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Radiation-Induced Emulsion Copolymerization of Tetrafluoroethylene with Propylene. The Behavior of the HF Formed

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ABSTRACT

The radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene was carried out at room temperature in the presence of gaseous monomers. The formation of hydrofluoric acid in the course of polymerization was observed. The amount of HF formed increased linearly with the irradiation time at various dose rates in the early stage. The tendency was similar to that of time-polymer yield curves. The rate of HF formation was proportional to the first order of the dose rate. The amount of HF formed increased in the presence of oxygen and decreased remarkably above 1 wt% emulsifier, while the polymer yield decreased in the presence of oxygen and increased with the emulsifier concentration. A remarkable decrease in the amount of HF formed in higher emulsifier concentration is mainly attributable to chemical absorption or electrostatic capture of H^+ ion on polymer particles produced. Hydrofluoric acid is mainly formed by reaction between primary products (e_{aq}^- and H) from the radiolysis of water and organic fluoride (tetrafluoroethylene and emulsifier), and is little formed by reaction between primary products and copolymer produced. The G value of HF formation was in the order of emulsifier-water system > suspension polymerization > emulsion polymerization, while the polymer yield was in the order of emulsion polymerization > suspension polymerization.

INTRODUCTION

In preceding papers [1-3] the effects of reaction conditions of the radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene were reported and the copolymerization mechanism was clarified. In the course of a study on radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene, it was found that hydrofluoric acid (HF) is formed in the course of polymerization. It is well known that acid is formed from the radiolysis of organic halide aqueous solutions [4-7]. As it is known [8] that the polymer yield and molecular weight in the emulsion polymerization are affected by acid, clarification of the behavior of HF formed in the course of polymerization was needed.

In this paper the behavior of HF formed under various conditions is discussed and is compared with that of the corresponding polymer yield.

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. The 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 [9] (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 emulsifier (0.8 g) (1 wt% to water) was put in the glass vessel. The autoclave was sealed, then purged twice by evacuating it and flushing it with nitrogen at 20 atm, and charged with 80 ml of nitrogen-saturated water and 15 g of tetrafluoroethylene-propylene mixture containing 50 mole % tetrafluoroethylene. In the case of experiments with the water-emulsifier system, nitrogen at 20 atm instead of monomer mixture was charged. This emulsion system was irradiated with ^{60}Co 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 with methanol, 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.

Analysis

The pH of the solution was obtained after irradiation 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.

Fluoride ion concentration in the solution was determined as follows. Twenty milliliters of solution and 20 ml of total ionic strength adjustment buffer solution [10] were pipetted into a 50-ml measuring flask, diluted with distilled water, and then mixed well. The electrode potential of the solution was measured with a Beckman fluoride ion selective electrode. F^- concentration was determined from a calibration curve between F^- concentration and electrode potential.

RESULTS AND DISCUSSION

Effect of Emulsifier Concentration

The effects of emulsifier concentration on the amount of HF formed are shown in Fig. 1 by open circles for the emulsion polymerization and open squares for the emulsifier-water system. In the emulsion polymerization the amount of HF formed was a maximum at 0.3 wt% emulsifier and decreased steeply at 1 wt%. In the emulsifier-water system the amount of HF formed was a maximum at 0.5 wt% emulsifier and decreased above 1 wt%. The tendency was similar to

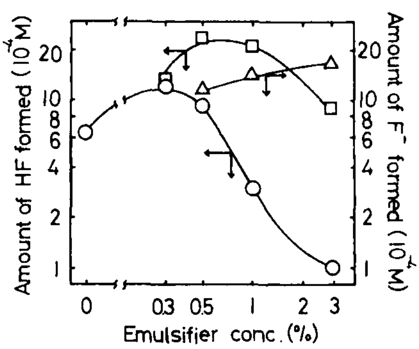


FIG. 1. Effect of emulsifier concentration on amount of HF formed and amount of F^- formed. Dose: 3.7×10^5 rad (○) Emulsion polymerization; (□) emulsifier-water system; (△) amount of F^- formed in the emulsion polymerization. C_2F_4 content in monomer mixture was 50 mole %.

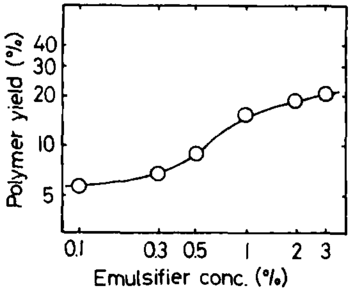


FIG. 2. Effect of emulsifier concentration on polymer yield. Dose: 3.7×10^5 rad. C_2F_4 content in monomer mixture was 50 mole %.

that of HF formed in the emulsion polymerization. However, the amount of HF formed in the emulsifier-water system was much larger than that in the emulsion polymerization. In both systems a remarkable decrease in the amount of HF formed in higher emulsifier concentration is noticeable.

