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Radiation-Induced Emulsion Copolymerization of Tetrafluoroethylene with Propylene. I

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ABSTRACT

Formulus and reaction conditions for the radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene were studied at room temperature in order to obtain higher molecular weight copolymer than those obtained in bulk or solution. It was found that ammonium perfluorooctanoate as an emulsifier is most suitable to obtain a stable latex of high molecular weight copolymer with good reactivity. The high molecular weight copolymer is obtained by using the emulsifier at high mole fraction of tetrafluoroethylene under the saturated vapor pressure of the monomer mixture. The molecular weight range of copolymers obtained in this experiment was from 3.0×10^4 to 8×10^4, and these are higher than those obtained in bulk or solution.

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It was found that low molecular weight copolymer is a by-product of the polymerization in monomer droplets when the radiation-induced emulsion copolymerization is carried out in the presence of excess monomer. This is a characteristic feature of the radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene and has not been observed in common emulsion polymerizations.

INTRODUCTION

In 1964 Tabata et al. reported the radiation-induced copolymerization of tetrafluoroethylene with propylene at low temperature in the liquid phase [1]. In 1969 a patent of E. I. du Pont about a process of emulsion copolymerization of the same monomer system initiated by ammonium persulfate was registered in the United States [2]. Both reports stated that the copolymers obtained consist essentially of tetrafluoroethylene units and propylene units in the mole ratio of about 1:1 and are convertible to elastomers.

In order to develop and improve the process of copolymerization of tetrafluoroethylene with propylene, considerable research work has been carried out at the Japan Atomic Energy Research Institute by means of radiation initiation since 1967. Several Japanese patents relating to the processes of radiation-induced copolymerization have been issued [3-6]. More detailed investigations on radiation-induced bulk and solution copolymerization were reported [7, 8]. These papers reported that the copolymerization of tetrafluoroethylene with propylene proceeds to give a highly alternating copolymer in the molecular weight range of 0.4×10^4 to 5×10^4 in bulk and 1.0×10^4 to 3×10^4 in solution.

Furthermore, in the bulk copolymerization of tetrafluoroethylene with propylene, the copolymer was insoluble in monomers. Although the viscosity of the liquid phase is not greatly altered by the separation of polymer phase, the polymerizing system as a whole becomes stiff and difficult to agitate.

In solution copolymerization the monomers are dissolved in an appropriate solvent and polymerization is brought about by radicals produced from the radiolysis of solvent. The copolymer is soluble in 1,1,2-trichloro-1,2,2-trifluoroethane (R-113) and is insoluble in tert-butyl alcohol. In solution polymerization the viscosity increases greatly as the polymerization proceeds. As the result, agitation of the polymerizing system becomes difficult and results in poor dispersion of the heat of polymerization.

This heat accumulation, of course, leads to an increased rate of polymerization, and the "run-away" reaction may culminate in serious explosions.

It is thought that emulsion polymerization is suitable for the production of sticky, rubbery polymers such as tetrafluoroethylene-propylene copolymer. One of the principal advantages of emulsion polymerization is to obtain high molecular weight polymers.

In order to achieve excellent properties in elastomers, the molecular weight of polymers should be high enough. Cross-linking is easily obtained in the high molecular weight polymers and results in good mechanical properties.

From the point of practical application of radiation methods, emulsion polymerization may be one of the most suitable processes. Not only are the kinetic chain lengths usually extremely high due to the inherent peculiarities of the mechanism, but also the G value of water are high enough, being 5.5. The high rate of polymerization is due to the high concentration of growing chains compared with homogeneous systems. This arises from the isolation of the growing radicals in the emulsified particles, and this delays the mutual termination process, resulting in high molecular weight polymers.

In view of these factors, the radiation-induced emulsion copolymerization process of tetrafluoroethylene with propylene has been investigated in detail.

In this paper, we describe the processing equipment and the reaction conditions that are suitable for the copolymerization of tetrafluoroethylene with propylene in an emulsion system in order to obtain higher molecular weight copolymers.

EXPERIMENTAL

Materials

The tetrafluoroethylene (C_2F_4) used was obtained from Asahi Glass Co. (stated purity 99.9%). Propylene (C_3H_6) was supplied as a research grade (purity 99.7%) by Takachiho Kagaku Co., Tokyo. Fluorosurfactants were obtained from Ryoko Kagaku Co., Tokyo, and were produced by Minnesota Mining and Manufacturing Co., United States. Distilled water was used.

