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K. Yoshida^{ab}; K. Ishigure^{ac}; H. Garreau^a; V. Stannett^a

^a Department of Chemical, Engineering North Carolina State University Raleigh, North Carolina ^b On leave from the Japanese Atomic Energy Research Institute, Takasaki, Japan ^c On leave from the Department of Nuclear Engineering, University of Tokyo,

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Radiation and Chemical Grafting of Styrene to Polybutadiene Latex

K. YOSHIDA,* K. ISHIGURE,[†] H. GARREAU, and V. STANNETT

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27650

ABSTRACT

Earlier studies of the gamma radiation and potassium persulfate grafting of styrene to uncrosslinked small particle size polybutadiene latices have been extended to a commercial crosslinked large particle size latex. The larger size particles and high gel content of the substrate latex was found to lead to a more complicated pattern of behavior. The conversion curves and the molecular weights were found to be complex functions of the initial monomer concentration, number of particles and temperature with both methods of initiation. The simple Smith-Ewart theory did not, in general, apply to these systems, and the k_p and E_p varied with conditions and were not in agreement with the generally accepted literature values. The molecular weights of the extracted polystyrene homopolymer were lower in the case of radiation initiation, in agreement with the previous work. This suggests that shorter but numerous grafted side chains are possible with radiation presumably due to the higher radical fluxes. (Some parallel experiments indicated that the

*On leave from the Japanese Atomic Energy Research Institute, Takasaki, Japan.

[†]On leave from the Department of Nuclear Engineering, University of Tokyo.

molecular weights of the extracted homopolystyrene are similar to those of the grafted side chains.) This phenomenon also leads to somewhat lower graft efficiency with radiation initiation. Nevertheless, radiation was found to give grafting efficiencies of more than 80% under the best conditions. The conversions were also quite efficient with economical yields per radiation dose. These results, coupled with the ease of control and other features of radiation, make it a viable alternative method of initiation for industrial use.

INTRODUCTION

In a previous paper [1] the results of a study of radiation and chemically initiated (potassium persulfate) grafting of styrene to two uncrosslinked polybutadiene latices of small particle size were reported. It was found that the Smith-Ewart theory applied and that the values obtained for the propagation rate constant for styrene were in good agreement with the accepted literature values. The molecular weights of the grafted side chains were found to be lower with radiation initiation than those formed under similar conditions with potassium persulfate. The possibility of forming more numerous but shorter grafted side chains is interesting and was attributed to the high radical fluxes obtainable with radiation.

In this paper, some similar studies, but with a commercial cross-linked polybutadiene latex of large particle size often used in industrial high impact polystyrene formulations are reported.

EXPERIMENTAL

Materials

Styrene was obtained from the Eastman Kodak Company. It was washed with a 5% aqueous solution of potassium hydroxide and distilled water, dried over Drierite, and then distilled under reduced pressure.

Polybutadiene latex was obtained from the Firestone Rubber Company. Its code name was Firestone FR-2004. In Table 1, the properties of the original latex are shown. The original latex was rather viscous and was used after dilution with distilled water. The number of particles N was calculated from the original particle size and concentration and the dilution ratio.

Experimental Methods

Measured amounts of latex and styrene were placed in glass ampoules of OD 2.0 cm and 15 cm long. The ampoules were then

TABLE 1. Properties of the Polybutadiene Latex Used (Firestone 2004)

Total solids (%)	60.1
Total soap (%)	2.16
pH	10.7
Coagulum - 80 mesh (%)	0.01
Toluene gel (Max) (%)	89
Avg particle diameter (Å)	2400
Specific gravity of latex (25°/25°)	0.95

placed in a dry box which was filled with nitrogen, Nitrogen gas was also passed into the latex-monomer mixture for about 10 min in order to remove the dissolved oxygen. The ampoules were then sealed off and stored under refrigeration until irradiation. The ampoules were irradiated in a ^{60}Co source which was placed in a swimming pool-type reservoir, using the agitation apparatus specially devised for this purpose and described previously [2]. The reaction temperature was controlled by circulating constant temperature water through the unit.

After irradiation, the ampoules were immersed in a Dry Ice-methanol mixture to stop the reaction. The ampoules were then opened and the reaction mixture thawed and poured into a saturated solution of sodium chloride in order to coagulate the latex. The precipitated polymers were filtered, washed with water and methanol, and dried under vacuum. From the weight increases of the polymer the reaction rates and the monomer conversions were calculated.

Extraction of Homopolymer

It was necessary to extract the homopolymer from the reaction products in order to estimate the grafting efficiency. Polybutadiene (PBD) and polystyrene (PSt) have almost the same solubility in various solvents. They have very similar solubility parameters; i. e., 8.4 for PBD [3] and 8.75 for PSt [4]. It is difficult, therefore, to separate mixtures of these two polymers. A few solvents have been used, however, for the separation of these two components. Acetone was used by Moore [5] for the separation of ABS resin. A mixture of benzene and methyl ethyl ketone (MEK) was used by Blanchette [6] for graft copolymers of GR-S and styrene, toluene - MEK mixtures were used by Cigna [7], and MEK alone was used by Manaresi [8], Toluene (or benzene)-MEK mixtures are good solvents for PSt but at the same time dissolve a considerable amount of PBD. PBD is also fairly soluble in MEK when Soxhlet extraction is used. Extraction with cold

