Emulsifier-Free Emulsion Polymerization of Tetrafluoroethylene by Radiation. IV. Effects of Additives on Polymer Molecular Weight

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Synopsis

Poly(tetrafluoroethylene) (PTFE) of high molecular weight, 4.5 × 10^7, was incidentally obtained at earlier study of an emulsifier-free emulsion polymerization of tetrafluoroethylene by radiation. In order to clarify this phenomenon, the effects of additives, in particular radical scavengers, on the molecular weight of PTFE and its polymerization behavior were studied. It was found that the molecular weight of PTFE is increased by the addition of hydroquinone, benzoquinone, α-pinene, *dl*-limonene, and ethylenediamine but is decreased by oxygen and triethylamine. A PTFE latex with molecular weight higher than 2 × 10^7 was obtained in the presence of hydroquinone. It is concluded that additives such as hydroquinone and benzoquinone, which rapidly scavenge the primary radicals (OH·, H·, and e_{aq}^-) in the aqueous phase but not the growing polymer radicals in PTFE particles, are most effective in increasing the molecular weight.

INTRODUCTION

In general the molecular weight of poly(tetrafluoroethylene) (PTFE) prepared by radiation-induced polymerization in solution and in emulsion is very low as compared with commercial PTFE. For example, PTFE molecular weight was ca. 1 × 10^6 in solution polymerization by Fujioka et al.[1] and Tabata et al.,[2,3] ca. 2 × 10^6 in emulsion polymerization by Yonetani,[4] and below 1 × 10^6 in emulsion polymerization with use of ammonium perfluorooctanoate (FC-143) by Suwa et al.[5] Furthermore, the molecular weight increases up to 3 × 10^6 in emulsifier-free emulsion polymerization as described in the first paper of this series.[6] This molecular weight is still lower than "dispersion" or "fine powder" grade PTFE (3 × 10^6 to 1 × 10^7) prepared by conventional emulsion polymerization with use of chemical initiators.

A few PTFE samples of molecular weight more than 10^7 were incidentally obtained during the course of an earlier study of an emulsifier-free system. This fact is noteworthy from the viewpoint of preparing PTFE latex of high molecular weight comparable to that of "molding powder" (above 2 × 10^7). We were then interested in the reason why such a high molecular weight PTFE was produced.

The present paper, the fourth of the series, deals with the effects of some additives such as oxygen, hydroquinone, benzoquinone, α-pinene, *dl*-limonene, triethylamine, and ethylenediamine on the polymer molecular weight and polymerization behavior.

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EXPERIMENTAL

Polymerization Procedure

The polymerization procedure was almost the same as that described in the previous paper.[6] The standard reaction conditions were: dose rate, 3.0×10^4 rad/hr; temperature, 70°C; initial pressure, 20 kg/cm^2; *n*-hexadecane, 4 ml; 150 ml twice-distilled water in 200-ml autoclave; agitation speed, 500 rpm.

Additives

Reagent-grade oxygen, cetyl iodide, Freon R-114, hydroquinone, benzoquinone, *dl*-limonene, α-pinene, triethylamine, and ethylenediamine were used as additives without further purification. Oxygen was charged into the reactor as air- or oxygen-saturated water through bubbling. In the case of large addition of O_2, oxygen was charged as TFE–O_2 mixed gas. Hydroquinone, benzoquinone, triethylamine, and ethylenediamine were charged each as aqueous solutions. Cetyl iodide, *dl*-limonene, and α-pinene were charged by pipetting. TFE monomer containing a stabilizer and Feon R-114 were charged at the required pressure.

Determination of Molecular Weight

The molecular weight of PTFE was determined from the heat of crystallization measured with a Perkin-Elmer 1B differential scanning calorimeter (DSC) by using the following relation between number-average molecular weight ($\overline{M}_n$) and heat of crystallization (ΔH_c in cal/g)[7]:

$$\overline{M}_n = 2.1 \times 10^{10}\, \Delta H_c{}^{-5.16}$$

Measurements of Particle Size and Distribution

An automatic particle analyzer PA-101 (Union Giken Co. Ltd.) was used. The detailed procedure was described in the previous paper of this series.[8]

RESULTS AND DISCUSSION

Polymerization Curve and Polymer Molecular Weight

As shown in Table I, though we incidentally found a high molecular weight PTFE ($\overline{M}_n$ 4.5×10^7) in run 186, no such high molecular weight product was obtained in subsequent experiments under the same conditions (run 219). Figure 1 shows the polymerization curves (polymer concentration versus reaction time). In run 186, the curve is sigmoid, that is, the rate of polymerization was very small at the initial stage and gradually accelerated with reaction time. On the other hand, in run 219, the rate increased rapidly in the initial stage and gradually decreased with reaction time. The reduced rate in the initial stage in run 186 suggests that the starting materials in this reaction system were contaminated by some impurity acting as a retarder.

