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Radiation-Induced Emulsion Copolymerization of Tetrafluoroethylene with Propylene. V. Formation of Acid and Its Effect

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Synopsis

In the radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene, it was found that hydrofluoric acid (HF) is formed in the course of polymerization. The amount of HF formed increased linearly with the irradiation time in all cases. The rate of HF formation was maximum at 0.3 wt-% emulsifier and increased linearly with tetrafluoroethylene content in the monomer mixture. On the other hand, the conversion and the molecular weight decreased remarkably by addition of 0.1*M* HF. The particle diameter of copolymer obtained in the presence of HF was larger than that obtained in the HF-free system. On the contrary, the number of polymer particles was less than that obtained in the HF-free system. The decrease in the conversion and the molecular weight was attributed mainly to the conversion of part of ammonium perfluorooctanoate to perfluorooctanoic acid by formation of acid or addition of acid.

INTRODUCTION

In the course of a study on radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene,[1] it was found that hydrofluoric acid (HF) is formed in the course of polymerization. It is well known that acid is formed from radiolysis of organic halide aqueous solutions.[2-5] It is considered that acid formation of this kind in the course of radiation-induced emulsion polymerization is responsible for a shift of the critical micelle concentration or the demulsification[6] in the system.

In order to clarify the effect of acid in detail, this study was carried out about several factors governing the radiation-induced emulsion copolymerization in the gaseous monomer system.

In this paper, we describe the relationship between the amount of HF formed and emulsifier concentration, tetrafluoroethylene content in the monomer mixture, and other factors. The effect of added HF is also discussed.

EXPERIMENTAL

Materials

The tetrafluoroethylene used was obtained from Asahi Glass Co. (stated purity 99.9%). Research-grade propylene (99.7%) was used without purification. The emulsifier used was ammonium perfluorooctanoate ($C_7F_{15}COONH_4$, 96%) obtained from Minnesota Mining & Mfg. Co. Hydrofluoric acid used was reagent grade, and the HF content was 46.5% ± 0.3%. Other chemicals used were reagent grade. The water was triply distilled[7] (pH 6.3 ± 0.2).

Apparatus and Procedure

A Pyrex reaction vessel with baffles was set tightly in a 200-ml stainless-steel autoclave equipped with a magnetic coupled agitator. Ammonium perfluorooctanoate, 0.8 g (1 wt-% of water), as emulsifier was put in the glass vessel. In some experiments, perfluorooctanoic acid as emulsifier was used. The autoclave was sealed, then purged twice by evacuating and flushing with nitrogen at 20 atm pressure, and charged with 80 ml nitrogen-saturated water and 15 g tetrafluoroethylene–propylene mixture containing 50 mole % tetrafluoroethylene. This emulsion system was irradiated with cobalt 60 gamma rays at room temperature. The dose rate was determined by Fricke dosimetry [$G(Fe^{3+}) = 15.6$]. The stirring speed was 500 rpm.

Polymers produced after irradiation were isolated from the latex by drying in an oven at 100°C. The polymer was washed thoroughly, first with methanol, and then dissolved in tetrahydrofuran and concentrated. The polymer was isolated from the concentrated solution by addition of methanol, then washed with methanol. The polymer yield was determined after drying in an oven at 100°C.

The solution viscosity was measured at 30°C in tetrahydrofuran.[8] The number-average molecular weight $\bar{M}_n$ was calculated from eq. (1):

$$[\eta] = 2.46 \times 10^{-4} \bar{M}_n^{0.70}. \quad (1)$$

Equation (1) differs from the relation given in bulk copolymerization.[8] This is mainly attributable to the difference of the composition of the copolymer produced. Tetrafluoroethylene content in the copolymer produced in emulsion copolymerization[9] is higher than that in bulk copolymerization.[8]

After irradiation, the pH of the solution was obtained by a Hitachi-Horiba M-5 pH meter, which was corrected with standard buffer solutions (pH 6.86 at 25°C, pH 4.01 at 25°C) before and after the measurements. HF concentration was determined from a calibration curve between HF concentration and pH.

