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Radiation-Induced Emulsion Copolymerization of Tetrafluoroethylene with Propylene.

II. Formulas and Conditions

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ABSTRACT

Formulas and reaction conditions for the radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene were studied at room temperature in the presence of gaseous monomers containing 50 mole % tetrafluoroethylene content. Stable latex was obtained by the use of ammonium perfluorooctanoate emulsifier. The resulting copolymer was a rubberlike material. A percentage of emulsifier greater than 1 wt% to water was suitable in this emulsion copolymerization. The conversion and the molecular weight were independent of the stirring speed above 400 rpm and decreased with a rise in temperature. An induction period was observed in the presence of oxygen. There was no effect of water purity on the emulsion copolymerization. When the stainless-steel reaction vessel was cleaned with a dilute acidic aqueous solution, the conversion was almost the same as that for a Pyrex reaction vessel.

INTRODUCTION

A few papers [1-3] have reported the radiation-induced copolymerization of tetrafluoroethylene with propylene.

Tabata et al. [1] studied the radiation-induced copolymerization of tetrafluoroethylene with propylene at low temperature in the liquid phase and found that the resulting copolymers ranged from viscous oils to rubberlike materials, depending on the polymerization conditions. They also observed that there were induction periods in these copolymerization, and that the rate of copolymerization was proportional to the square root of the dose rate.

Kojima et al. [2, 3] studied the radiation-induced bulk copolymerization and solution copolymerization of tetrafluoroethylene with propylene in chlorofluorohydrocarbon solvents and found that the resulting copolymers were amorphous and alternative over a wide monomer composition range. A remarkable accelerating effect of rate was also observed in these solution systems. The maximum values of molecular weights in solution systems are almost the same (12,000 ~ 14,000 at a polymerization temperature of 0°C), whereas the molecular weight observed in bulk polymerization is 23,000 at -23°C.

On the other hand, it is well known that in emulsion polymerization [4, 5] the rate of polymerization and the molecular weight are usually higher than those obtained in bulk or suspension. Therefore, the same effect is expected in the emulsion copolymerization of tetrafluoroethylene with propylene.

We [6] have studied the radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene in the presence of monomer droplets of 75 mole % tetrafluoroethylene content. It was found that ammonium perfluorooctanoate as emulsifier is suitable for obtaining a stable latex, and that the polymerization does not take place in the gaseous phase. The molecular weight was higher than those obtained in bulk and solution polymerization.

In order to elucidate the reaction mechanisms in detail, this study was carried out on several factors governing the emulsion copolymerization reaction in the gaseous monomer system of 50 mole % tetrafluoroethylene content. In this case it is considered that bulk polymerization does not take place and the ratio of monomer composition is kept constant during copolymerization.

In this paper we describe the relationships between the conversion or the molecular weight and the amount of monomer mixture added, stirring speed, and other factors. Information on the initiating species, the effect of acid, and hydrogen-peroxide photosensitized emulsion copolymerization will be reported later.

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 (FC-143, 96%) obtained from Minnesota Mining and Manufacturing Co. Other chemicals used were of reagent grade. The water was triply distilled [7] (ordinary distillation followed by distillations from acidic permanganate and dilute alkaline permanganate solutions). The water pH was 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. Emulsifier (0.8 g) (1 wt% to water) was put in the glass vessel. The autoclave was sealed, purged twice by evacuating and flushing with nitrogen pressure at 20 atm, and finally charged with 80 ml of nitrogen-saturated water and with 15 g of the tetrafluoroethylene-propylene mixture from the monomer reservoir (pressure of about 21 atm at room temperature). The temperature of the monomer reservoir was kept at 70°C throughout the experiment.

This emulsion system was irradiated with ^{60}Cobalt 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, 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 [2].

The number-average molecular weight $\overline{M}_n$ was calculated from

$$[\eta] = 2.46 \times 10^{-4} \overline{M}_n^{0.70} \tag{1}$$

RESULTS AND DISCUSSION

Amount of Monomer Mixture Added

In order to determine the optimum weight of the tetrafluoroethylene-propylene mixture in 80 ml of 1% ammonium perfluorooctanoate

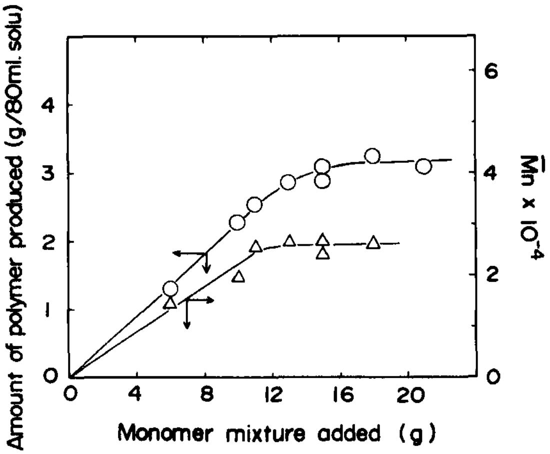

FIG. 1. Amount of polymer produced and molecular weight as functions of amounts of monomer mixture added. Irradiation dose: 5.9×10^5 R.

aqueous solution, the amount of monomer mixture added was changed from 6 to 30 g.