As shown in Fig. 2, in the emulsion polymerization the polymer yield increased steeply in the range of 0.3 to 1 wt% emulsifier, and increased linearly above 1 wt%, in contrast to the remarkable decrease in the

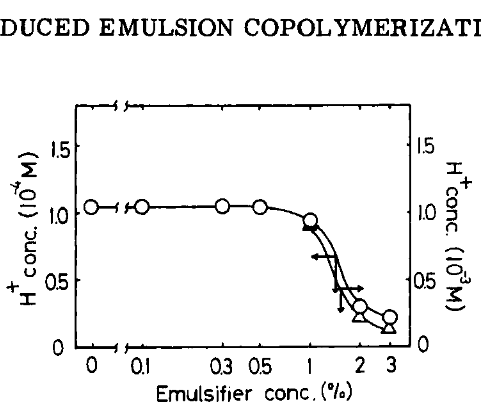


FIG. 3. Change of H^+ concentration by addition of emulsifier.

amount of HF formed above 1 wt%. This indicates that the polymer produced affects the behavior of HF formed.

On the other hand, as shown in Fig. 3, when emulsifier in the range of 0.1 to 3 wt% was added in an aqueous solution containing a known H^+ concentration, H^+ concentration was kept constant up to 1 wt% emulsifier and decreased steeply above 1 wt%. A critical micelle concentration is 0.68 wt% [11]. It can be assumed from the result that in the emulsifier-water system a decrease in the amount of HF formed above 1 wt% emulsifier is attributable to chemical absorption or electrostatic capture of H^+ ion on micelle. In the emulsion polymerization, as shown in Fig. 1, F^- ion concentration in an aqueous solution after irradiation increased with the emulsifier concentration even above 1 wt%. The amount of HF formed in the emulsion polymerization was much smaller than that in the emulsifier-water system. Consequently, it can be assumed that a remarkable decrease in the amount of HF formed in the emulsion polymerization is mainly attributable to chemical absorption or electrostatic capture of H^+ ion on polymer particles produced.

Dose Rate Dependence

The relation between amount of HF formed and irradiation time at various dose rates is shown in Fig. 4. The amount of HF formed increased linearly with the irradiation time at dose rates of 1.8×10^5 and 3.7×10^5 rad/hr. However, at a dose rate of 9.5×10^5 rad/hr, the amount of HF formed increased linearly up to 3 hr and then the slope of the straight line fell to half. In this case a noticeable drop in pressure was observed. The tendency of HF formation was similar to that of the time-polymer yield curves shown in Fig. 5. At a dose

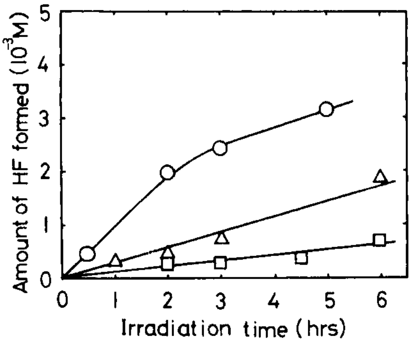


FIG. 4. Relation between amount of HF formed and irradiation time at various dose rates. Dose rate: (□) 1.8 × 10^5 rad/hr; (△) 3.7 × 10^5 rad/hr; (○) 9.5 × 10^5 rad/hr. Emulsifier concentration: 1 wt% to water; C_2F_4 content in monomer mixture was 50 mole %.

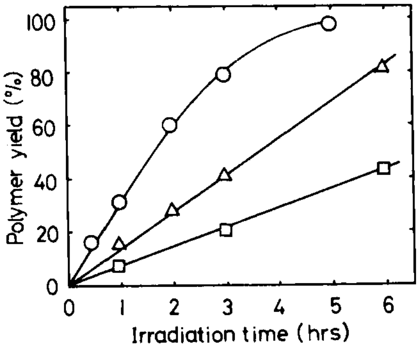


FIG. 5. Relation between polymer yield and irradiation time at various dose rates. Dose rate: (□) 1.8 × 10^5 rad/hr; (△) 3.7 × 10^5 rad/hr; (○) 9.5 × 10^5 rad/hr. Emulsifier concentration: 1 wt% to water; C_2F_4 content in monomer mixture was 50 mole %.