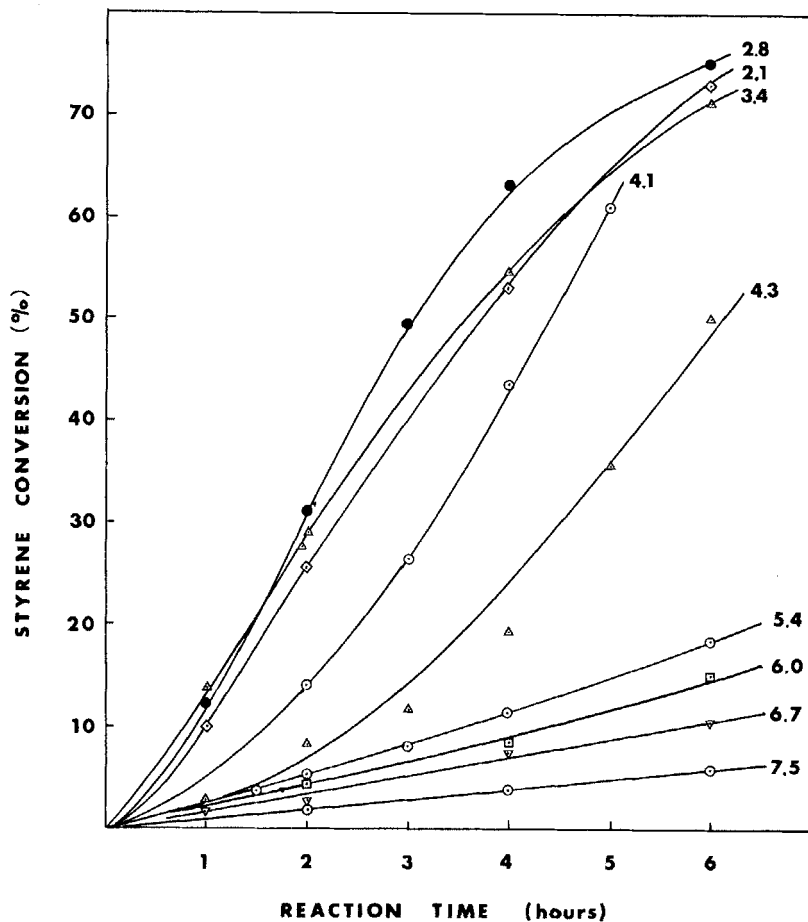


FIG. 1. Conversion curves for the polymerization of styrene in PBD latex at 25°C, $N = 7.3 \times 10^{14}$, dose rate = 0.12 Mrad/hr. The numbers refer to the monomer concentration (mole/liter).

MEK is more suitable and only a limited amount of PBD is extracted, whereas PSt is essentially completely extracted.

This extraction method is very sensitive to the extraction condition such as temperature, amount of solvent, the extraction time and the state of the polymer. After an initial rapid decrease, the weight unextracted with MEK was found to be almost constant for eight days.

The following extraction method was therefore used: about 1 g of the crude polymer was mixed with 60 ml of MEK in a glass bottle. The mixtures were agitated for 8 days at room temperature. The

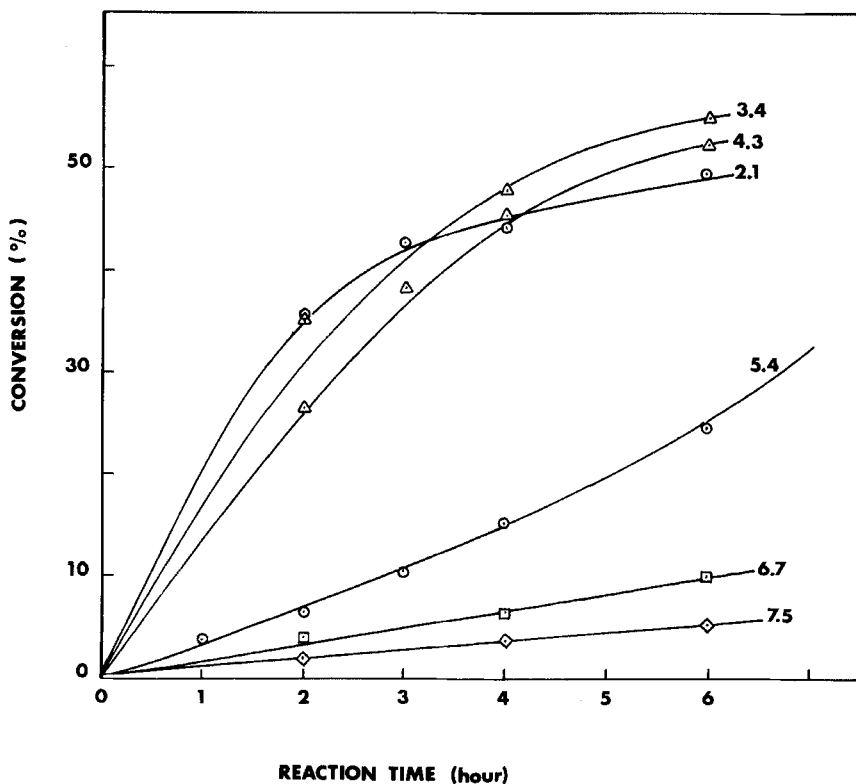


FIG. 2. Conversion curves for the polymerization of styrene in PBD Latex at 25°C, $N = 3.2 \times 10^{14}$, dose rate = 0.12 Mrad/hr. The numbers refer to the monomer concentration (mole/liter).

insoluble polymer was then filtered, washed with cold MEK, and dried under vacuum.