TABLE I

Effect of Oxygen on Polymer Yield, Molecular Weight, and Particle Diameter[a]

Run no.	O_2 Added		Polymer yield			$\overline{M}_n \times 10^{-6}$	Particle diameter	
	Procedure	Amounts (moles/l.) × 10^5	W_c, (g)	V_1, g/l.	V_t, g/l.		D_n, Å	D_w, Å
186	—	0	0.76	39.5	44.6	45.0	1890	2180
219	—	0	0	45.9	45.9	0.69	2040	2190
260	air bubbling	3.94	2.66	28.8	46.5	1.70	2300	2530
261	O_2 bubbling	18.5	2.88	17.8	37.0	0.96	—	—
265	5 ml	20.4	2.34	20.9	36.5	0.95	1560	1830
262	10 ml	40.9	1.60	2.54	35.2	0.48	—	—

[a] W_c, amount of polymer coagulated during polymerization; V_1, polymer concentration in latex; V_t, polymer concentration containing the coagulated polymer. Reaction conditions: initial pressure, 20 kg/cm^2; temperature, 70 °C; dose rate, 3×10^4 rad/hr; reaction time, 150 min; n-hexadecane, 4 ml; 150 ml water in 200-ml autoclave.

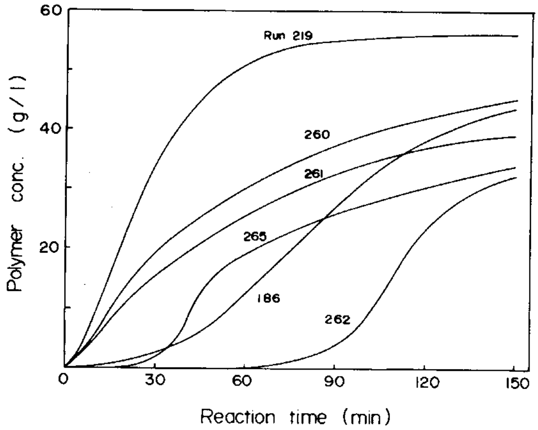

Fig. 1. Polymerization curves in the absence of additive and in the presence of oxygen. Reaction conditions are given in Table I.

Effect of Possible Impurities

The starting materials in this reaction system were TFE monomer, water, and a small amount of n-hexadecane. Possible impurities were (1) oxygen; (2) residual α-pinene or dl-limonene used as a stabilizer of TFE; (3) cetyl iodide contained in n-hexadecane; (4) Freon contained in TFE. The polymerization curve and polymer molecular weight in the presence of these possible impurities were compared with those in run 186.

Oxygen

Figure 1 shows the polymerization curves in the presence of various amounts of oxygen. The reaction conditions and the polymer molecular weight are shown in Table I. As the amount of oxygen increases, the initial polymerization rate decreases and the induction period increases. The curve of run 265 is similar to that of run 186 in the initial stage; rate reduction due to coagulation of the latex was observed near 50 min of reaction time. However, the polymer molecular weight of run 265 was much lower than that of run 186. The behavior of run 186 cannot be explained by the effect of oxygen.

Since oxygen can easily diffuse into PTFE particles,[9] it reacts not only with the primary radicals in the aqueous phase but also with the growing polymer radicals in the particles. Consequently, both chain initiation and propagation are retarded.

TFE Stabilizer, Cetyl Iodide, and Freon R-114

The results of the polymerization of TFE containing a TFE stabilizer, cetyl iodide, and Freon R-114 are summarized in Table II. The polymerization curves in Figure 2 are not remarkably changed, and the polymer molecular weight increases to some extent in the presence of the additives.

