerated when the surfactant concentration is too high, due to the steric effect.²⁸ This results from the increase in viscosity of the bulk phase and the structural effect of the surfactant on the particle surface.

In the second type, in the range from 3.48×10^{-3} to 32.48×10^{-3} mol/liter, the polymerization rate increases continuously over the entire reaction time. It is related to the phenomenon that causes the number of particles to increase steadily during polymerization;²⁷ the particle size decreases by the increase of the surfactant concentration, which leads to an increase in the rate of supply of the monomer and initiating radicals from the aqueous phase to the particles.

The third type occurs when the polymerization rate increases in the initial stage and remains almost constant; this was found with the surfactant concentration of 3.48×10^{-3} mol/liter. It is similar to a conventional emulsion polymerization.

The last type is when the polymerization rate decreases after reaching the maximum rate, which was found to be below 1.39×10^{-3} mol/liter. The decrease in polymerization rate in the later stage is caused by a coagulation of the particles due to the inadequate surface potential by the lack of surfactant.

To discuss the relationship between polymerization and agitation speed, experiments were carried out at another agitation speed (350 rpm), as shown in Figure 10. From a comparison of Figures 9 and 10, it is expected that polymerization rates depend on the surfactant rather than agitation speed. The coagulation that occurs in low-PTFE dispersion, irrespective of the agitation speed, is characteristic of emulsion polymerization of TFE when the surfactant concentration is above CMC (Fig. 5). Furthermore, the morphology of the polymers formed is remarkably affected by the surfactant concentration.²⁷ The results suggest that the mechanism of the emulsion polymerization with TFE differs from the typical rules of emulsion polymerization.

Figure 11 shows the effects of surfactant concentration on R_p with agitation speeds of 350 and 500 rpm. The relationships are divided into two parts on the border of the CMC. R_p increases with increasing surfactant concentration (about 39.44 imes 10⁻³ mol/liter), while the surfactant concentration approaches CMC, regardless of agitation speed. R_p is proportional to the 0.12 power of the surfactant concentration at 500 rpm, and to the 0.18 power of the surfactant concentration at 350 rpm. Generally, the low exponent found for the surfactant concentration is common in the case of water-soluble monomers such as vinyl acetate.¹⁴ Our experiments appeared have similar results. regardless of the fact that TFE has a very low solubility in water. It suggests that the polymerization occurs principally by a direct gas-solid reaction between TFE gas and colloid particles in the aqueous phase, indifferent to the presence of surfactant micelles.

To summarize, when the surfactant concentration in the range of 1.39×10^{-3} to 32.48×10^{-3}

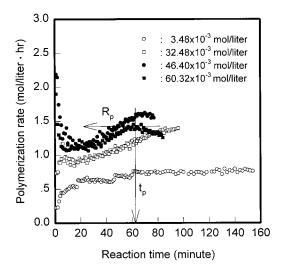


Figure 10 Polymerization rate vs. reaction time at various surfactant concentrations when the agitation speed is fixed at 350 rpm. Other reaction conditions are given in Table I, except agitation speed.

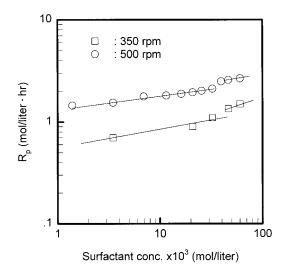


Figure 11 Effects of surfactant concentrations on R_p at 350 and 500 rpm. Other reaction conditions are given in Table I.

mol/liter, PTFE dispersion particles of 80 to 220 nm were obtained as described previously.²⁷

Effects of Initiator Concentrations

Figure 12 shows the polymerization rate as a function of reaction time at various initiator concentrations, ranging from 0.53×10^{-4} to 39.43 $\times 10^{-4}$ mol/liter, and agitation speeds of 430, 500, and 750 rpm. Figure 12(a) shows that when the agitation speed is 430 rpm, the polymerization rate increases in the initial stage as the initiator concentration increases and becomes constant in the final stage, regardless of the initiator concen-

tration. At an agitation speed of 500 rpm [see Fig. 12(b)], the polymerization rate increases up to the initiator concentration of 8.79 imes 10⁻⁴ mol/liter and then decreases after attaining the maximum value of 39.43×10^{-4} mol/liter. The decrease in the high concentration results from a little coagulation of the polymer particles. These phenomena suggest that increasing concentration of initiator (ammonium persulfate) markedly enhances the formation of hydrogen fluoride (HF) by increasing initiator decomposition.¹⁵ Therefore, it is reasonable to expect the PTFE dispersion to be unstable by decreasing pH or increasing ionic strength among particles. Similar phenomena were also obtained in a surfactant-free emulsion polymerization of TFE by radiation, in which the polymerization rate decreases with the addition of HF, owing to the coagulation of the particles.³⁰