The homopolystyrene in the filtrate was recovered by precipitation in methanol. The viscosities of the homopolymer were measured at 30°C using a toluene as a solvent. The molecular weights were calculated from the equation [9]:

$$[\eta] = 12.0 \times 10^{-5} M^{0.71} \quad (1)$$

RESULTS

A number of variables were studied for both radiation-initiated and chemical-initiated grafting; these included the influence of

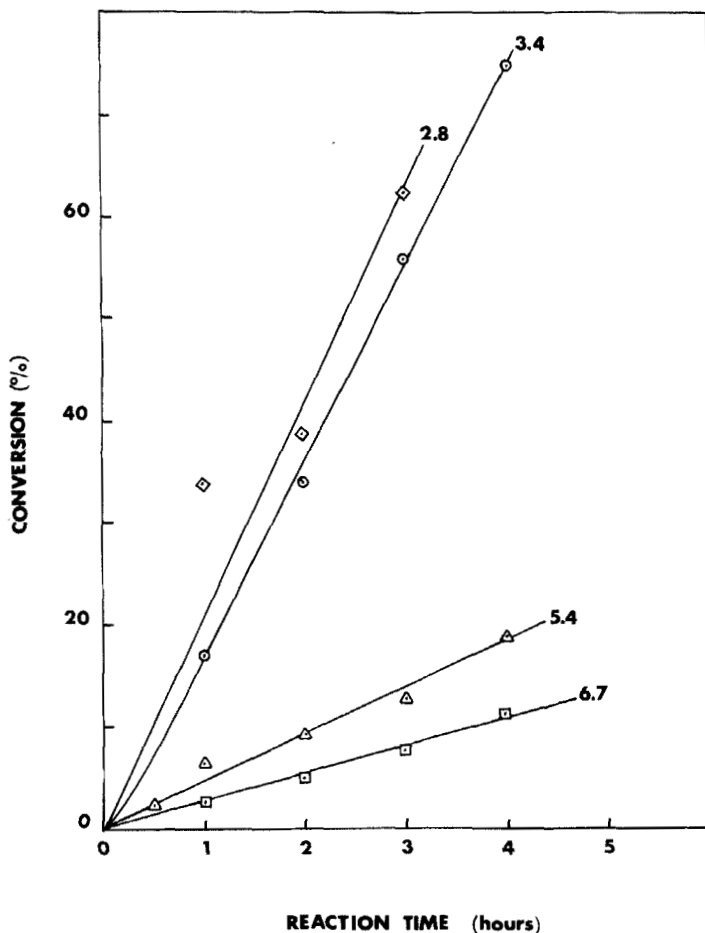


FIG. 3. Conversion curves for the polymerization of styrene in PBD Latex at 40°C , $N = 7.3 \times 10^{14}$, dose rate = 0.12 Mrad/hr . The numbers refer to the monomer concentration (mole/liter).

monomer concentration, the number of particles, the dose rate or initiator concentration, and the temperature on the rates of polymerization. The molecular weights of the extracted homopolystyrene were also determined.

In these experiments, the monomer concentrations were calculated with the assumption that all the monomer dissolved in the polymer particles. This is reasonable, since the experiments were carried out at lower concentrations than the maximum solubility of styrene in PBD; i. e., 7.5 mole/liter at 25°C .

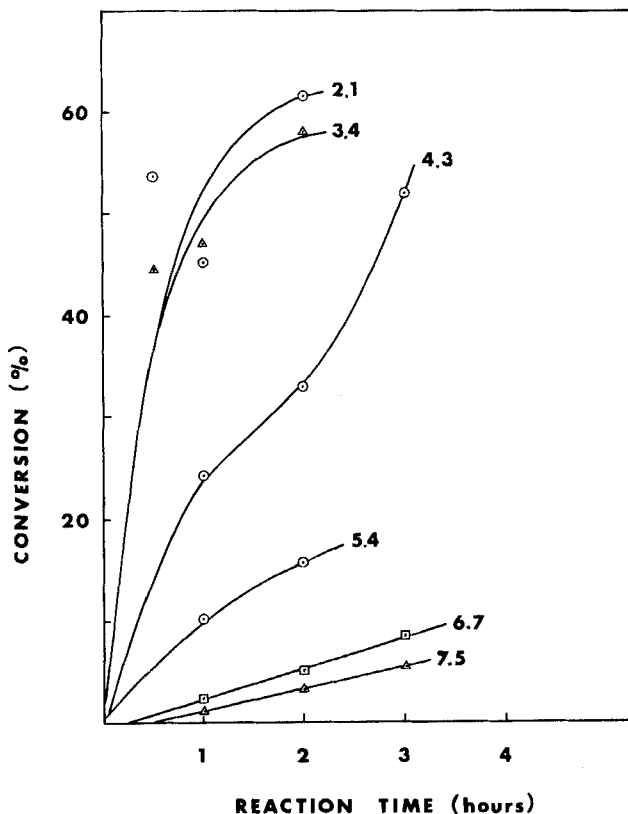


FIG. 4. Conversion curves for the polymerization of styrene in PBD Latex at 40°C , $N = 3.2 \times 10^{14}$, dose rate = 0.12 Mrad/hr . The numbers refer to the monomer concentration (mole/liter).

Radiation-Induced Grafting

The influence of the initial monomer concentration in the latex particles on the rate was studied by measuring the weight increase of PBD as a function of reaction time, for different initial monomer concentrations at 25°C , the number of particles N , being 3.2×10^{14} and 7.4×10^{14} particles/cm³. Similar experiments were also run at 40°C ; from these studies, the time-conversion curves were calculated and are presented in Figs. 1 to 4.

In Fig. 1, we can see that at very high monomer concentrations, the curves were almost linear, the weight increases were linear when plotted versus reaction time for $[M] = 6.7$ and $[M] = 7.5$ mole/liter. When the concentration was lowered, an acceleration in the rate was

TABLE 2. G Values for the Polymerization of Styrene in PBD Latex, $N = 3.2 \times 10^{14}$

Dose rate (Mrad/hr)	Monomer concn (mole/liter)	G value	
		25° C	40° C
0.12	2.1	1.4×10^4	4.0×10^4
	3.4	1.3×10^4	3.8×10^4
	4.3	9.6×10^3	1.8×10^4
	5.4	2.7×10^3	6.5×10^3
	6.7	1.3×10^3	2.5×10^3
	7.5	7.2×10^2	1.7×10^3
0.053	2.1	2.7×10^4	4.8×10^4
	3.4	2.7×10^4	7.9×10^4
	4.3	2.2×10^4	4.5×10^4
	5.4	5.8×10^3	-
	6.7	2.9×10^3	-
	7.5	1.6×10^3	-

observed; this is especially apparent at 4.1 and 4.3 mole/liter. In the low monomer concentration range, a slight saturation in the reaction rate was found to occur when the monomer conversion reached 40-60%.