rate of 9.5 × 10^5 rad/hr, the polymer yield was about 80 wt% at 3 hr of reaction. It is assumed from these results that, in the case of the dose rate of 9.5 × 10^5 rad/hr, such a decrease in the rate of HF formation above 3 hr of reaction is attributable to the decrease of monomer concentration in the aqueous phase. It is also assumed that HF from reaction between primary products from the radiolysis

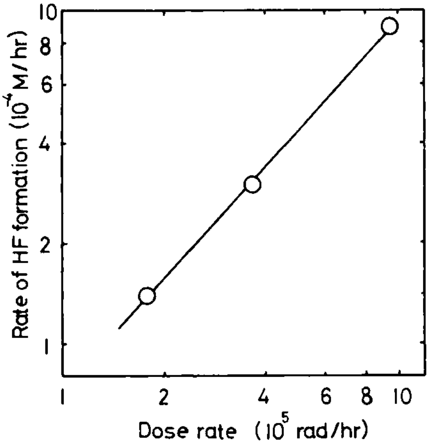


FIG. 6. Dose rate dependence of the rate of HF formation.

of water and copolymer produced will be very small, since the energy of radiation is mostly absorbed in water and the rate of HF formation decreases in high polymer yield as mentioned above.

Figure 6 shows the dose-rate dependence of the rate of HF formation obtained from the slope of the straight line in Fig. 4. The rate of HF formation was proportional to the first order of the dose rate.

Effect of Oxygen

Figure 7 shows the effect of oxygen on the amount of HF formed and polymer yield. The amount of HF formed increased in the presence of oxygen, while the polymer yield decreased. In this system, oxygen was consumed during the first hour, and the rate of HF formation and the rate of polymerization after the consumption of oxygen was consistent with that obtained in a nitrogen-saturated system.

It is well known that the oxidation of tetrafluoroethylene induced by heat, UV light, and ionizing radiation gives carbonylfluoride, tetrafluoroethylene oxide, and perfluorocyclopropane [12, 13]:

$$C_2F_4 + O_2 \xrightarrow[\text{heat, light, radiations}]{} COF_2,\ (CF_2)_2O,\ (CF_2)_3 \qquad (1)$$

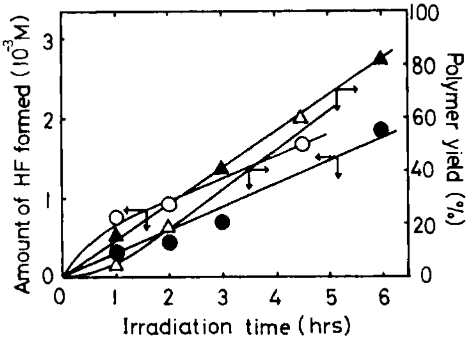
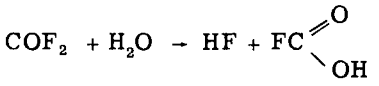


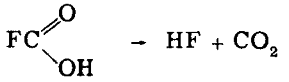
FIG. 7. Effect of oxygen on amount of HF formed and polymer yield. Dose rate: 3.7×10^5 rad/hr. Emulsifier concentration: 1 wt% to water. (○, △) Air saturation; (●, ▲) N_2 saturation. C_2F_4 content in monomer mixture was 50 mole %.

Subsequent hydrolysis of the carbonylfluoride formed gives HF [7]:



$$COF_2 + H_2O \rightarrow HF + FC(=O)OH \qquad (2)$$

and then elimination of HF from FCOOH must take place [7]:



$$FC(=O)OH \rightarrow HF + CO_2 \qquad (3)$$

Consequently, it can be assumed that the increase in the amount of HF formed in the presence of oxygen is attributable to the above reactions.

On the other hand, the inhibition or retardation of free radical polymerization by oxygen is well known in the liquid phase. It is due to the addition of oxygen to the propagating radicals. These radicals have a lower reactivity with monomer and finally disappear as nonradical products. Therefore, oxygen contributes to both the HF formation and the inhibition or retardation of radical polymerization.