Diameter Measurement of Polymer Particle

The diameter of polymer particle was measured by using a JEOL JEM-7 electron microscope.[10] The latex was irradiated with an electron beam (50

Mrad), and the polymer particle was crosslinked to prevent the softening before the electron microscopy.

RESULTS AND DISCUSSION

Effect of Emulsifier Concentration on HF Formation

The relation between amount of HF formed and irradiation time at various emulsifier concentrations is shown in Figure 1. The amount of HF formed increased linearly with irradiation time in all cases. The rate of HF formation, obtained from the slope of the straight line in Figure 1, indicated a maximum at 0.3 wt-% emulsifier, and decreased steeply at 1 wt-%. On the other hand, as shown in Figure 2, the rate of polymerization obtained from the slope of the time–conversion curve increased steeply in the range of 0.5 wt-% to 1 wt-% and increased with emulsifier concentration above 1 wt-%. It may be assumed that such decrease in the rate of HF formation above 0.5 wt-% emulsifier is mainly attributable to the formation of micelle. In this emulsion system, the critical micelle concentration is

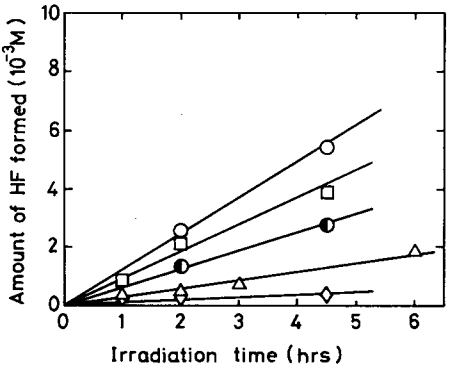

Fig. 1. Relation between amount of HF formed and irradiation time at various emulsifier concentrations: dose rate, 3.8×10^5 R/hr; emulsifier concentration, (◐) 0%; (○) 0.3%; (□) 0.5%; (△) 1%; (◇) 3%; C_2F_4 content in monomer mixture, 50 mole-%.

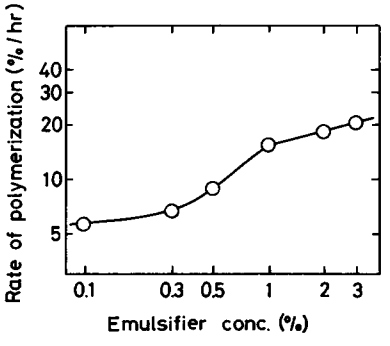

Fig. 2. Relation between rate of polymerization and emulsifier concentration: irradiation dose, 3.8×10^5 R; C_2F_4 content in monomer mixture, 50 mole-%.

0.68-wt-%.[11] Also, in this emulsion system, as the amount of water was much larger than the amount of monomer and emulsifier, the energy of radiation is mostly absorbed in water. Consequently, it can be assumed that HF is mainly formed by reaction between primary products from radiolysis of water and organic fluoride (monomer and emulsifier).

Effect of Monomer Composition on HF Formation

The relation between amount of HF formed and irradiation time at various tetrafluoroethylene contents in the monomer mixture is shown in Figure 3. The amount of HF formed increased linearly with the irradiation time in all cases. Figure 4 shows the effect of monomer composition on the rate of HF formation. The rate of HF formation, obtained from the slope of the straight line in Figure 3, increased linearly with tetrafluoroethylene content in the monomer mixture. It is apparent from the above results that part of the HF is formed by reaction between primary products from radiolysis of water and tetrafluoroethylene. Also, the tendency of HF

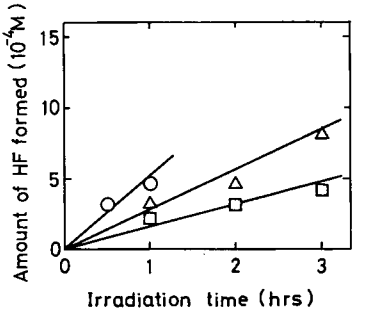

Fig. 3. Relation between amount of HF formed and irradiation time at various tetrafluoroethylene contents in monomer mixture: dose rate, 3.8×10^5 R/hr; C_2F_4 content, (□) 25 mole-%; (△) 50 mole-%; (○) 75 mole-%; emulsifier concentration, 1 wt-% of water.