On the other hand, at an agitation speed of 750 rpm [see Fig. 12(c)], the polymerization rate decreases rapidly after the maximum value, regardless of the initiator concentration.²⁷ An increase in the intensity of the agitation causes a reduction in the polymerization rate; this is caused by the strong shearing force of agitation, which breaks up the dispersion, forming the coagulated polymer.

Figure 13(a) shows a log-log plot of initiator concentration vs. R_p . R_p is proportional to the 0.3 power of the initiator concentration at 750 rpm, and is independent of the initiator concentration at 430 rpm. On the other hand, R_p is proportional to the 0.18 power of initiator concentration up to an initiator concentration of 4.38×10^{-4} mol/ liter, and remains constant beyond 500 rpm. The

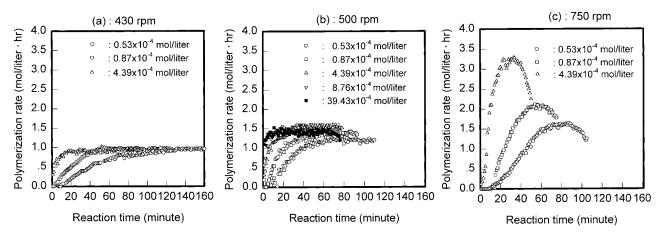
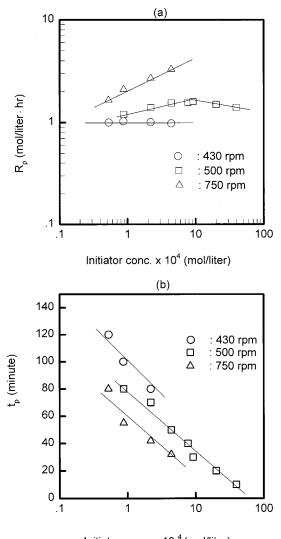


Figure 12 Plots of polymerization rate as a function of reaction time at various initiator concentrations and agitation speeds. Other reaction conditions are given in Table I.



Initiator conc. x 10⁴ (mol/liter)

Figure 13 Plots of (a) R_p and (b) t_p as a function of initiator concentration at various agitation speeds. Other reaction conditions are given in Table I.

low exponents found with the low agitation speeds may be ascribed to the decomposition of radicals accompanied with high initiator concentration; this, in turn, may be due to the contact difficulty of the monomer with a low agitation speed.

Figure 13(b) shows t_p as a function of initiator concentration at various agitation speeds. The t_p decreases as initiator concentration and agitation speed increase.

Effects of Reaction Temperature (T)

Figure 14 represents the polymerization rate as a function of the reaction time at various reaction

temperatures, ranging from 55 to 105°C. As shown in Figure 14, the polymerization rate increases with reaction time and levels off at the temperature of below 95°C. When the temperature is 105°C, the polymerization rate decreases rapidly after the maximum value. This results from the coagulation of the particles, which is easily seen at a high temperature.

Further tests were made with various agitation speeds at a constant temperature (105°C) to find the effect of coagulation on agitation speed. Figure 15 shows the polymerization rate as a function of the reaction time at the agitation speeds of 350, 430, and 500 rpm. As shown in Figure 15, the polymerization rate decreases rapidly after the maximum value, regardless of agitation speed. This supports the idea that the decrease of the polymerization rate is caused by the coagulation of the dispersion particles.²⁷ This behavior may be related to the decomposition rate of initiators like APS. The decomposition rate can be estimated to remarkably increase within 10 min at 105°C.³³ Therefore, the particles formed rapidly in the nucleation period may be unstable, and hence, easy to coagulate; the surface area of the particles is large, and there is not enough surfactant to cover the nucleated particles.