HF Formation in Various Systems

The amount of HF formed and polymer yield as functions of irradiation time in various systems are shown in Fig. 8. The amount of HF formed increased linearly with the irradiation time in all cases. The

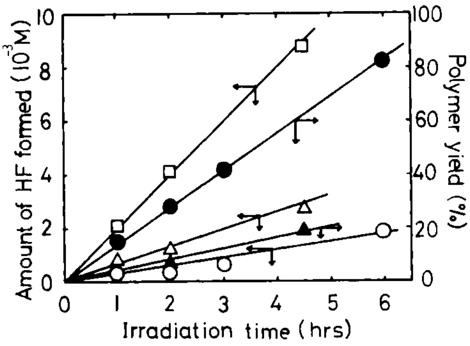
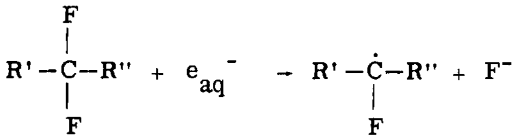


FIG. 8. Amount of HF formed and polymer yield as functions of irradiation time in various systems. Dose rate: 3.7×10^5 rad/hr. Emulsifier concentration: 1 wt% to water. Amount of monomer mixture: 15 g. (□) Emulsifier-water system; (△, ▲) suspension polymerization; (○, ●) emulsion polymerization. C_2F_4 content in monomer mixture was 50 mole %.

G values of HF, estimated as the number of HF molecules formed per 100 eV of energy absorbed, from the values plotted in Fig. 8, are summarized in Table 1. The G(HF) was in the order of emulsifier-water system > suspension polymerization > emulsion polymerization. On the other hand, the polymer yield increased linearly with the irradiation time and was in the order of emulsion polymerization > suspension polymerization.

Emulsifier-Water System

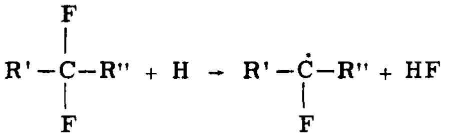
In the case of the emulsifier-water system, as the energy of radiation is mostly absorbed in water, HF would be scarcely formed from direct radiolysis of emulsifier and would be formed by reaction between primary products (e_{aq}^- and H) from the radiolysis of water [14] and emulsifier. Consequently, the mechanism of HF formation proposed for the emulsifier-water system can be represented by [6, 7, 15-17]



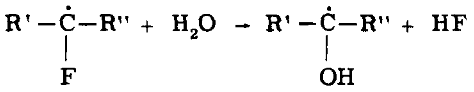
$$R'-\underset{F}{\overset{F}{C}}-R'' + e_{aq}^- \rightarrow R'-\underset{F}{\dot{C}}-R'' + F^- \qquad (4)$$

TABLE 1. G-Value of HF Formation

Experimental conditions	G(HF)
Emulsifier-water system	5.2
Suspension polymerization	2.1
Emulsion polymerization	0.6



$$R'-\underset{F}{\overset{F}{C}}-R'' + H \rightarrow R'-\underset{F}{\dot{C}}-R'' + HF \qquad (5)$$



$$R'-\underset{F}{\dot{C}}-R'' + H_2O \rightarrow R'-\underset{OH}{\dot{C}}-R'' + HF \qquad (6)$$

where R'FCFR'' is emulsifier $[CF_3-(CF_2)_6-COONH_4]$.

Reactions (4), (5), and (6) are dissociative electron capture, fluorine atom abstraction by H radical, and hydrolysis reaction, respectively. As seen from the above reactions, e_{aq}^- forms one molecule of HF, and H radical forms two molecules of HF. Therefore, on the basis of the G value $[G(e_{aq}^-) = 2.8,\ G(H) = 0.5]$ of primary products [18] from the radiolysis of water and the ratio of fluorine atoms in $-(CF_2)_6-$ to total fluorine atoms in $CF_3-(CF_2)_6-COONH_4$, the G value of HF formation can be represented as

$$G(HF) = \frac{4}{5}[G(e_{aq}^-) + 2G(H)] = 3.0 \qquad (7)$$

In addition to the above consideration, reactions between CF_3- in $CF_3-(CF_2)_6-COONH_4$ and e_{aq}^- or H radical have to be considered and can be repesented as

$$R'''-CF_3 + e_{aq}^- \rightarrow R'''-\dot{C}F_2 + F^- \qquad (8)$$

$$R'''-CF_3 + H \rightarrow R'''-\dot{C}F_2 + HF \qquad (9)$$

$$R'''-\dot{C}F_2 + H_2O \rightarrow R'''-\dot{C}FOH + HF \qquad (10)$$

$$R'''-\dot{C}FOH \rightarrow R'''-\dot{C}=O + HF \qquad (11)$$

where R‴$-CF_3$ is emulsifier $[CF_3-(CF_2)_6-COONH_4]$. In the case of the above reactions, e_{aq}^- forms two molecules of HF and H radical forms three molecules of HF. According to the same consideration mentioned above, the ratio of fluorine atoms in CF_3- to total fluorine atoms in $CF_3-(CF_2)_6-COONH_4$ is 0.2. The G value of HF formation can be represented as

$$G(HF) = \frac{1}{5}[2G(e_{aq}^-) + 3G(H)] = 1.4 \tag{12}$$

Consequently, total G value of HF formation calculated from primary products from the radiolysis of water can be represented as

$$G(\text{total HF}) = \frac{4}{5}[G(e_{aq}^-) + 2G(H)] + \frac{1}{5}[2G(e_{aq}^-) + 3G(H)] = 4.4 \tag{13}$$

The G value of HF formation was almost consistent with the G value (5.2) observed, shown in Table 1. It is concluded from these facts that in the emulsifier-water system, HF is mainly formed by reactions (4)-(6) and (8)-(11).