In Fig. 2, corresponding to a smaller value of N , saturation was reached at a lower conversion. At 40°C, for high particle numbers, the conversion was linear versus time at any monomer concentration, while in Fig. 4 (small N) the same saturation effect was observed: briefly, low temperatures and small values of N lowered the conversion. The origin of this saturation effect will be discussed further.

To measure the efficiency of the polymerization process the G value for the reaction has been calculated and the results are summarized in Table 2. They range from 10^3 to 10^5 , higher G values being obtained for lower monomer concentrations.

But as a measure of the real graft efficiency G_r the value G_r was calculated from the extraction (with MEK at room temperature) data. The definition of G_r is as given in Eq. (2):

$$G_r = [T(1 - s) - B(1 - X)]/S \quad (2)$$

where S = amount of styrene polymerized, T = amount of crude polymer

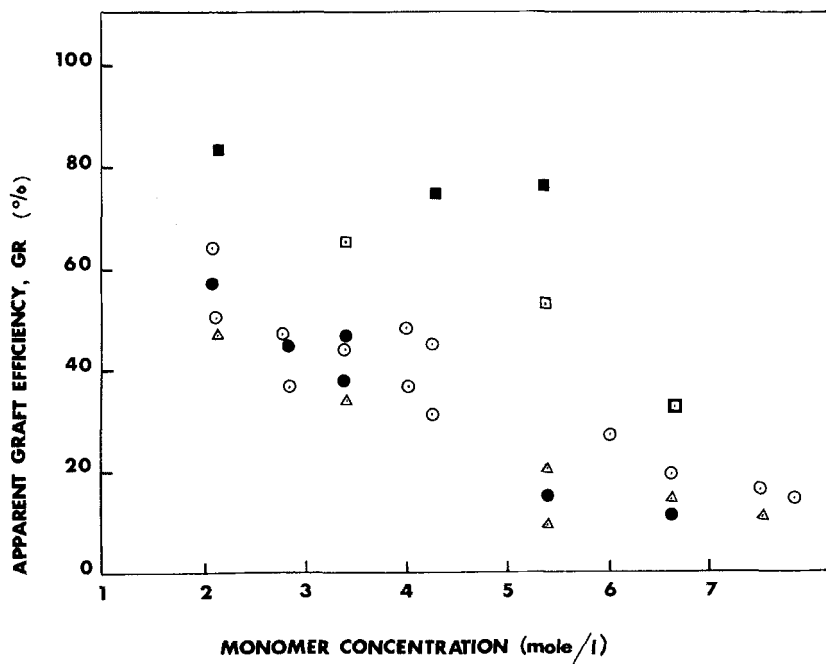


FIG. 5. Apparent graft efficiencies for radiation-induced polymerizations: (○) 25°C, $N = 7.3 \times 10^{14}$, dose rate = 0.12 Mrad/hr; (●) 40°C, $N = 7.3 \times 10^{14}$, dose rate = 0.12 Mrad/hr; (△) 25°C, $N = 3.2 \times 10^{14}$, dose rate = 0.12 Mrad/hr; (□) 25°C, $N = 3.2 \times 10^{14}$, dose rate = 0.053 Mrad/hr; (■) 40°C, $N = 3.2 \times 10^{14}$, dose rate = 0.053 Mrad/hr.

used for extraction, B = amount of PBD in crude polymer, X = fraction of PBD soluble in MEK, and s = weight decrease fraction with extraction.

In Fig. 5, the calculated G_r values are shown plotted against the monomer concentration. The data are widely scattered; however, the values of G_r decrease with increasing monomer concentration, while the changes in N and the reaction temperatures do not greatly affect the G_r value. In contrast, the dose rate strongly affects the graft efficiency, lower dose rates always yielding higher G_r values.

The molecular weight of the extracted homopolymer has also been measured, and is shown on Fig. 6. At high dose rates, the change of the molecular weights was rather small when the monomer concentration changed and very flat curves were obtained. A decrease in the number of particles caused a decrease of the molecular weight

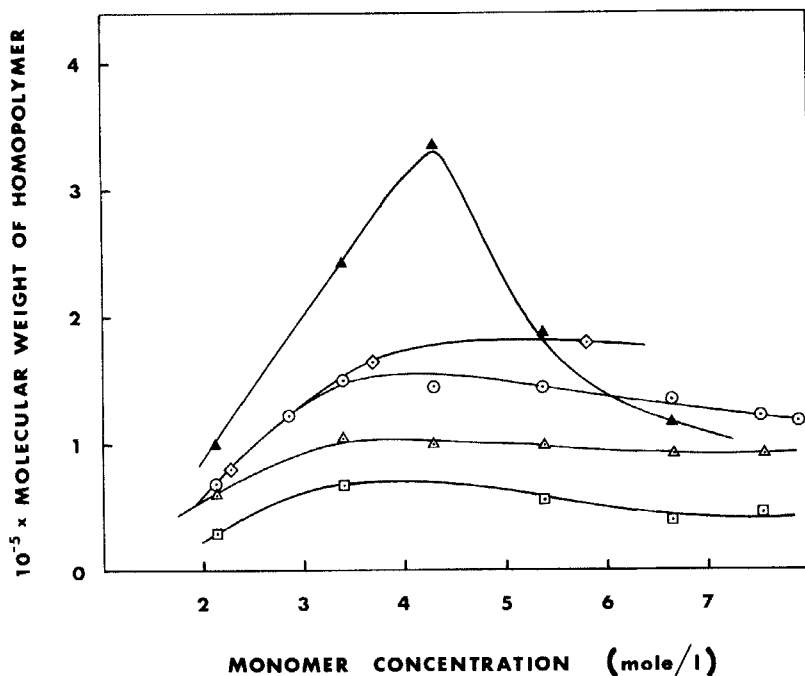


FIG. 6. Molecular weights of polystyrene extracted from the radiation polymerizations at 25°C: (◊) dose rate 0.12 Mrad/hr, $N = 2.6 \times 10^{15}$; (○) dose rate 0.12 Mrad/hr, $N = 7.3 \times 10^{14}$; (△) dose rate 0.12 Mrad/hr, $N = 3.2 \times 10^{14}$; (◻) dose rate 0.12 Mrad/hr, $N = 1.1 \times 10^{14}$; (▲) dose rate 0.053 Mrad/hr, $N = 3.2 \times 10^{14}$.