Apparatus and Procedure

The polymerization vessel used was a 200-ml stainless steel autoclave equipped with a magnetic coupled paddle-type agitator, the Bourdon gauge, a rupture disk for safety, and a valve for charge or purge of gases. The maximum pressure of the autoclave was 200 kg/cm^2. The schema is shown in Fig. 1.

Monomers and water were introduced into the autoclave by using a

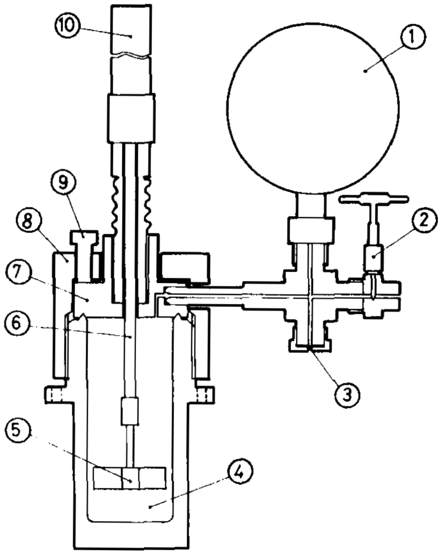

FIG. 1. A 200-ml autoclave with a magnetic coupled agitation system. (1) Pressure gauge, (2) valve, (3) rupture disk, (4) inside of autoclave, (5) paddle-type agitator, (7) flange, (8) cover of flange, (9) bolt, (10) magnetic coupled agitator.

stainless steel pressure line designed for the operation of gases at high pressure.

The autoclave was connected with the pressure line, and air in the autoclave was purged twice by evacuating and flushing with nitrogen gas and finally evacuated. Then monomer gases were supplied into the autoclave at liquid nitrogen temperature by the trap method in the order from propylene to tetrafluoroethylene. The amount of monomer introduced was determined from both the pressure drop of monomer gas in the reservoir and its volume. Then 100 ml of oxygen-free water was injected into the autoclave by a compressor through the pressure line. The necessary amounts of the emulsifier were put in the autoclave and it was sealed.

Irradiation

The irradiation was carried out at room temperature by γ-rays from ^{60}Co sources. In order to promote the diffusion of monomers in the aqueous phase, the reaction system was stirred for about 10 min before irradiation.

The dose rate inside of the autoclave was determined by the Fricke dosimeter.

Purification of Copolymers

After irradiation, residual monomer gases were removed.

Copolymers were isolated from the emulsion in an air oven at 90 to 100° C. The residues consist of copolymers and emulsifiers. Then the copolymers were dissolved in tetrahydrofuran. The solution was concentrated by the evaporation of solvent on a hot plate, and it was poured into a large quantity of methanol. Only copolymers were precipitated in methanol and washed by methanol more than two times. Then the copolymers were dried at 100° C for 16 hr and weighed.

Elemental Analysis

The carbon, fluorine, and hydrogen content in copolymers was measured by means of the elemental analysis to determine the copolymer composition. Fluorine was generated by combustion of copolymers in an oxygen-filled flask. After combustion, the HF formed was absorbed in water. The aqueous solution was titrated with 0.01 N sodium hydroxide by using a glass electrode and a caromel electrode.

Molecular Weight and Molecular Weight Distribution

Molecular weights were determined by measuring the viscosity of copolymers in tetrahydrofuran at 30° C, and using [7].

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

Molecular weight distribution was measured by GPC, Model 200, Waters Associates, at 30° C with tetrahydrofuran as the solvent.

RESULT AND DISCUSSION

Emulsifier

In emulsion polymerization, the emulsifier plays two important roles: the loci of polymerization and the stabilizer of the latex particles produced. Accordingly, it is important to select suitable emulsifier which promote the emulsion polymerization without coagulation of the polymers.