The relation between the amount of polymer produced and the amount of monomer mixture added is shown in Fig. 1. The amount of polymer increased linearly with the amount of monomer mixture up to 15 g of monomer mixture. Above 15 g of monomer mixture added, the amount of polymer was independent of the amount of monomer mixture added. Also, as shown in Fig. 1, the molecular weight was independent of the amount of monomer mixture above 11 g of monomer mixture. The effect on the amount of polymer produced suggests that the solubility of the monomer mixture reaches a saturation value in an aqueous solution. On the basis of the results, 15 g of monomer mixture per 80 ml of aqueous solution is suitable in this emulsion copolymerization. All experiments described hereafter were carried out in the presence of 15 g of monomer mixture.

Effect of Stirring Speed

Because this emulsion copolymerization is carried out in the presence of a gaseous monomer mixture, the contact area between the gaseous phase and the aqueous phase affects the conversion and the molecular weight. In order to clarify the effect of the stirring speed, the emulsion copolymerization was carried out from 200 to 600 rpm.

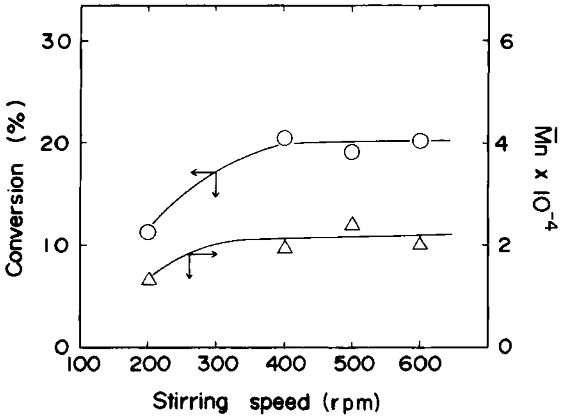

FIG. 2. Effect of stirring speed. Irradiation dose: 5.9×10^5 R.

Figure 2 shows the conversion and molecular weight vs stirring speed. Below 400 rpm, the conversion and the molecular weight were lower. These results suggest that the dissolution of gaseous monomer is a rate-determining step in this emulsion copolymerization up to 400 rpm. Above 400 rpm, the conversion and the molecular weight were independent of the stirring speed. In this case the copolymerization reaction is a rate-determining step.

Effect of Oxygen

Tabata et al. [1] have reported that there is an induction period in the radiation-induced copolymerization of tetrafluoroethylene with propylene at low temperature in the liquid phase. This seems to be due to the presence of trace amounts of oxygen in the system. In the case of emulsion polymerization, it must be considered that the polymerization reaction is affected by trace amounts of oxygen in the water.

Figure 3 shows the time conversion curves obtained in an air-saturated system and in a nitrogen-saturated system. It was observed that there is an induction period in the presence of air. In this system, oxygen is consumed during the first hour, and the rate of polymerization after the consumption of oxygen was consistent with that obtained in a nitrogen-saturated system. This suggests that the copolymerization may proceed by a free radical mechanism as is the case in bulk and solution copolymerization of tetrafluoroethylene with propylene.

In general, 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 to form the peroxy radical (RO_2).

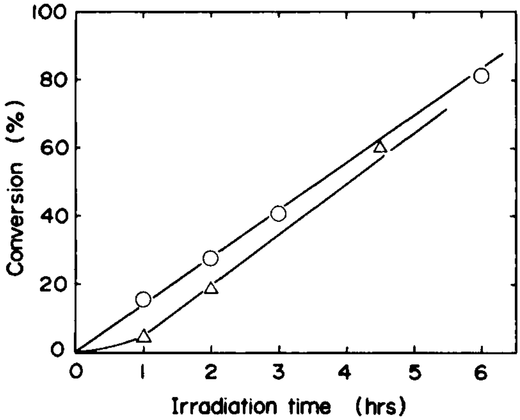

FIG. 3. Effect of air on conversion. Dose rate: 3.8×10^5 R/hr; (○) nitrogen saturation; (△) air saturation.