In summary, high molecular weight PTFE and a polymerization curve similar to that of run 186 could not be obtained by the addition of the above possible impurities. The difference between run 186 and run 219 is not due to the impurities and not yet clear. However, it should be noted that the polymer mo-

TABLE II

Effect of Impurities on Polymer Yield, Molecular Weight, and Particle Diameter[a]

Run	Additives			Polymer yield				Particle diameter	
		Amount,							
no.	Additive	vol-%	ml	W_c, g	V_1, g/l	V_t, g/l.	$\overline{M}_n \times 10^{-6}$	D_n, Å	D_w, Å
274	Stabilizer	1.7		1.71	39.9	51.3	0.93	—	—
275	Stabilizer	8.3		1.76	41.3	53.0	1.37	—	—
278	Stabilizer	16.7		2.13	37.2	51.4	2.50	—	—
279	Stabilizer	83.3		1.20	49.6	57.6	5.95	1650	1840
302	cetyl iodide		0.08	2.49	37.1	53.7	2.67	—	—
303	cetyl iodide		0.20	0	42.9	42.9	1.71	1810	1970
304	cetyl iodide		0.80	2.03	39.9	53.5	2.32	—	—
305	cetyl iodide		2.0	0	46.6	46.6	1.40	2240	2410
313	Freon R-114	1.5		0	49.5	49.5	4.26	—	—
314	Freon R-114	5.0		1.53	43.5	53.7	2.97	2290	2460

[a] Symbols and reaction conditions same as in Table I.

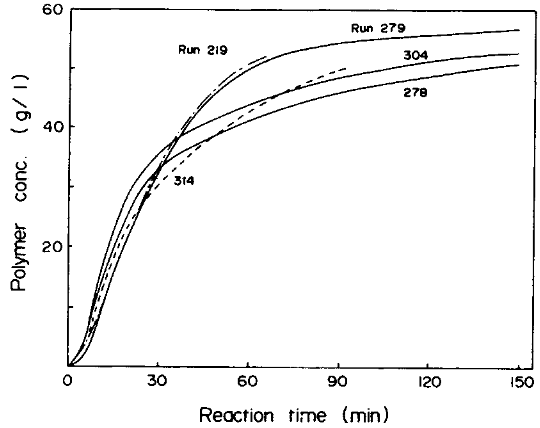

Fig. 2. Polymerization curves in the presence of TFE containing a stabilizer, cetyl iodide, and Feon R-114. Reaction conditions are given in Table II.

lecular weight is increased by the addition of stabilizer, cetyl iodide, and Freon R-114, contrary to the usual effect of inhibitors.

Effect of Radical Scavengers

In the emulsion polymerization, high molecular weight polymer may be obtained by the addition of radical scavengers which capture primary radicals in the aqueous phase but cannot diffuse into the polymer particles to terminate growing radicals.

The polymerization was carried out in the presence of the following additives: (1) hydroquinone (QH_2) and benzoquinone (Q), which are highly soluble in water and scarcely soluble in PTFE particles and have very large rate constants for the reaction with OH·, H·, and e_{aq}^-; (2) ethylenediamine (EDA) and triethylamine (TEA), which are also soluble in water, but whose rate constants with OH· and H· are smaller than those of QH_2 and Q; (3) α-pinene and *dl*-limonene, which are used as a stabilizer of TFE monomer and whose rate constants with OH·, H·, and e_{aq}^- are unknown.

The rate constants of all the reactions involved in the radiolysis of water are now known.[10,11] All of the radical–radical reactions of OH·, H·, and e_{aq}^- are extremely fast (ca. $10^{10}M^{-1}$ sec^{-1}). The rate constants of QH_2, Q, TEA, and EDA for the reaction with OH·, H·, and e_{aq}^- are shown in Table III. Benzoquinone reacts rapidly with both OH· and e_{aq}^-, while QH_2 reacts rapidly with OH· but slowly with e_{aq}^-.[11] In alkaline solutions, at pH values where amines are deprotonated, the rate constants of amines with OH· are greatly increased and close to $10^{10}M^{-1}$ sec^{-1}, while the rate constants of amines with e_{aq}^- are rather low, 10^6M^{-1} sec^{-1} for deprotonated amines and two to three times larger for protonated amines.[13] Since the aqueous phase of this polymerization system is acidic due to the formation of HF,[15] the reactivities of amines with OH· and e_{aq}^- are much lower than those of QH_2 and Q.