TABLE 1. Effects of Surfactants on Reactivity of the Emulsion Copolymerization[a] and on Latex Stability

Kind of surfactant	Notation	Main component	Ionic	CMC (wt%)	Polymer conversion (wt%)	Selective ratio of latex (wt%)	R_p[b] [g/(liter)(hr)]	$\overline{M}_n$[c]
Hydrocarbon	LT-221	Polyoxiethylene-monolaurate	Nonion	-	12.6	45.0	4.76	3.2×10^4
	NaLS	$C_{12}H_{25}NaSO_4$	Anion	-	14.7	56.1	6.90	3.4×10^4
Fluorocarbon	FC-95	$C_8F_{17}SO_3K$	Anion	0.22	15.1	56.2	7.15	7.8×10^4
	FC-98	$C_nF_{2n+1}SO_3NH_4$, $n = 4, 6, 8, \ldots$	Anion	Above 1.0	15.8	54.0	7.14	-
	FC-128	$C_8F_{17}SO_2N(C_2H_5)CH_2COOH$	Anion	0.38	14.0	56.3	6.61	-
	FC-143	$C_7F_{15}COONH_4$	Anion	0.68	15.4	75.5	9.73	7.8×10^4
	FC-170	$C_8F_{17}SO_2N(C_2H_5)(C_2H_4O)_{14}H$	Nonion	0.1	10.7	43.5	3.91	-
	FC-176	-	Nonion	-	12.7	69.5	5.83	5.6×10^4
Mixture	FC-143 + FC-170	FC-143 1.5%, FC-170 1.5%,	Anion + nonion		9.1	49.0	3.75	5.1×10^4
	FC-143 + NaLS	FC-143 1.0%, NaLS 2.0%			12.8	53.7	5.79	3.4×10^4

[a] Irradiation was carried out at a dose rate of 2.0×10^4 R/hr at room temperature for 10 hr.

[b] Rate of polymerization.

[c] The number-average molecular weight.

The polymerizations were carried out by using anionic surfactants, nonionic surfactants, and their mixtures. The results are summarized in Table 1.

The emulsion copolymerizations shown in Table 1 were carried out with C_2F_4/C_3H_6 in a molar ratio of 75/25, with an emulsifier concentration of 3.0% and at a dose rate of 5.0×10^4 R/hr. The irradiation time was 10 hr. A total of 84 g of monomer mixture was used.

It is obvious from the results of Table 1 that the rate of polymerization in the presence of anionic surfactants such as FC-143, FC-95, FC-98, and sodium lauryl sulfate is larger than in the case of a nonionic surfactant system, and that the selective ratio of latex (see Appendix) is usually low in polymerizations in which nonionic surfactants are used as the emulsifier. The latex stability was evaluated by the selective ratio of latex.

The molecular weights of copolymers obtained in the hydrocarbon surfactant system are lower than that in the fluorocarbon surfactant system. It is assumed that the hydrocarbon surfactant has small affinity with tetrafluoroethylene monomer or copolymer. In the case of copolymerization using FC-143, the molecular weight is the highest and the rate of polymerization is the largest. The reactivity in the FC-95 system is good, but the stability is not good. Neither reactivity nor stability is good in the mixed surfactant systems, that is, FC-143 and 170, or FC-143 and sodium lauryl sulfate, and the molecular weight is very low in these systems. The copolymer is colored by the impurity in the FC-128 system.

It was the main purpose of this work to obtain a stable latex of high molecular weight copolymers with a high polymerization rate. From this viewpoint, ammonium perfluorooctanoate of the anionic fluorocarbon surfactant FC-143 or FC-126 is a suitable emulsifier for reactivity and latex stability, and FC-143 is excellent for obtaining high molecular weight copolymer. Therefore, the surfactant FC-143 was used as the emulsifier in this study.

Effect of Stirring Speed

In emulsion polymerization, how the monomer is transferred to the chief loci of polymerization, i.e., the micelles and polymer particles, is an important problem. It appears that it must be transferred chiefly by diffusion through the true aqueous phase. The dominant determining factors of the diffusion process are the solubility of monomer in the aqueous phase and the surface area of monomer droplets.

In the emulsion copolymerization of tetrafluoroethylene with propylene, both monomers are slightly soluble in water. Therefore, stirring speed is a very important factor to determine whether the reaction proceeds as the rate- or the diffusion-determining process.

Effects of stirring speed on the conversion and the selective ratio of latex are shown in Fig. 2.