These radicals have a lower reactivity with monomer and finally disappear as nonradical products. The radiation-induced emulsion polymerization would be mainly initiated by primary radicals (H, OH radicals) from the radiolysis of water [8], and oxygen is a very efficient scavenger for hydrogen atoms, combining with them to give the perhydroxyl radical:

$$H + O_2 \longrightarrow HO_2 \qquad (2)$$

The HO_2 radical is not as reactive as the hydrogen atom. Therefore, the total initiating species concentration decreases and the conversion decreases in the presence of oxygen.

Also, as shown in Fig. 4, the molecular weight decreased in the presence of oxygen and was almost consistent with that obtained in a nitrogen-saturated system after the consumption of oxygen.

Effect of Temperature

In the radiation-induced emulsion polymerization of methyl methacrylate, vinyl acetate, and styrene [4], the rate of polymerization increases with a rise in temperature. A similar effect can be expected in this emulsion copolymerization of tetrafluoroethylene with propylene. The polymerization was carried out at a dose rate of 4.1×10^5 R/hr in the range from 25 to 50°C.

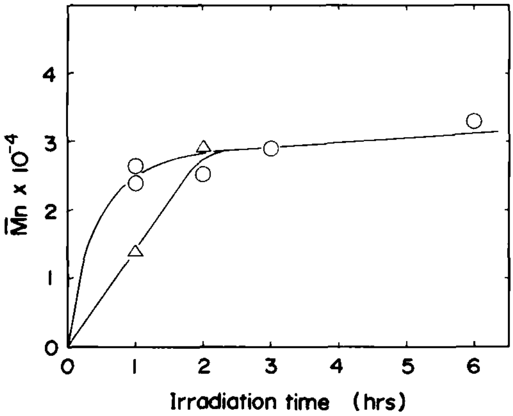

FIG. 4. Effect of air on molecular weight. Dose rate: 3.8 × 10^5 R/hr; (○) nitrogen saturation; (△) air saturation.

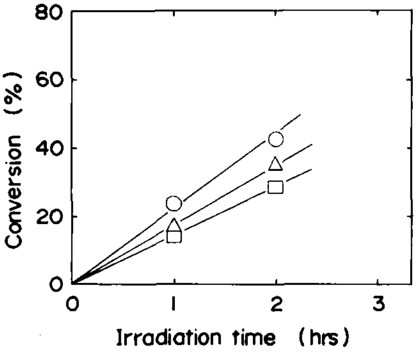

FIG. 5. Effect of temperature on conversion. Dose rate: 4.1 × 10^5 R/hr; (○) 25°C; (△) 40°C; (□) 55°C.

The relationship between conversion and irradiation time is shown in Fig. 5. The conversion increased linearly with the irradiation time, and decreased slightly with the rise in temperature. However, in the emulsion copolymerization of tetrafluoroethylene with propylene in the presence of monomer droplets [6], the conversion increased slightly with the rise in temperature. It may be assumed that such a difference is attributable to the solubility of monomer in an aqueous solution; that is, the solubility of monomer decreases with the rise in temperature because this emulsion copolymerization is carried out in

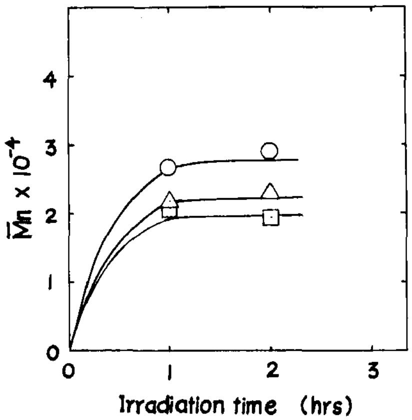

FIG. 6. Effect of temperature on molecular weight. Dose rate: 4.1×10^5 R/hr; (○) 25°C; (△) 40°C; (□) 55°C.

the absence of monomer droplets. It can therefore be assumed that the conversion decreases with the rise in temperature.

Figure 6 shows the effect of temperature on molecular weight. The molecular weight decreased slightly with a rise in temperature. This tendency was consistent with that in the emulsion copolymerization of tetrafluoroethylene with propylene in the presence of monomer droplets reported in the preceding paper.

It should be noticed that the result is remarkably different from that of the emulsion polymerization of methyl methacrylate, vinyl acetate, and styrene. Furthermore, the temperature dependence of the time conversion curve was different from that in bulk [3] and solution [4] copolymerizations of tetrafluoroethylene with propylene.

Amount of Emulsifier Added

In order to determine the optimum concentration of emulsifier, the copolymerization was carried out at a dose rate of 3.8×10^5 R/hr in the range from 0 to 3 wt% emulsifier to water.