TABLE III

Comparison of Rate Constants for OH·, e_{aq}^-, and H· Reactions with Some Solutes[a]

Solute	Rate constant, M^{-1} sec^{-1}			Reference
	OH· (pH)	e_{aq}^- (pH)	H· (pH)	
Hydroquinone	1.2×10^{10} (7)	$< 10^7$ (13)	— —	11, 12
Benzoquinone	1.2×10^9 (ca. 7)	1.35×10^9 (6.6)	3.1×10^9 (1)	12
Ethylamine	3.0×10^8 (3.1)	1.0×10^6 (13)	— —	13
Ethylamine	1.3×10^{10} (12)	— —	— —	13
Ethylenediamine	ca. 3.5×10^7 (4)	— —	— —	11
Triethylamine	3.5×10^8 (3.6)	— —	— —	13
Triethylamine	8.0×10^9 11.0	— —	— —	13

[a] The rate constants for e_{aq}^- with amines are ca. $10^6 M^{-1}$ sec^{-1}.[13,14]

Hydroquinone and Benzoquinone

Table IV and Figure 3 show the results of polymerization at various concentrations of QH_2 and Q. In the presence of QH_2 (solid line), the curve of run 272 at the concentration of 2.20×10^{-4} mole/l. is similar to that of run 186. Moreover, the molecular weight of polymer formed is very high (2×10^7), comparable to that of run 186. With increasing concentration of QH_2, this polymerization gives not only high molecular weight but also a long induction period.

In the presence of Q (dotted line), the curve is also similar to that of run 186. However, when comparing QH_2 and Q at the same concentration (runs 264 and 324, runs 272 and 322), it can be seen that the Q gives longer induction period and lower polymer molecular weight. The induction period decreases with increasing dose rate from 3.0×10^4 rad/hr (run 322) to 8.0×10^4 rad/hr (run 323); and even at a higher dose rate (run 323), Q gives a longer induction period than QH_2 (run 273).

As shown in Table III, the rate constant of QH_2 with OH· is extremely large compared with H· and e_{aq}^-. Therefore, the polymerization is mainly initiated by H· and e_{aq}^- in the presence of QH_2. On the other hand, since the reactivity of Q with the above three species is considerably large, most of the species may be captured by Q and the induction period becomes longer than that of QH_2.

Triethylamine and Ethylenediamine

Table V and Figure 4 show the results of polymerization in the presence of TEA and EDA. The induction period with TEA is longer than that with EDA, but shorter than with QH_2 and Q. As shown in Table III, since the rate constants of amines with OH· and e_{aq}^- are smaller than those of QH_2 and Q, the initiating radicals are less effectively captured by the amines than by QH_2 and Q.

The marked decrease in the polymerization rate is observed in all polymerization curves at relatively low conversion. This is due to the coagulation of the latex.[6] As shown in Table IV and V, pH and conductivity of aqueous solutions of the amines are higher than those of QH_2 and Q aqueous solutions. The large ionic strength of the amine solutions causes the coagulation of the latex.

The polymer molecular weight is increased by the addition of EDA, while it is decreased by TEA. Since TEA has a low surface tension (below 18 dynes/cm above 40°C[16]) and is easily adsorbed on the surface of PTFE particles, it may effectively react with the growing radicals on the surface leading to a decrease in molecular weight.

TABLE IV

Effects of Hydroquinone (QH_2) and Benzoquinone (Q) on Polymer Yield, Molecular Weight, and Particle Diameter[a]

Run	Reaction conditions					Polymer yield				Particle diameter	
no.	Additive	(moles/l.) ×10^4	pH	$\kappa \times 10^5$	Time, min	W_c, g	V_1, g/l.	V_t, g/l.	$M_n \times 10^{-6}$	D_n, Å	D_w, Å
264	QH_2	0.55	—	—	150	1.36	42.7	51.7	3.38	1740	1950
271	QH_2	1.10	6.45	0.565	150	1.79	33.3	45.2	5.00	1670	1910
272	QH_2	2.20	6.25	0.303	150	0	34.0	34.0	20.8	1610	1890
273	QH_2	4.41	6.05	0.710	150	0	37.0	37.0	27.5	1760	2130
324	Q	0.55	6.15	0.281	120	0.84	36.2	41.8	2.73	1430	1720
322	Q	2.20	5.65	0.175	225	0	17.5	17.5	3.96	1320	2100
323[b]	Q	4.60	5.55	0.220	240	0	34.5	34.5	3.39	1580	2100

[a] κ, Conductivity of aqueous solution in Ω^{-1} cm^{-1}; other symbols same as in Table I. Reaction conditions: initial pressure, 20 kg/cm^2; temperature, 70°C; dose rate, 3 × 10^4 rad/hr; *n*-hexadecane, 4 ml; 150 ml aqueous solution in 200-ml autoclave.