Figure 16 is a plot of $\ln R_p$ and t_p against the reciprocal of the reaction temperatures ranging from 55 to 105°C. R_p increases with the rising reaction temperature. On the other hand, R_p at 105°C is found to be much lower than that at 55°C. This means that the higher temperature

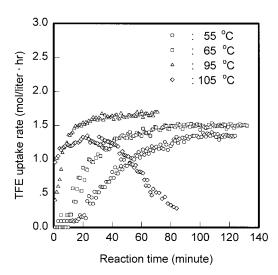


Figure 14 Polymerization rate vs. reaction time at various reaction temperatures. Other reaction conditions are given in Table I.

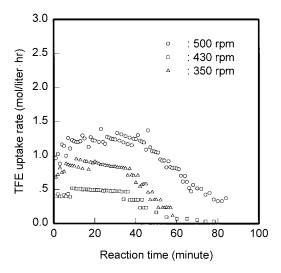


Figure 15 Polymerization rate vs. reaction temperature at various agitation speeds when the reaction temperature is constant as 105°C. Other reaction conditions are given in Table I.

can cause a higher degree of coagulation. This behavior is different from that found in Suwa et al.¹⁸ results; in that study, emulsion polymerization of TFE by radiation showed that the rate increases with the rising reaction temperature (70°C) and then decreases. Consequently, it is shown as the behavior of the typical radical polymerization. t_p decreases sharply with the increases ing reaction temperature, and smoothly increases at higher reaction temperatures.

The apparent activation energy obtained by a slope of a plot of $\ln R_p$ vs. 1/T of Figure 16 is -0.7

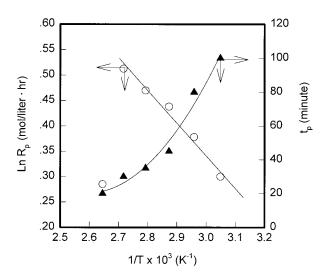


Figure 16 Effect of reaction temperature on R_p and t_p . Other reaction conditions are given in Table I.

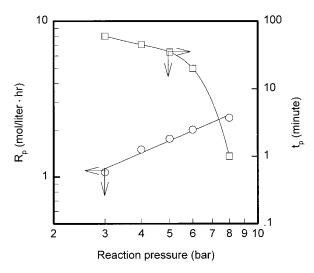


Figure 17 Effect of reaction pressure on R_p and t_p . Other reaction conditions are given in Table I.

kcal/mol, between 55 to 95°C. This value is lower than that obtained by Suwa et al. (-5.2 kcal/ mol),¹⁸ compared to the range of negative dependence of 1/T for the rate of polymerization. This difference may be due to the initiator or agitation speed. In fact, our experiment was carried out in the range of mass transfer limitation (at 500 rpm in standard conditions) because the coagulant polymers increase sharply with increasing agitation speed (Fig. 5). t_p decreases rapidly with an increase in reaction temperature.

Effects of Reaction Pressure

Figure 17 shows the effects of reaction pressures ranging from 2 to 8 bar on R_p and t_p . R_p increases linearly and t_p decreases with the pressure. This is due to an increase of the concentration of the TFE monomer with the rising reaction pressure in the reactor. R_p is proportional to a 0.85 power of the pressure. It is expected that R_p may be proportional to the first order of monomer concentration in polymer particles, or reaction loci in typical radical polymerization.

Effects of Stabilizer Type and Concentration

First, the effects of stabilizer types on the polymerization were studied, and are shown in Table II. The curves of the polymerization rates show the same pattern with the curve in the standard conditions, irrespective of stabilizer types. The reactivity of the stabilizer is in the order of *n*hexadecane (1.2 mol/liter \cdot h) < p-wax(3) (1.47 mol/ liter \cdot h) < p-wax(1), p-wax(2) (1.55 mol/liter \cdot h).

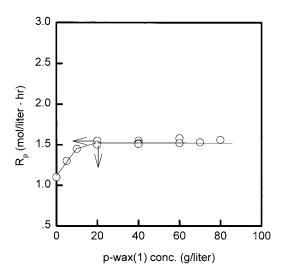


Figure 18 Effect of stabilizer [p-wax(1)] concentration on R_p . Other reaction conditions are given in Table I.

These behaviors result from the difference in the viscosity of the stabilizer, which is immiscible with water at reaction temperature (75°C). As a result, *n*-hexadecane (thought to contact with the PTFE particles because of its viscosity) is relatively lower than that of p-wax. Therefore, the PTFE particles result in the limitation in the contact with TFE. On the other hand, p-wax(3) does not disperse in the aqueous phase because of a relatively high viscosity in water, which is expected by its high melting point (Table II).