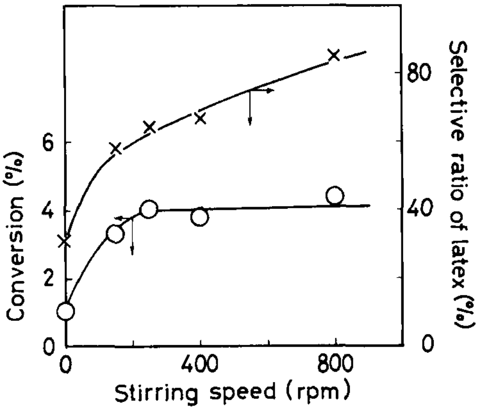

FIG. 2. Effect of stirring speed on polymerization rate and selective ratio of latex in emulsion copolymerization. Irradiation was carried out in the monomer mixture of C_2F_4/C_3H_6 with a molar ratio of 75/25 at room temperature at a dose rate of 1.0×10^4 R/hr for 5 hr. Fifty grams of the monomer mixture with emulsifier (concentration of 1.0% vs H_2O) was used.

The conversion rises up to about 250 rpm and then appears to level off. It was found that the polymerization proceeds by the monomer diffusion-determining step below 250 rpm. At stirring speeds above 250 rpm the monomers are supplied efficiently to the loci of polymerization. Conversion was observed even at 0 rpm. This indicates that monomers initially solubilized into micelles with stirring before irradiation polymerize slightly.

Emulsion polymerization using water-soluble initiators can generally be distinguished from suspension polymerization by using oil-soluble initiators. In the former, all of the initiators are generated in the aqueous phase. On the other hand, suspension polymerization is merely the normal bulk reaction occurring in small globules. However, high-energy radiation penetrates both the aqueous phase and monomer droplets, its energy is absorbed in the medium, along the path, and radicals are generated. The radicals directly generated in monomer droplets cause initiation in the normal bulk polymerization. Accordingly, in emulsion polymerization by radiation, both emulsion and suspension processes coexist in the reaction system when monomer droplets exist.

A comparison of the molecular weights of copolymers formed in bulk and emulsion copolymerization of tetrafluoroethylene with propylene under similar conditions is given in Table 2. Similar results were

TABLE 2. Comparison of Bulk and Emulsion Copolymerization of Tetrafluoroethylene with Propylene[a]

	Bulk	Emulsion
Dose rate	3×10^5 R/hr	3×10^5 R/hr
Polymerization rate	1.0%/hr	5.2%/hr
Molecular weight	2.1×10^4	6.0×10^4

[a] The reactions were carried out with C_2F_4/C_3H_6 in a molar ratio of 66/34.

obtained in the polymerization of styrene [9]. It is an inherent characteristics of the mechanism of emulsion polymerization that the kinetic chain length is usually extremely high. The long kinetic chain lengths are due to the high concentration of growing chains compared with homogeneous systems. This arises from the isolation of growing radicals in the emulsified particles, thus delaying the mutual termination process.

The molecular weight of the copolymer of nonlatex in this emulsion copolymerization, as described in the next section, is apparently much lower than that of latex. It seems, in view of the low molecular weight, that the copolymer of nonlatex was produced by a bulk reaction in droplets of excess monomer.

The selective ratio of latex increased with increased stirring speed. This can be explained as follows. Under the condition of low stirring speed, there are a small number of monomer droplets of large volume in the reaction system together with solubilized large amounts of monomers in micelles and water. In this case, polymerization in the monomer droplets cannot be neglected. Since several growing radicals are generated in the same large droplet, they easily recombine, and as the result the low molecular weight copolymer is produced. Under high stirring speed conditions, these monomer droplets are crushed to a large number of small particles. If the size of the monomer droplet is small enough, polymerization conditions become similar to emulsion polymerization as far as the number of radicals produced in the droplet is concerned. Then none or one radical is generated in each particle, and polymerization in the particles proceeds as in emulsion polymerization. A radical in one particle cannot terminate with radicals in another particle or propagate until another radical invades the particle. Consequently, the number of loci of polymerization is apparently increased by means of high stirring speed. The long propagation time of each radical is preserved, and the stable emulsion of the high molecular weight copolymer is obtained.

Although two kinds of polymers are formed in radiation-induced emulsion polymerization in most cases, they are indistinguishable each other.

In our system, copolymers obtained in latex can be clearly distinguished from those obtained in monomer droplets. This is the characteristic feature of the radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene. This is discussed later.

The following experiments were carried out at 800 rpm to obtain highly selective ratios of latex.