[b] Dose rate of 8.0 × 10^4 rad/hr.

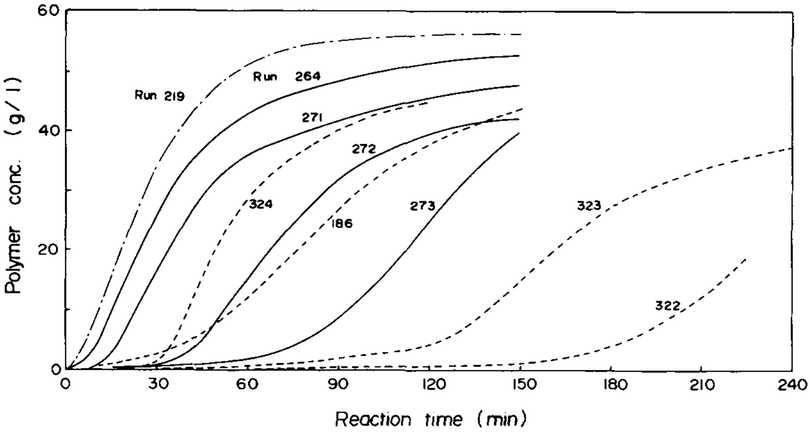

Fig. 3. Polymerization curves in the presence of hydroquinone and benzoquinone. Solid and dotted lines show the additions of hydroquinone and benzoquinone, respectively. Reaction conditions are given in Table IV.

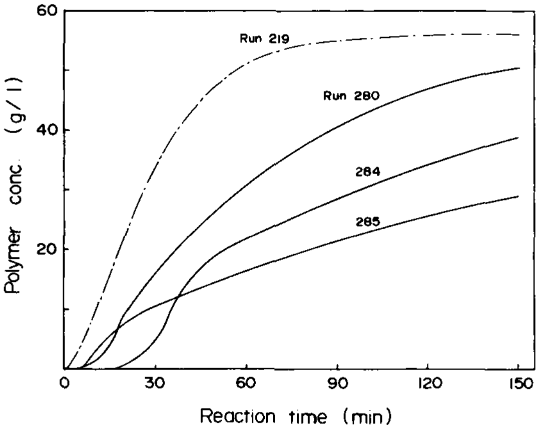

Fig. 4. Polymerization curves in the presence of ethylenediamine and triethylamine. Reaction conditions are given in Table V.

dl-Limonene and α-Pinene

Table VI and Figure 5 show the results of polymerization in the presence of *dl*-limonene and α-pinene. As the amount of *dl*-limonene increases in the order of runs 282, 281, and 277, the induction period increases, and especially in run 277 the polymerization scarcely proceeds. *dl*-Limonene (run 281) gives a longer induction period and a higher molecular weight PTFE than α-pinene (run 283) at the same concentration. The molecular weight of polymer obtained in the presence of these additives is comparable to that of "fine powder."

The effect of the additives on the molecular weight of the polymer is summarized in Figure 6. Taking into consideration some factors such as induction period, stability of the latex, and rate of polymerization, the addition of QH_2 is most preferable for obtaining the high molecular weight PTFE.

TABLE V

Effects of Triethylamine (TEA) and Ethylenediamine (EDA) on Polymer Yield, Molecular Weight, and Particle Diameter[a]

Run	Reaction conditions					Polymer Yield				Particle diameter	
no.	Additive	(moles/l.) × 10^4	pH	$\kappa \times 10^5$	Time, min	W_c, g	V_1, g/l.	V_2, g/l.	$M_n \times 10^{-6}$	D_n, Å	D_w, Å
280	TEA	2.20	9.65	2.20	150	1.69	33.7	45.0	0.32	—	—
284	TEA	4.61	10.3	5.00	150	1.95	22.8	35.8	0.25	1490	1620
285	EDA	4.61	9.90	3.40	150	3.12	6.98	27.8	3.20	2220	2340

[a] Symbols and reaction conditions same as in Table IV.

TABLE VI

Effects of *dl*-Limonene and α-Pinene on Polymer Yield, Molecular Weight, and Particle Diameter[a]

Run	Additives		Polymer yield				Particle diameter	
no.	Additive	Amounts (moles/l.) × 10^5	W_c, g	V_1, g/l.	V_t, g/l.	$\overline{M}_n \times 10^{-6}$	D_n, Å	D_w, Å
277	*dl*-Limonene	12.3	0	0.3	0.3			
281	*dl*-Limonene	3.08	0	53.3	53.3	7.15	1460	1690
282	*dl*-Limonene	0.617	1.94	41.1	54.0	4.20		
283	α-Pinene	3.15	0	47.9	47.9	5.70	1720	1930

[a] Symbols and reaction conditions same as in Table I.