Suspension Polymerization

In the case of suspension polymerization, where the copolymer is produced by irradiation as shown in Fig. 8, most of H and OH radicals take part in the initiation of polymerization. Therefore, it is assumed that HF is mainly formed by reaction between e_{aq}^- and tetrafluoroethylene [6, 19, 20]:

$$CF_2CF_2 + e_{aq}^- \rightarrow CF_2\dot{C}F + F^- \tag{14}$$

$$CF_2\dot{C}F + H_2O \rightarrow CF_2\dot{C}OH + HF \tag{15}$$

In the case of above reactions, e_{aq}^- forms one molecule of HF. As shown in Table 1, the G value of HF formation was 2.1. A slight difference between the G(HF) observed and the G value (2.8) of the hydrated electron from the radiolysis of water may be attributable to chemical absorption or electrostatic capture of H^+ ion on the polymer particles produced.

Emulsion Polymerization

In the case of emulsion polymerization, as shown in Table 1, the G value (0.6) observed is very small in comparison with that obtained in other systems. However, the polymer yield is larger than that obtained in suspension polymerization as shown in Fig. 8. Also, according to the authors [8], the number of polymer particles produced (1.1×10^{14}/ml) in emulsion polymerization is much larger than that (1.1×10^{12}/ml) in suspension polymerization. Consequently, it can be assumed that in emulsion polymerization a remarkable decrease in higher emulsifier concentration is mainly attributable to chemical absorption or electrostatic capture of H^+ ion on the polymer particles produced.

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REFERENCES

[1] O. Matsuda, M. Ito, N. Suzuki, J. Okamoto, and Y. Tabata, J. Macromol. Sci.—Chem., A8, 775 (1974).
[2] N. Suzuki, O. Matsuda, and J. Okamoto, Ibid., A8, 793 (1974).
[3] N. Suzuki, O. Matsuda, and J. Okamoto, J. Polym. Sci., 12, 2045 (1974).
[4] J. Jeply, Collect. Czech. Chem. Commum., 25, 24 (1960).
[5] R. J. Woods and J. W. T. Spinks, Can. J. Chem., 38, 77 (1960).
[6] T. I. Balkas, J. H. Fendler, and R. H. Schuler, J. Phys. Chem., 75, 455 (1971).
[7] J. Lilie, D. Behar, R. J. Sugdak, and R. H. Schuler, Ibid., 76, 2517 (1972).
[8] N. Suzuki, O. Matsuda, and J. Okamoto, J. Appl. Polym. Sci., 18, 2457 (1974).
[9] G. R. A. Johnson and J. Weiss, Proc. Roy. Soc., A, 240, 189 (1957).
[10] M. Fukushima, H. Fukushima, and T. Kuroda, Japan Analyst, 21, 522 (1972).
[11] O. Matsuda, M. Ito, A. Danno, G. Kojima, H. Wachi, and Y. Tabata, Paper Presented at Symposium of High Polymer, Japan, Osaka, November 1972.
[12] D. Cordischi, M. Lenzi, and A. Mele, Trans. Faraday Soc., 60, 2047 (1964).
[13] V. Caglioti, A. D. Site, M. Lenzi, and A. Mele, J. Chem. Soc., 1964, 5430.

[14] M. S. Matheson, Radiat. Res., Suppl., 4, 1 (1964).
[15] M. B. Fallgatter and R. J. Hanrahan, J. Phys. Chem., 69, 2059 (1965).
[16] R. M. Reese, V. H. Dibeler, and F. L. Mohler, J. Res. Nat. Bur. Stand., 57, 367 (1956).
[17] L. A. Rajbenbach, J. Phys. Chem., 73, 356 (1969).
[18] A. O. Allen, Radiat. Res., Suppl., 4, 54 (1964).
[19] J. C. J. Thynne and K. A. G. Macneil, J. Phys. Chem., 75, 2584 (1971).
[20] J. C. J. Thynne and K. A. G. Macneil, Int. J. Mass Spectrom. Ion Phys., 5, 329 (1970).

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