Figure 18 shows the effects of stabilizer concentrations ranging from 0 to 80 g/liter of H_2O on R_p using p-wax(1). The coagulated polymer was rapidly increased in the absence of stabilizer (Fig. 5) and completely eliminated by adding 20 g/liter of p-wax(1). R_p increases with amounts of p-wax(1), and remains constant beyond the value of 20 g/liter of p-wax(1).

Influences of Reaction Conditions on Molecular Weight

Effects of Agitation Speed and Reaction Pressure

Figures 19 and 20 show the effects of agitation speed and reaction pressure on ΔH_c , respectively. These experimental ranges are almost the same as those described in the chapter "influence of reaction conditions on the polymerization rate."

As seen in Figure 19, ΔH_c barely affects the agitation speeds less than 500 rpm, whereas it increases slightly with agitation speeds less than

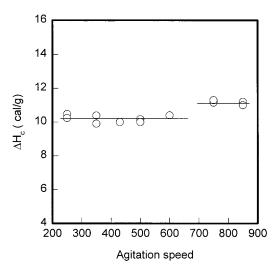


Figure 19 ΔH_c vs. agitation speed. Other reaction conditions are given in Table I.

500 rpm, due to coagulation. In Figure 20, ΔH_c barely affects the rate, with a reaction pressure of 2 to 8 bar; coagulation does not occur. These behaviors are different from the results of the surfactant-free emulsion polymerization of TFE by radiation obtained by Suwa et al.¹³ They posited that the molecular weight increases with agitation speed and reaction pressure, and levels off when coagulation occurred.

Effects of Surfactant and Initiator Concentrations

Figures 21 and 22 show the effects of concentrations of surfactant and initiator on ΔH_c . First,

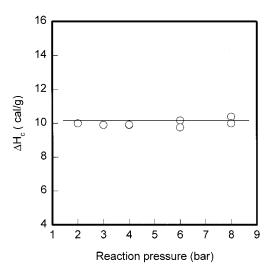


Figure 20 ΔH_c vs. reaction pressure. Other reaction conditions are given in Table I.

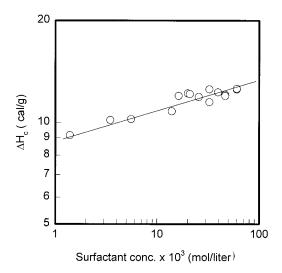


Figure 21 Effect of the surfactant concentration on ΔH_c . Other reaction conditions are given in Table I.

 ΔH_c steadily increases with an increase in surfactant (Fig. 21) and initiator concentration (Fig. 22) in the range investigated. Thus, the initiator and surfact ant concentration dependencies of the ΔH_c can be expressed as follows:

$$\Delta H_c \coloneqq [I]^{0.09} [C_s]^{0.07} \tag{4}$$

where I is the initial initiator concentration (mol/ liter) and C_s the surfactant concentration (mol/ liter).

The initiator and surfactant concentration dependence of the ΔH_c (molecular weight) are very low and not in accordance with the Smith-Ewart theory. Therefore, it does not follow the characteristic behaviors of the conventional emulsion polymerization in which the polymerization rate and molecular weight are simultaneously increased by increasing the number of polymer particles (by increase of surfactant concentration) at a constant initiator rate.

These facts support the results observed in our previous article;²⁷ the particle numbers increase with reaction time in the whole experimental range to avoid coagulation, which is different from the conventional emulsion polymerization.

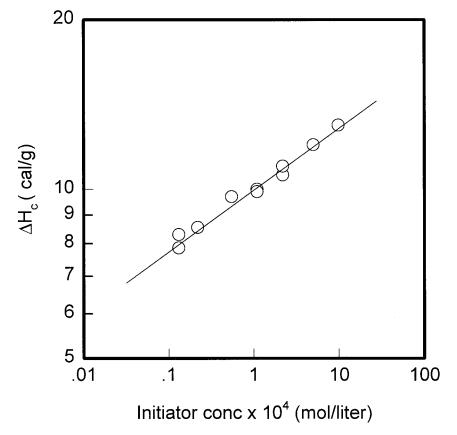


Figure 22 Effect of the initiator concentration on ΔH_c . Other reaction conditions are given in Table I.