throughout the whole monomer concentration range. The molecular weights were also markedly influenced by the dose rate, they increased sharply with decreasing dose rate, and a distinct maximum was observed.

Chemically Induced Grafting

Using similar methods to those used for the radiation-induced grafting experiments, the time-conversion curves for the polymerization of styrene initiated by potassium persulfate were measured (Figs. 7 and 8). The reactions were carried out at 40 and 50°C, since the decomposition rate of persulfate was too slow at 25°C. In the case of chemical initiation, accelerations in the rates were not obvious.

To measure the graft efficiency, G_r values were calculated (G_r as

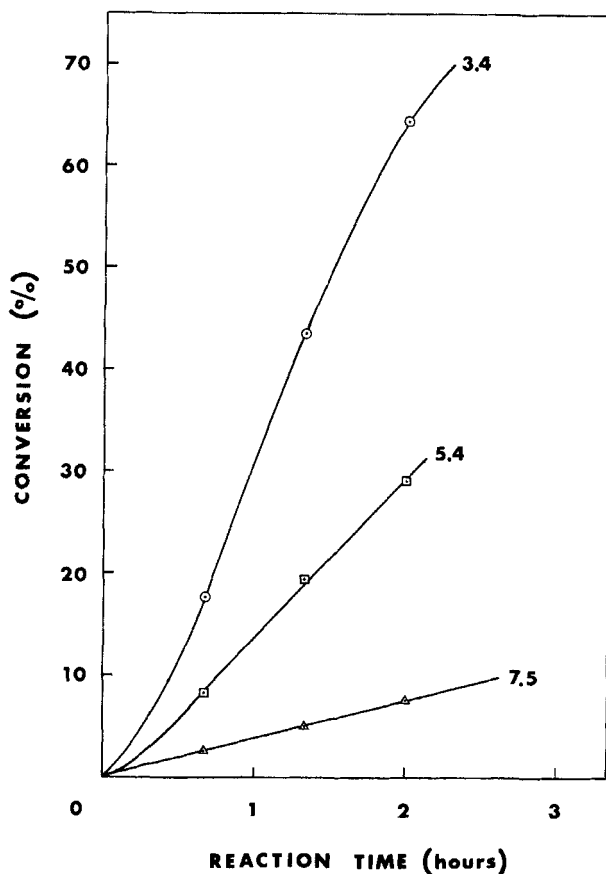


FIG. 7. Conversion curves for the $K_2S_2O_8$ -initiated polymerization of styrene in PBD latex at $50^\circ C$; $K_2S_2O_8 = 0.06$ mole/liter, $N = 3.2 \times 10^{14}$. The numbers refer to the monomer concentration in (mole/liter).

defined for the radiation-induced experiments) and are shown in Fig. 9. The dependence of G_p values on the monomer concentration is very similar to that of the radiation system, but the values for chemical systems tend to be slightly larger than that for radiation.

The molecular weights of the extracted homopolymers have also been determined (Fig. 10): they increased linearly with the increase of monomer concentration when the initiator concentration is low, but with higher initiator concentrations the molecular weights sharply decreased when monomer concentrations increased. At low monomer concentrations, the molecular weights did not change with increasing initiator concentration.

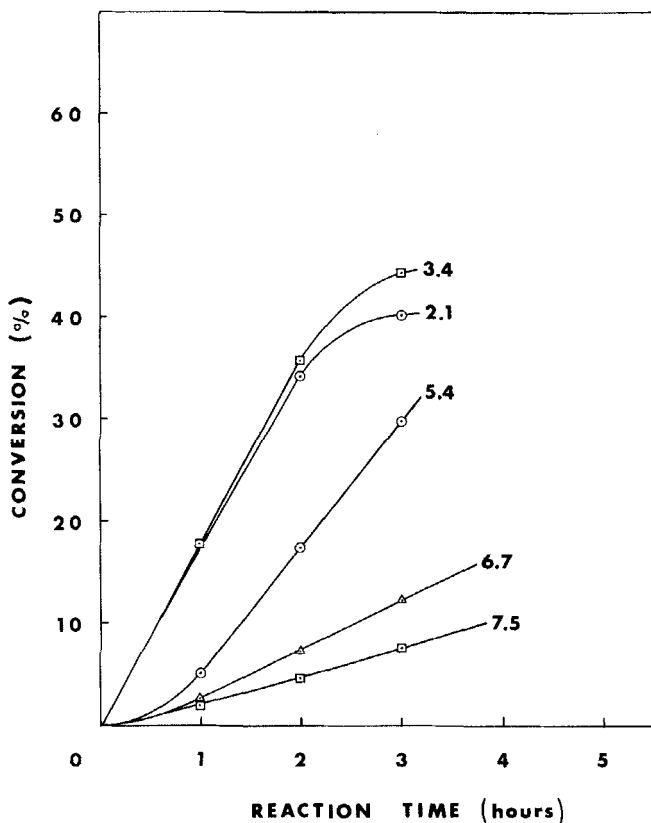


FIG. 8. Conversion curves for the $K_2S_2O_8$ -initiated polymerization of styrene in PBD latex at $40^\circ C$; $K_2S_2O_8 = 0.06$ mole/liter, $N = 3.2 \times 10^{14}$. The numbers refer to the monomer concentration (mole/liter).