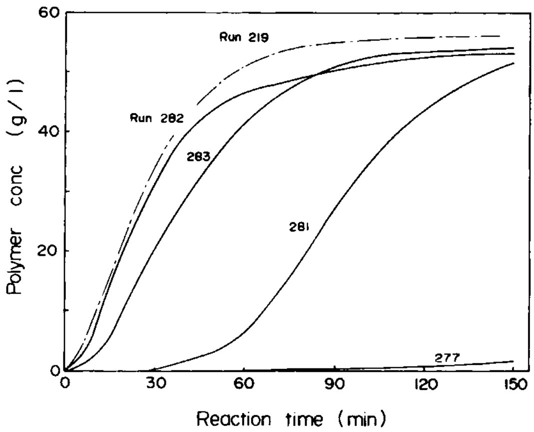

Fig. 5. Polymerization curves in the presence of *dl*-limonene and α-pinene. Reaction conditions are given in Table VI.

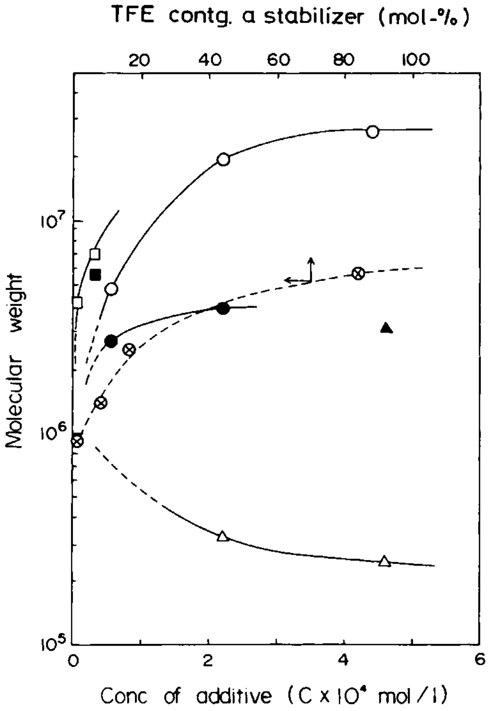

Fig. 6. Effect of additives on molecular weight of PTFE. Additives: (●) benzoquinone; (○) hydroquinone; (▲) ethylenediamine; (△) triethylamine; (■) α-pinene; (□) *dl*-limonene; (⊗) TFE containing a stabilizer. Reaction conditions are the same as in Table IV.

Effects of Dose Rate and Temperature in the Presence of QH_2

Table VII and Figure 7 show the results of the polymerization in the presence of QH_2 at various dose rates and temperatures. As the dose rate increases in the order of runs 273, 286, and 291 at QH_2 concentrations of 4.61×10^{-4} mole/l., the induction period decreases, the rate of polymerization increases, and the polymer molecular weight considerably decreases.

TABLE VII

Effects of Dose Rate and Temperature on Polymer Yield, Molecular Weight, and Particle Diameter in the Presence of Hydroquinone[a]

Run	Reaction Conditions			Polymer Yield				Particle diameter	
Run no.	Dose rate, (rad/hr) × 10^{-4}	Temp., °C	QH_2 concn., (moles/l.) × 10^4	W_c, g	V_1, g/l.	V_t, g/l.	$\overline{M}_n \times 10^{-6}$	D_n, Å	D_w, Å
289	3.0	50	4.61	0	34.7	34.7	18.3	1700	2030
273	3.0	70	4.41	0	37.0	37.0	27.5	1760	2130
290	3.0	80	4.61	0.06	4.99	5.36	3.11	1650	2580
288[b]	3.0	90	4.61	0.05	1.70	2.01	—	—	—
286	8.0	70	4.61	0.44	39.0	41.9	14.9	1740	2070
287	8.0	70	10.0	0.52	27.2	30.7	16.1	1760	2190
291	14.6	70	4.61	0	43.9	43.9	3.77	1590	1880

[a] Symbols same as in Table I. Reaction conditions: initial pressure, 20 kg/cm^2; n-hexadecane, 4 ml; 150 ml aqueous solution in 200-ml autoclave; reaction time, 150 min.