The relationship between conversion and emulsifier concentration is shown in Fig. 7. The conversion increased steeply in the range from 0.3 to 1 wt% emulsifier, and increased linearly above 1 wt%. The relationship between molecular weight and emulsifier concentration is shown in Fig. 8. A similar tendency was observed in molecular weight in the range from 0.3 to 1 wt% emulsifier, and indicated a constant value above 1 wt%. These results suggest that the initiation

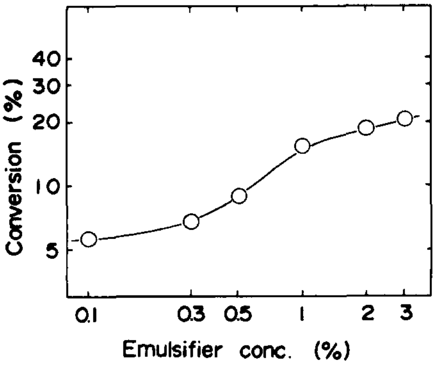

FIG. 7. Influence of emulsifier concentration on conversion. Irradiation dose: 3.8 × 10^5 R.

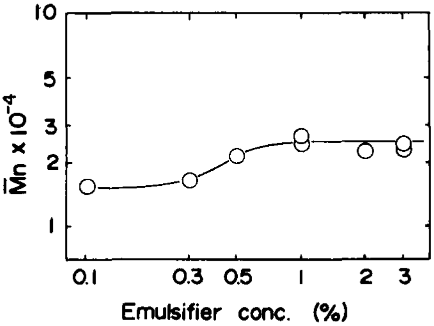

FIG. 8. Influence of emulsifier concentration on molecular weight. Irradiation dose: 3.8 × 10^5 R.

of copolymerization takes place in the micelle above 1 wt% emulsifier. Therefore, a percentage of emulsifier greater than 1 wt% to water is suitable for the emulsion copolymerization of tetrafluoroethylene with propylene.

Influence of the Purity of Water

The emulsion copolymerization is initiated by primary radicals (H, OH radicals) from the radiolysis of water. When some reactive organic impurities (RH) are present in water, they usually react rapidly with H and OH radicals [9]:

$$RH + H \longrightarrow R\ (\text{stable}) + H_2 \qquad (3)$$

$$RH + OH \longrightarrow R\ (\text{stable}) + H_2O \qquad (4)$$

and the conversion decreases.

In order to examine the influence of the purity of water, the emulsion copolymerization was carried out by using ordinary distilled water and triply distilled water.

The results are shown in Table 1. The conversion for ordinary distilled water was slightly higher than that for triply distilled water. On the other hand, the molecular weight was slightly lower. However, these were almost within experimental error. Consequently, there is no effect of the purity of water on emulsion copolymerization.

Influence of the Material of Reaction Vessel

In order to examine the influence of the material of the reaction vessel, emulsion copolymerization was carried out using a Pyrex reaction vessel and a stainless-steel reaction vessel.

The results are shown in Table 2. The conversion for the stainless-steel reaction vessel decreased remarkably, but the molecular weight did not change.

The phenomenon can be explained as follows. The emulsion copolymerization is initiated by primary radicals from the radiolysis of water. It is well known that OH and H radicals are scavenged by metallic ions [10]:

$$M^{+} + OH \longrightarrow M^{2+} + OH^{-} \qquad (5)$$

$$M^{2+} + H \longrightarrow M^{+} + H^{+} \qquad (6)$$

Therefore, OH and H radicals are scavenged by metallic ions eluted in the aqueous phase from the walls of the stainless-steel reaction

TABLE 1. Influence of Purity of Water[a]

Experimental conditions	Conversion (%)	Molecular weight ($\overline{M}_n$)
Triple-distilled water	14.7	2.8×10^4
Distilled water	15.5	2.7×10^4

[a] Irradiation dose: 3.8×10^5 R.

TABLE 2. Influence of Material of Reaction Vessel[a]

Experimental conditions	Conversion (%)	Molecular weight ($\overline{M}_n$)
Glass reaction vessel	15.5	2.7×10^4
Stainless-steel[b] reaction vessel	14.6	2.5×10^4
Stainless-steel[c] reaction vessel	11.8	2.4×10^4

[a] Irradiation dose: 3.8×10^5 R.
[b] Treatment with dilute acidic aqueous solution.
[c] Without treatment.

vessel, and the conversion decreases. However, when the stainless-steel reaction vessel was cleaned with a dilute acidic aqueous solution, the conversion was almost the same as that for the Pyrex reaction vessel.

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