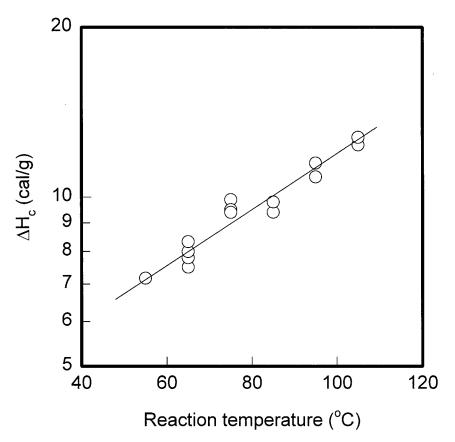


Figure 23 Effect of reaction temperature on ΔH_c . Other reaction conditions are given in Table I.

Therefore, the molecular weight is nearly independent of the number of polymer particles or the rate of radical generation, i.e., the interval number of polymer particles or the rate of radical generation, i.e., the interval of radical entrances irrespective of CMC.

Accordingly, the PTFE dispersion with a high molecular weight can be obtained by lowering both the initiator and surfactant concentration.

Effects of Reaction Temperature

Figure 23 shows the effects of the reaction temperatures on ΔH_c . ΔH_c decreases with the rising reaction temperature. Thus, the PTFE dispersion polymer of high molecular weight could be obtained by possibly decreasing the reaction temperature. The upper limit of the molecular weight is set by the melting point of the stabilizer (p-wax) used. Therefore, the molecular weight of the PTFE dispersion polymer is lower than that of the polymer produced by the suspension polymerization (Table IV). This result may be due to the increase in the mobility of polymer chain radicals

at higher temperatures, which leads to a reduction in radical accumulation and its lifetime.

Effects of Stabilizer Type and Concentration

n-Hexadecane (14.98 cal/g) is found to affect more than just the p-wax (9.61 cal/g) regarding ΔH_c . This behavior suggests the fact that the impurities of low molecular weight hydrocarbons (like the double-bond compounds in *n*-hexadecane) induce the chain transfer reaction.³² But p-waxs shows the same molecular weight irrespective of stabilizer types, though they have a slight difference in the melting point.

Figure 24 shows the effects of stabilizer concentration on ΔH_c using p-wax(1) in the range of 0 to 80 g/liter of H₂O. ΔH_c increases with increasing amounts of p-wax(1) and levels off at 20 g/liter.

CONCLUSIONS

In this work, the emulsion polymerization of TFE was carried out at different reaction conditions.

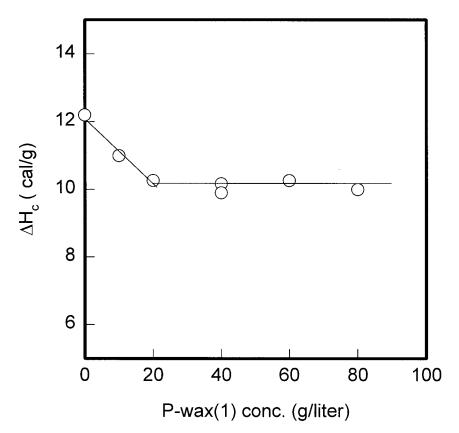


Figure 24 Effect of the concentration of the stabilizer [p-wax(1)] on ΔH_c . Other reaction conditions are given in Table I.

The effects of the process conditions and each ingredient introduced in the reaction system have been investigated in regard to the polymerization kinetics and the geometric properties of the polymer particles produced. Several conclusion can be drawn from this study:

- 1. The mechanism of the TFE polymerization can be represented as follows. When TFE was pressurized in the reactor, TFE monomer radicals were produced by association with a decomposed anionic initiator. The monomer radicals grew by reaction with TFE monomers and produced PTFE particles. The particles were stabilized by the anionic surfactant.
- 2. The polymerization rate was reduced when the polymer particles were coagulated due to a decrease in the adsorption amounts of the monomer and initiator introduced into the reactor system; this was caused by a decrease in the surface area of the resultant particles.
- 3. The PTFE particles produced were 80–220

nm in size. A stable dispersion could be obtained at surfactant concentrations below CMC, which is an abnormal observation in ordinary emulsion polymerization.

4. The molecular weight of PTFE particles tends to decrease as the concentration of the surfactant or the initiator increases or when the temperature is high.

The emulsion polymerization of TFE was quite different from conventional emulsion polymerization.

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