[b] Reaction time 210 min.

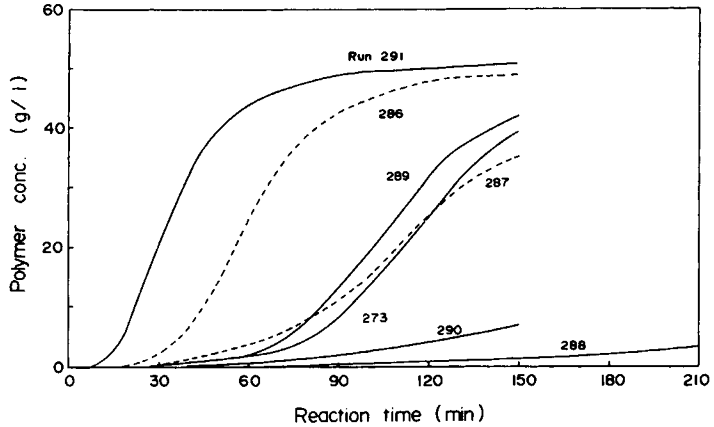

Fig. 7. Polymerization curves in the presence of hydoquinone at various dose rates and temperatures. Reaction conditions are shown in Table VII.

Figure 8 shows the induction period divided by QH_2 concentration (t_{ind}/c) versus dose rate (I) and the rate of polymerization (R_p) versus QH_2 concentration (c). The value of t_{ind}/c varies inversely with the dose rate, as usually observed. As the concentration of QH_2 increases the polymerization rate decreases, while the molecular weight increases as described above. The QH_2 concentration exponent of the polymerization rate after the induction period is −0.28 and −0.8 at dose rates of 3×10^4 rad/hr and 8×10^4 rad/hr, respectively.

As shown in Figure 7, the polymerization rate decreases with rising temperature from 50 to 70°C and markedly decreases from 70 to 80°C. The extremely low polymerization rate above 80°C may be due to the prolonged induction period. On the other hand, the polymerization rate slightly decreases with temperature above 70°C in the absence of QH_2 as described in the previous paper.[6] These results may be ascribed to the complex behavior of QH_2.

Adams and Michael have proposed the following reaction mechanism of QH_2 aqueous solution[12]:

$$QH_2 + \cdot OH \rightarrow QH_2OH \tag{1}$$

$$QH_2OH \rightarrow QH + H_2O \tag{2}$$

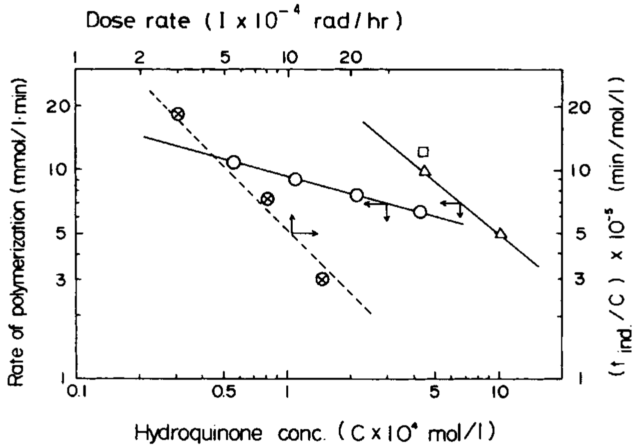

Fig. 8. Logarithmic plots of rate of polymerization vs. hydroquinone concentration and t_{ind}/c vs. dose rate. Reaction conditions are given in Table VII.

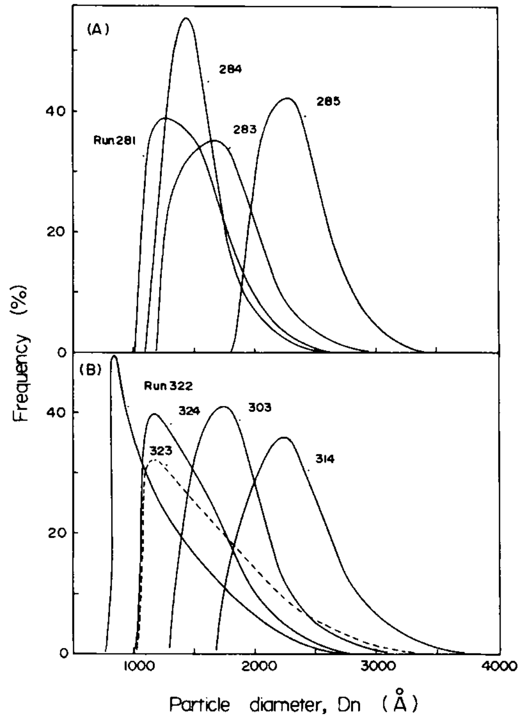

Fig. 9. Particle size distributions of PTFE prepared in the presence of various additives. See tables for identification of runs.