Polymerization Rate and Molecular Weight of Copolymer

The relation between concentration of latex (see Appendix) and irradiation time is shown in Fig. 3.

In the presence of monomer droplets, the experimental data give linear plots. The copolymerization is considered to proceed in a stationary state up to the limiting conversion (see Appendix), which is about 41.5% in this experiment.

The emulsion copolymerization of tetrafluoroethylene with propylene proceeds in the aqueous phase regardless of the amounts of monomer mixture added.

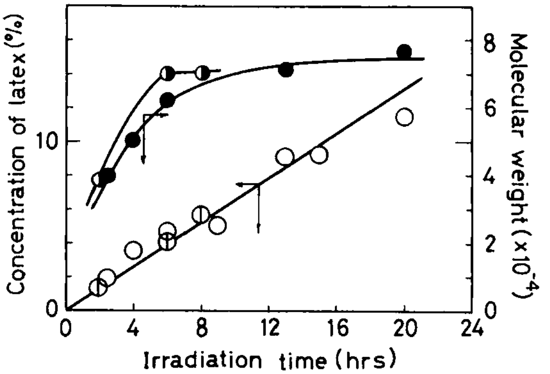

FIG. 3. Polymerization rates and molecular weights of copolymers in emulsion copolymerization. Irradiation was carried out in the monomer mixture of C_2F_4/C_3H_6 with a molar ratio of 75/25 including emulsifier (concentration of 3.0% vs H_2O) at a room temperature at a dose rate of 2.0×10^4 R/hr under stirring at 800 rpm.

In general, at the early stage of reaction the polymer particles are produced from the micelles at a constant rate; that is, the reaction proceeds in a nonstationary state. In this experiment the so-called induction reaction period was not observed in the polymerization.

The molecular weight of copolymer obtained is also shown in Fig. 3 as a function of irradiation time.

The molecular weight increases gradually and then reaches a constant value. In contrast to the polymer yield, the variation of molecular weight increased only at the early stage of the reaction. In this region the reaction is in the diffusion-determining step. After all the micelles have disappeared, the number of polymer particles and the rate of polymerization are kept constant, and it is assumed that equilibrium is established between the propagating and the terminating reactions.

Effects of Amounts of Monomer Mixture Added

Figure 4 shows the effects of the amounts of monomer mixture on

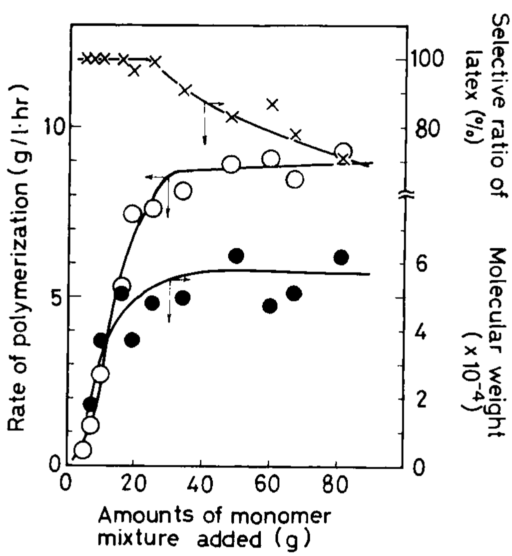

FIG. 4. Polymerization rates, molecular weights of copolymers, and selective ratio of latex as functions of amounts of monomer added in emulsion copolymerization. Irradiation was carried out in a monomer mixture of C_2F_4/C_3H_6 with a molar ratio of 75/25 in the presence of the emulsifier (concentration of 3.0% vs H_2O) at room temperature at a dose rate of 2.0×10^4 R/hr for 6 hr under stirring at 800 rpm.

the rate of polymerization, the molecular weight of copolymers, and the selective ratio of latex.

The rate of polymerization increases rapidly with the monomer concentration and level off above 20 g. The amount of monomer mixture in 20 g of this reaction system is equal to the maximum liquefied quantity of the monomer mixture at room temperature [10]. The rate of polymerization increases linearly with the pressure of monomer gas below the maximum liquefied concentration of monomer mixture, and saturates above that concentration. Its value is kept constant at 9 g/liter hr in the system of 0.75 mole fraction of tetrafluoroethylene. And above the liquefied concentration, excess monomer mixture exists in the state of liquid monomer droplets.