DISCUSSION

Many investigators [10, 11] have applied the theory of Smith and Ewart [10] to the emulsion polymerization of styrene. Vanderhoff [13], for example, studied the γ -ray-induced emulsion polymerization of styrene and found some deviations from the theory. It is interesting to test the applicability of the theory to the graft polymerization of styrene with this PBD latex, especially to the case using radiation as the initiator. Similar comparisons were made with smaller particle size uncrosslinked latices in the previous paper [1].

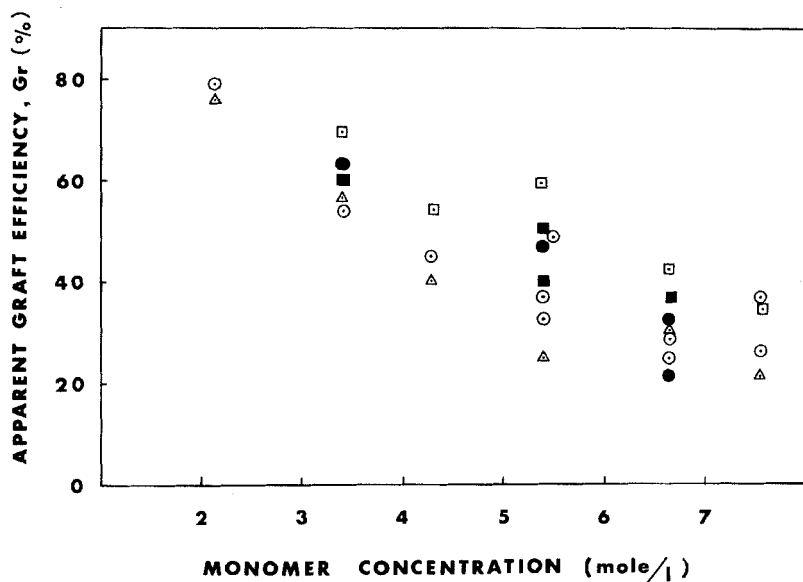


FIG. 9. Apparent graft efficiencies for the $K_2S_2O_8$ -initiated systems, $N = 3.2 \times 10^{14}$: (Δ) $40^\circ C$, $K_2S_2O_8 = 0.12$ mole/liter; (\circ) $40^\circ C$, $K_2S_2O_8 = 0.06$ mole/liter; (\square) $40^\circ C$, $K_2S_2O_8 = 0.015$ mole/liter; (\bullet) $40^\circ C$, $K_2S_2O_8 = 0.010$ mole/liter; (\blacksquare) $50^\circ C$, $K_2S_2O_8 = 0.010$ mole/liter.

According to Smith-Ewart theory, (Case II), the reaction rate R_p is expressed by the Eq. (3)

$$R_p = (1/2N) k_p [M] \quad (3)$$

where R_p is the reaction rate (number of molecules reacted/1 ml of H_2O , sec), N is the particle number (number of particle/ml of H_2O), k_p is the reaction constant (liter/mole-sec), and $[M]$ is the monomer concentration (mole/liter).

The monomer concentrations have been calculated with the assumption that all monomer dissolves into the particles and no volume change occurs. Thus, $[M]$ can be expressed as

$$[M] = \text{moles of styrene/volume of St} + \text{volume of PBD} \quad (4)$$

In Fig. 11, the relation between k_p and the monomer concentrations is presented. At $25^\circ C$, k_p is constant in the higher monomer concentration regions with a value of 14 liter/mole-sec. This is rather low

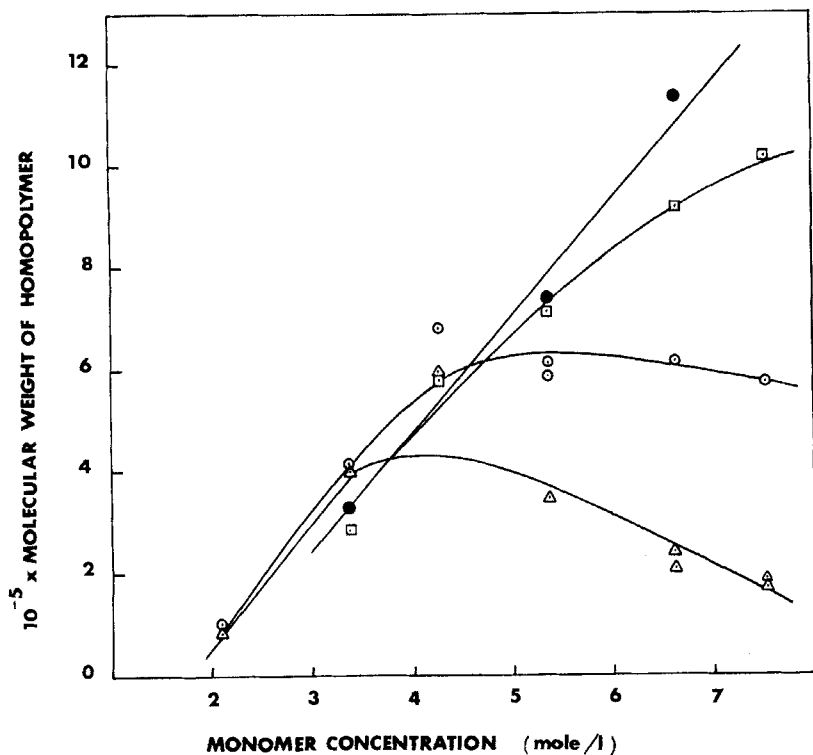


FIG. 10. Molecular weights of polystyrene extracted from the $K_2S_2O_8$ -initiated polymerizations at $40^\circ C$, $N = 3.2 \times 10^{14}$: (Δ) $K_2S_2O_8 = 0.12$ mole/liter; (\circ) $K_2S_2O_8 = 0.06$ mole/liter; (\square) $K_2S_2O_8 = 0.015$ mole/liter; (\bullet) $K_2S_2O_8 = 0.010$ mole/liter.

compared with the literature values of 30-46 liter/mole-sec. The most reliable values are probably those obtained by Matheson [14]; i. e., 46 at $25^\circ C$, 83 at $40^\circ C$, and 124 at $50^\circ C$. In the low concentration ranges, k_p can be seen to vary with the monomer concentration.