$$QH \rightleftharpoons Q^- + H^+ \tag{3}$$

$$QH + QH \rightleftharpoons Q + QH_2 \tag{4}$$

The semiquinone (QH) produced via reactions (1) and (2) regenerates QH_2, accampanied by the formation of Q. These species again capture the initiating radicals produced during polymerization. The rate of production of OH· radicals by radiolysis is independent of temperature. However, reactions (2) and (4) may have large temperature dependence, and the increase in induction period at high temperatures is probably due to increase in the regeneration of QH_2 and Q.

Particle size and distribution

The number-average diameter (D_n) and weight-average diameter (D_w) measured by the centrifugation method are shown in the previous tables. Typical distribution curves of the latex particles prepared in the presence of various additives are shown in Figure 9.

The values of D_w/D_n for most latices that lie in the range from 1.05 to 1.20 show the distributions are considerably sharp. The latices prepared in the presence of Q have broad distributions. In the case of QH_2, the particle diameter is $D_n = 1700$ Å, $D_w = 1900$–2100 Å, and is almost independent of the QH_2 concentration. The diameter decreases slightly with increasing dose rate. The diameter of particles obtained in the presence of Q is smaller than that in the presence of QH_2. As shown in Figure 9(d) the distribution curve of high molecular weight PTFE prepared in the presence of QH_2 (run 273) is similar to that of run 186 and broader than that of run 219 obtained in the absence of additives. The particle

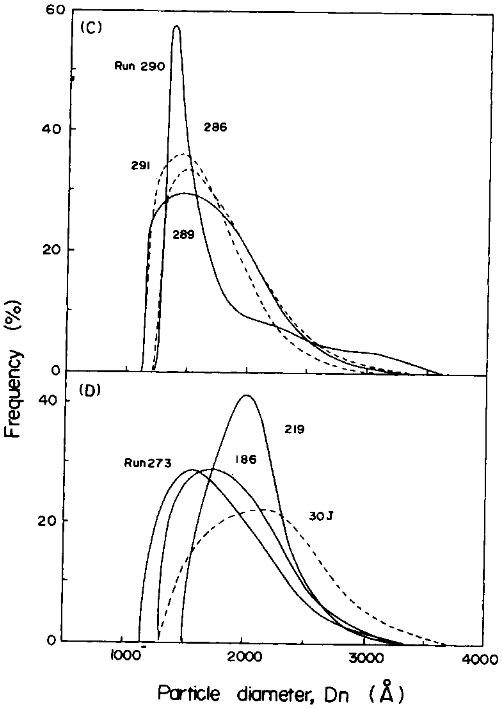

Fig. 9. (*Continued from previous page.*)

diameter of run 273 is smaller than that of "dispersion 30J" of the Mitsui Fluoro Chemical Co.

Reaction Mechanism of Radical Scavengers

As shown in Figures 3 and 4, the polymerization of TFE in the presence of QH_2, Q, and EDA slowly proceeds in the early stage or in the induction period; then the rate increases to the maximum, which is lower than that in the absence of the scavenger and decreases with the amount of scavenger. It should be noted that the polymer molecular weight is increased by the addition of scavengers.

In the early stage of the reaction, most of the primary radicals formed from the radiolysis of water are trapped by the scavenger, but some start the polymerization. The polymer thus early produced forms latex particles, e.g., particles with 350-Å diameter at polymer concentration of 0.1 g/l.[8] After the latex particles are formed, the polymerization mainly proceeds in the particles by the radicals entered from the aqueous phase. The radical scavengers QH_2, Q, and EDA having poor affinity to PTFE cannot scavenge growing radicals in the polymer particles, and mainly scavenge radicals in the aqueous phase. Accordingly, the polymerization in the particles proceeds at a reduced initiation rate leading to the formation of higher molecular weight polymer. On the other hand, TEA and O_2 having larger affinity for PTFE probably scavenge the radicals in the polymer particles; therefore the polymerization with these additives shows a lower polymerization rate and gives lower molecular weight products.

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