From the results the copolymerization in polymer particles emulsified proceeds as a rate-determining process above the liquefied concentration; that is, above the saturated vapor pressure of the monomer mixture at the temperature. Below this point, polymerization proceeds as a diffusion-determining process.

The molecular weights of copolymers show the same tendency as the rate of polymerization and may be similarly explained. The value of the molecular weight leveled off at 6×10^4 in Fig. 4.

The selective ratio of latex is 100% below the liquefied point, and gradually decreases above it. In the presence of excess monomer above 20 g, both emulsion and suspension polymerization coexist in the same reaction system as described in the section on the stirring speed. Two kinds of copolymers were obtained above the concentration of 20 g. One is high molecular weight copolymer in latex and the other is a sticky low molecular weight copolymer which adhered to the wall of the reactor as a nonlatex. The low molecular weight copolymers obtained as a nonlatex are produced by bulk reaction in monomer droplets. A comparison of the two forms of copolymers are shown in Table 3, and their molecular weight distributions are shown in Fig. 5.

Molecular weights and their distributions are distinctly different.

The fraction of polymerization in monomer droplets increased with the amounts of monomer mixture above the liquefied point. Sticky copolymers adhered to the walls of the reactor and the stirrer, and disturbed smooth stirring. Furthermore, irregularity of the molecular weights is caused by homogeneous mixing of the latex above the liquefied point.

It is desirable, therefore, that the reaction be carried out at the saturated vapor pressure of the monomer mixture without excess monomer droplets.

In this experiment the reactions were carried out at a concentration of 25 g. The most desirable condition is that the reactions are carried out at the liquefied point and that the consumed monomer mixture is constantly led into the reactor during irradiation. The study of this continuous feed experiment will be reported later.

TABLE 3. Molecular Weight and Its Distribution in Two Kind of Copolymers Obtained in Emulsion Copolymerization in the Presence of Monomer Droplets[a]

Copolymer	Yield (g)	Molecular weight $\overline{M}_n$ ($\times 10^4$)	$\overline{M}_n/\overline{M}_w$
Latex	10.0	8.1	3.54
Nonlatex	2.0	2.9	3.07

[a] Irradiation was carried out at room temperature at a dose rate of 2×10^4 R/hr for 13 hr. The molar ratio of C_2F_4 to C_3R_6 was 75/25, and 84 g of the monomer mixture with 3.0% emulsifier was used. The reactants were stirred at a rate of 800 rpm.

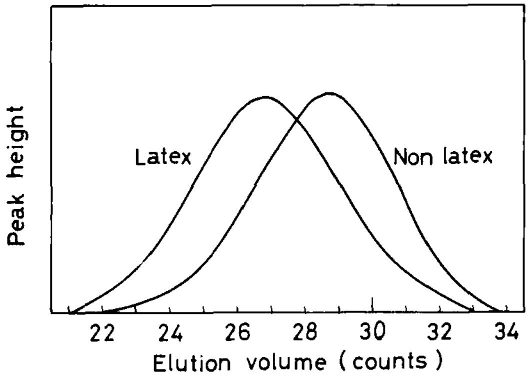

FIG. 5. Distributions of molecular weights of copolymers from latex and nonlatex.

Effects of Concentration of Tetrafluoroethylene in Monomer Mixture

Both the polymerization rate and the molecular weight of the copolymers were profoundly affected by the initial monomer composition as shown in Fig. 6.

The polymerization rate increases rapidly with the concentration of tetrafluoroethylene in the monomer mixture. It increases about 14 times as the tetrafluoroethylene concentration varies from 10 to 90 mole %. The molecular weight of the copolymer also increases remarkably with tetrafluoroethylene concentration in the initial monomer mixture.

The composition curve of tetrafluoroethylene-propylene copolymers is shown in Fig. 7.