A maximum occurs at 3 mole/liter. This result is very interesting, perhaps, factors other than those included in Eq. (3) were changing although no coagulation for example occurred during the reaction. It can be concluded that the number of radicals in the particles may be increasing with decreasing monomer concentration. According to Smith-Ewart theory, (Case II), the radical number is $1/2$. However, in our experiments, it could be larger than $1/2$. There are a number of reasons why this could be so. Essentially they are mainly based on the decreased rate of termination of the radicals in the particles. In particular this could be due to large size particles or a reduced

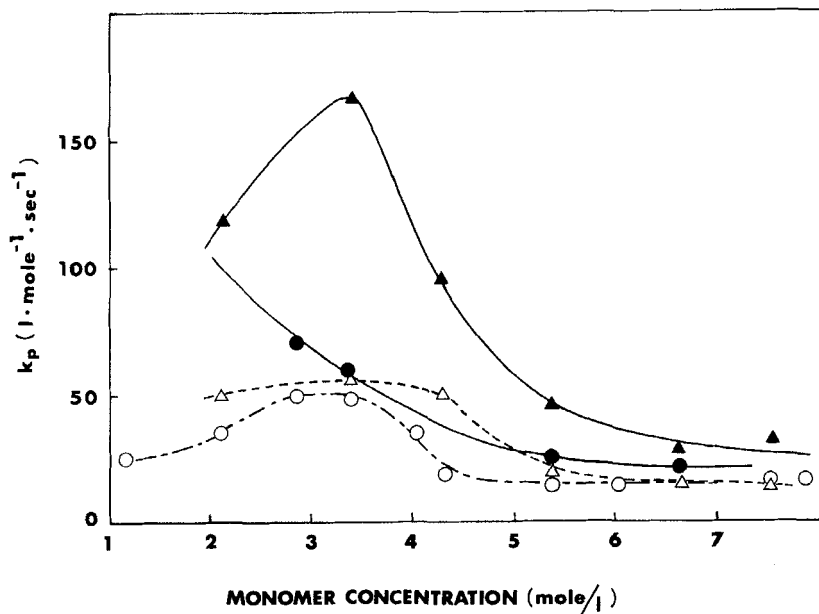


FIG. 11. Relationship between the monomer concentration and the k_p values in the radiation polymerizations: (○) 25°C, $N = 7.3 \times 10^{14}$; (●) 40°C, $N = 7.3 \times 10^{14}$; (△) 25°C, $N = 3.2 \times 10^{14}$; (▲) 40°C, $N = 3.2 \times 10^{14}$.

termination rate constant, k_t . As the amount of monomer in the particle is reduced, k_t decreases due to diffusion control. This leads to the so-called "gel" effect. In the case of latex systems it also leads to a buildup in the average number of particles beyond the 0.5 value of Smith-Ewart Case II kinetics. An excellent general review of the deviations which can occur from the standard Smith-Ewart approach has been presented recently by Ugelstad and Hansen [15].

At extremely low monomer concentrations, k_p decreases with a decrease of monomer as shown in Fig. 11. At such low concentrations, even the diffusion of the monomer may be restricted by the highly crosslinked polybutadiene molecules. This could cause the apparent decrease of k_p .

In Table 3, the apparent activation energies calculated from Fig. 11 are shown. These values may include the effect of the temperature dependency of the diffusion process so they should not, perhaps, be compared with the literature values of E_p : 7.8 kcal/mole by Matheson

TABLE 3. Apparent Activation Energies for Styrene-PBD Graft Copolymerizations Initiated by γ -Radiation^a

Particles (no./cm ³) $\times 10^{-4}$	Monomer concentration (mole/liter)	Activation energy (kcal/mole)
7.3	2.85	4.4
7.3	3.40	2.6
7.3	5.37	7.2
7.3	6.65	5.0
3.2	2.12	13.0
3.2	3.40	14.0
3.2	4.27	8.0
3.2	5.37	11.0
3.2	6.65	7.7
3.2	7.53	11.0

^aCalculated from k_p (25°C) and k_p (40°C); dose rate = 0.12 Mrad/hr.

et al. [12], 7.4 to 8.4 kcal/mole by Morton et al. [9], and 11.7 kcal/mole by Smith [8]. The results at lower particle numbers, however, show fairly good agreement with the literature values.

Now, if a rather simple model is assumed, where t is the average of the entry of radicals into the particle and τ is the average lifetime of the radicals in a particle and if the radicals produced directly in a particle with the radiation are considered as negligible [1], t can be expressed as by Eq. (5):

$$t = N/\rho \quad (5)$$

where N is the number of particles and ρ is the rate of radical formation in the aqueous phase. Then $1/\tau$ is the probability of the disappearance of a radical within unit time. The rate of disappearance in the whole system therefore is $N\bar{n}(1/\tau)$, where \bar{n} is the average number of radicals in a particle. In the steady state, the radical formation rate is equal to the disappearance rate; then