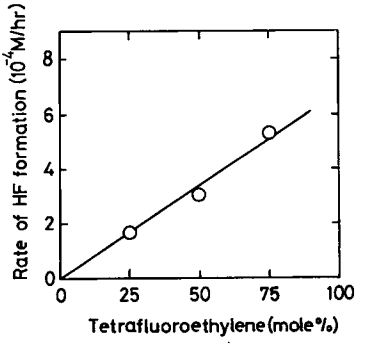

Fig. 4. Relation between rate of HF formation and tetrafluoroethylene content in monomer mixture: irradiation dose, 3.8×10^5 R; emulsifier concentration, 1 wt-% of water.

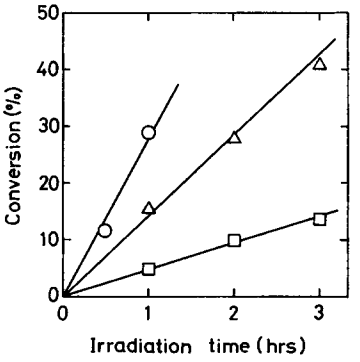

Fig. 5. Relation between conversion and irradiation time at various tetrafluoroethylene content in monomer mixture: dose rate, 3.8 × 10^5 R/hr; C_2F_4 content; (□) 25 mole-%; (△) 50 mole-%; (○) 75 mole-%; emulsifier concentration, 1 wt-% of water.

formation in Figure 3 was similar to that of the time conversion curve shown in Figure 5.

Effect of Acid

As described above, a considerable amount of HF was formed in this emulsion system. It is considered that in the emulsion polymerization, HF formation of this kind is responsible for the shift of the critical micelle concentration or the demulsification,[6] and complicating features may take place in emulsion.

Figure 6 shows the effect of HF added on conversion at various emulsifier concentrations. The conversion decreased slightly by addition of 0.01*M* HF and decreased steeply by addition of 0.1*M* HF. At various emulsifier concentrations, a similar tendency was observed. Also, the effect of HF decreased with increase in emulsifier concentration. At 0.5 wt-% emulsifier, the ratio of conversion at 0.1*M* HF added to that in the absence of HF was about 0.56.

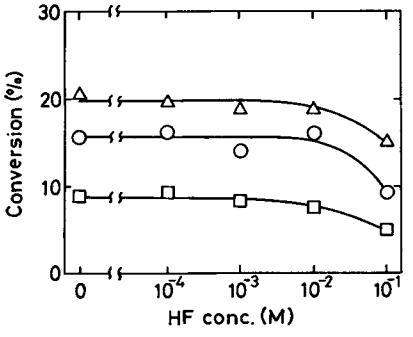

Fig. 6. Effect of HF added on conversion at various emulsifier concentrations; irradiation dose, 3.8 × 10^5 R; emulsifier concentration, (□) 0.5%; (○) 1%; (△) 3%.

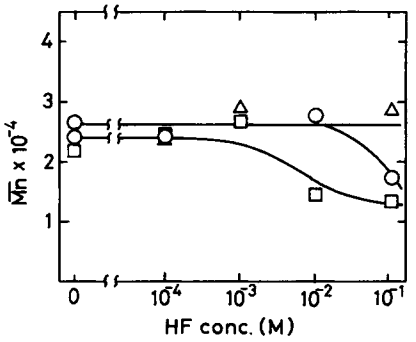

Fig. 7. Effect of HF added on molecular weight at various emulsifier concentrations: irradiation dose, 3.8×10^5 R; emulsifier concentration, (□) 0.5%; (○) 1%; (△) 3%.

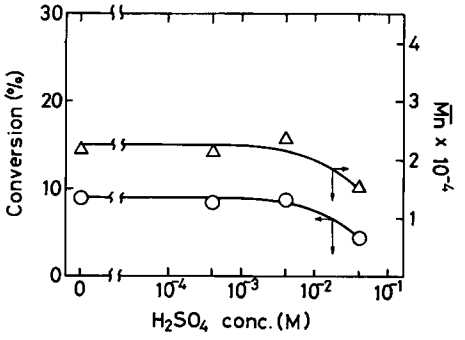

Fig. 8. Effect of H_2SO_4 added on conversion and molecular weight: irradiation dose, 3.8×10^5 R; emulsifier concentration, 0.5 wt-% of water.