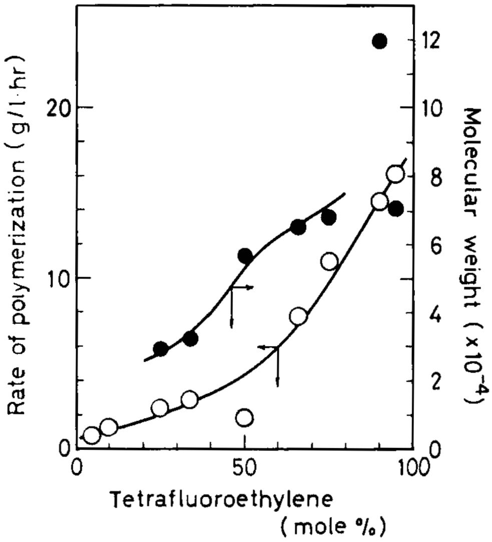

FIG. 6. Relation between concentration of C_2F_4 in copolymer and that in monomer mixture in emulsion copolymerization. Irradiation was carried out at room temperature at a dose rate of 3.0 × 10^4 R/hr under stirring at 800 rpm. Eighty-four grams of the monomer mixture was used with the emulsifier (3.0% vs H_2O) in this experiment.

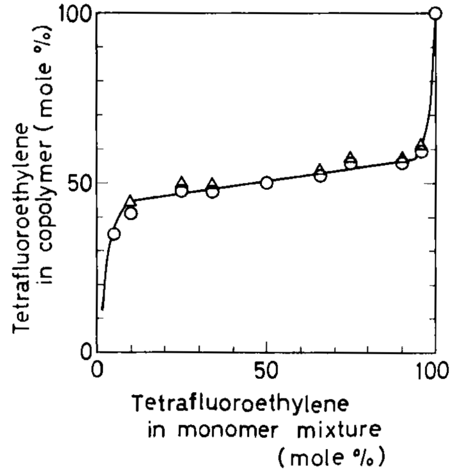

FIG. 7. Polymerization rate and molecular weight of copolymers as a function of molar concentration of C_2F_4 in monomer mixture in emulsion copolymerization.

TABLE 4. Effects of Temperature on Polymerization Rate and Molecular Weight[a]

Temperature (°C)	Dose rate (R/hr)	Concentration of emulsifier (% vs H_2O)	Rate of polymerization [g/(liter)(hr)]	Selective ratio of latex (%)	Molecular weight ($\times 10^4$)
0	2×10^4	3.0	6.0	70	7.2
25			7.0	61	7.1
50			7.5	-	4.7

[a] Content of tetrafluoroethylene in monomer mixture: 75 mole %. Stirring speed: 800 rpm.

It is abvious that copolymer composition changes very slightly with the concentration of tetrafluoroethylene in the initial monomer mixture in a wide range of monomer composition. In the range from 0.1 to 0.9 mole fraction of tetrafluoroethylene, the copolymer obtained consist essentially of tetrafluoroethylene units and propylene units in a mole ratio of about 1:1. It seems that the copolymers have the same alternative construction as do those in bulk or solution [7, 8].

The experimental results mentioned above were analyzed below a conversion of 18 wt%. However, at higher conversions the polymerization becomes rather complicated. With an initial molar ratio of tetrafluoroethylene to propylene of 3.0, homopolymerization of tetrafluoroethylene starts to take place at about 41.5 wt% conversion, since almost equal moles of both monomers are consumed.

Temperature Dependency of Polymerization

The effects of temperature on the copolymerization are summarized in Table 4.

It is apparent from the results that the rate of polymerization is not strongly dependent on temperature. However, the average molecular weight decreases with increasing temperature. In order to obtain high molecular weight copolymers with a high rate of polymerization, emulsion polymerization is better carried out at room temperature.

It is concluded that for the purpose of obtaining a high molecular weight copolymer with a high polymerization rate, it is desirable for the reaction to be carried out at the saturated vapor pressure and with a high content of tetrafluoroethylene in the monomer mixture. High molecular weight copolymers of 6×10^4 to 8×10^4 were obtained in this study.

APPENDIX

The definitions of terms used in this report:

(1) Limiting conversion (wt%) = conversion when either tetrafluoroethylene or propylene is consumed completely. For example, when copolymerization is carried out with an initial molar ratio of tetrafluoroethylene and propylene of 3, the limiting conversion is 41.5 wt%, since an almost equal number of moles of both monomers are consumed.

(2) Selective ratio of latex (wt%) = weight of copolymer in latex (g)/weight of total copolymer (g) (× 100). Note: Total copolymer = copolymer in latex + sticky copolymer as nonlatex.

(3) Concentration of latex (wt%) = concentration of copolymer in

latex = weight of copolymer in latex (g)/weight of latex (g) (× 100).

(4) Rate of polymerization (g/liter hr) = weight of copolymer in latex (g)/unit volume of water in latex (liter) unit hour (hr).

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