A remarkable effect of HF on molecular weight is shown in Figure 7. The molecular weight indicated a constant value in the range of $10^{-4}M$ to $0.1M$ HF at 3 wt-% emulsifier. However, below 1 wt-% emulsifier, the molecular weight decreased considerably by addition of $0.1M$ HF. Especially, at 0.5 wt-% emulsifier, the molecular weight decreased considerably even by addition of $0.01M$ HF. As shown in Figure 7, the effect of HF on molecular weight decreased with increase in emulsifier concentration. It is apparent from the above results that HF plays an important role in such a reaction system. It can be assumed that the interaction between HF and emulsifier takes place upon addition of HF or accumulation of HF formed in the course of irradiation.

On the other hand, the copolymerization was carried out in the presence of H_2SO_4. Figure 8 shows the effect of H_2SO_4 added on conversion and molecular weight. Conversion and molecular weight decreased remarkably by addition of $5 \times 10^{-2}M$ H_2SO_4, and the tendency was similar to that in the presence of HF. It is considered that such decrease in the conversion and the molecular weight by addition of acid is attributable to the stability of latex.

TABLE I
Effect of Added HF[a]

Expt. no.	Emulsifier	Emulsifier concns., wt-% of water	Diameter of particles, Å	Number of particles, ml^{-1}	Polymer yield, %	Molecular weight, $\bar{M}_n$
1	$C_7H_{15}COONH_4$	0.5	990	2.5×10^{13}	8.9	2.3×10^4
2		1	730	1.1×10^{14}	15.5	2.6×10^4
3		3	750	1.1×10^{14}	20.6	2.5×10^4
4	$C_7H_{15}COONH_4$ $-0.1M$ HF	0.5	1330	5.3×10^{12}	4.9	1.3×10^4
5		1	1100	1.8×10^{13}	9.3	1.9×10^4
6		3	1000	3.8×10^{13}	15.1	2.8×10^4
7	$C_7H_{15}COOH$	0.5	1670	2.0×10^{12}	3.6	1.5×10^4
8		1	1580	2.5×10^{12}	3.9	1.0×10^4
9		3	1640	4.3×10^{12}	7.5	1.9×10^4
10	None		1970	1.1×10^{12}	3.2	1.2×10^4

[a] Irradiation dose: 3.8×10^5 R.

In order to clarify the above phenomenon, the relationship between polymerization conditions and diameter of polymer particles formed, number of polymer particles formed per unit volume, conversion, and molecular weight was examined. The results are summarized in Table I. It is apparent from Table I that the diameter of polymer particles obtained in the presence of HF (expts. 4–6, Table I) was larger than that obtained in the HF-free system (expts. 1–3, Table I). On the contrary, the number of polymer particles (expts. 4–6, Table I) was less than that obtained in the HF-free system (expts. 1–3, Table I). Furthermore, the conversion and the molecular weight obtained in the HF-free system (expts. 1–3, Table I) were higher than those obtained in the presence of HF (expts. 4–6, Table I). Consequently, it can be assumed from these results that part of ammonium perfluorooctanoate is converted into perfluorooctanoic acid by addition of acid as shown in the following reaction:

$$C_7F_{15}COONH_4 \xrightarrow{H^+} C_7F_{15}COOH$$

and its inherent action as emulsifier becomes very weak.

In fact, when perfluorooctanoic acid was used as emulsifier instead of ammonium perfluorooctanoate, the diameter of polymer particles was larger and the number of polymer particles was less, and the conversion and the molecular weight were lower (expts. 7–9, Table I). These results were similar to that obtained in a suspension system (expt. 10, Table I).

Consequently, it is concluded from these results that the decrease in conversion and molecular weight is mainly attributable to the conversion of part of ammonium perfluorooctanoate to perfluorooctanoic acid by addition of acid and formation of acid in the course of polymerization. As described above, in the emulsion polymerization, conversion and molecular weight are affected by the formation of acid. Especially, in radiation-induced

emulsion polymerization with organic halide as monomer and an emulsifier, the effect of acid formed should be adequately noted.

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