$$\rho = N(\bar{n}/\tau) \quad (6)$$

If the disappearance process is by recombination, then

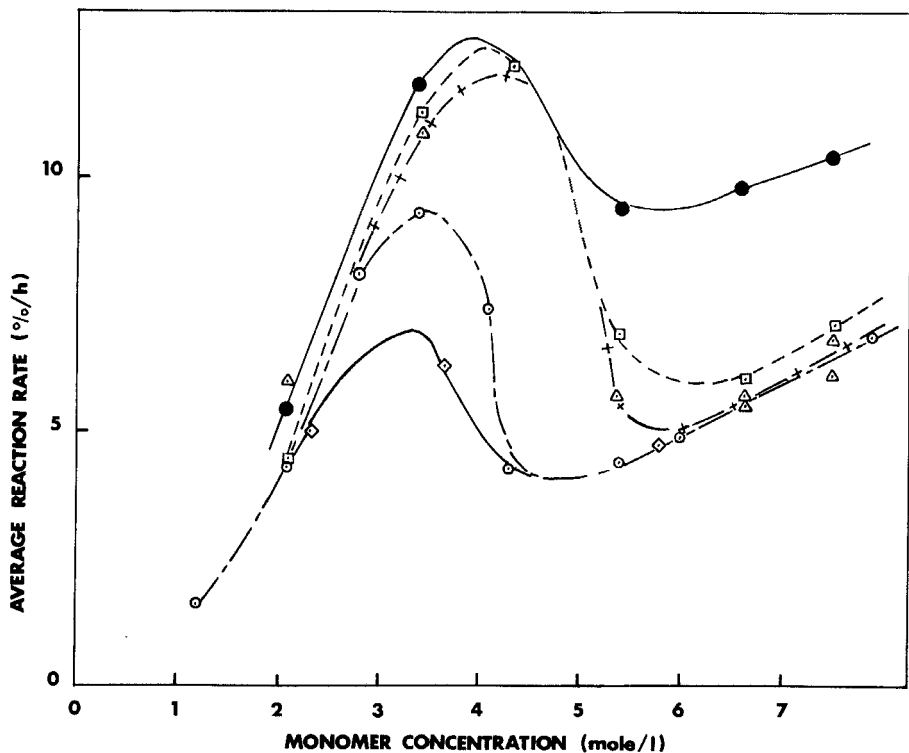


FIG. 12. Effect of N on the rate of polymerization at 25°C , dose rate = 0.12 Mrad/hr: (\diamond) $N = 2.6 \times 10^{15}$; (\circ) $N = 7.3 \times 10^{14}$; (\triangle) $N = 3.2 \times 10^{14}$; (\square) $N = 1.1 \times 10^{14}$; (\bullet) $N = 5.5 \times 10^{13}$.

$$\rho = k_t \bar{n}^2 N^2$$

Therefore

$$\tau = 1/\sqrt{k_t \rho} \quad (7)$$

The degree of gelling depends on the time in which two or more radicals exist in one particle. Therefore, the value τ/t is an important factor relating to the degree of the gel effect. From Eqs. (5)-(7),

$$\tau/t = (1/N)\sqrt{\rho/k_t} \quad (8)$$

On the basis of this model, it is expected that the gel effect occurs

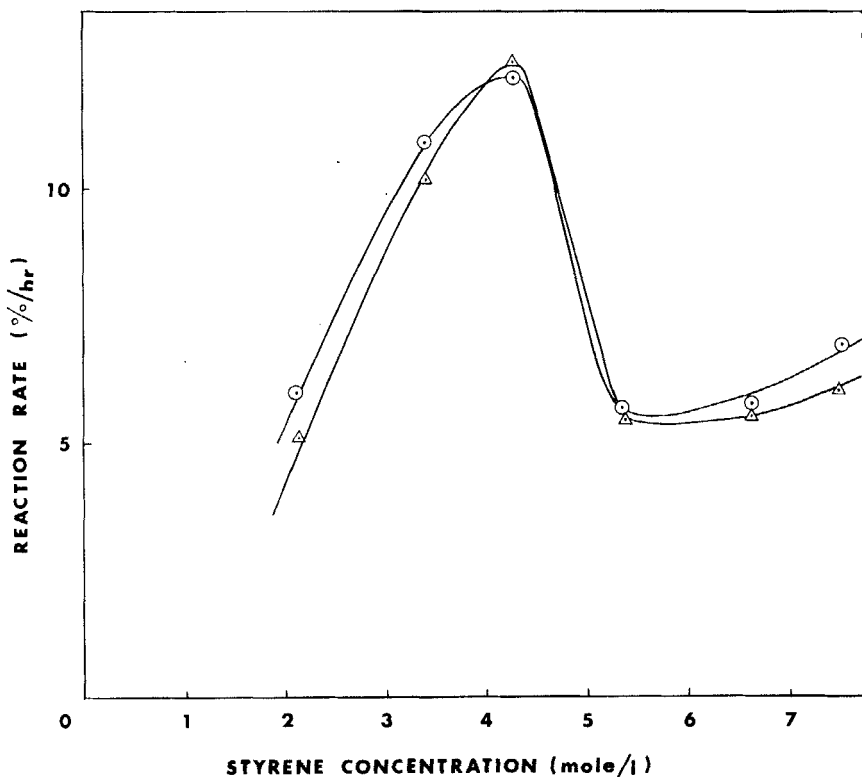


FIG. 13. Effect of dose rate on the rate of polymerization at 25°C, $N = 3.2 \times 10^{14}$ at various monomer concentrations: (○) dose rate = 0.12 Mrad/hr; (△) dose rate = 0.053 Mrad/hr.

with a decrease in k_t when the value $\sqrt{\rho}/N$ is kept larger than some critical values. The most important factor is the particle number. The gel effect occurs more easily when the particle number is low. In Fig. 12, the effect of particle number is shown. The data on the particle numbers of 1.13×10^{14} and 5.49×10^{13} are obtained from the conversion after 3 hr reaction, not from the time-conversion curves. If the curves are not linear, the error is considerably larger.

As expected by the model, the increase in the reaction rate due to the gel effect is larger when the particle number is low. The concentration range where the gel effect occurs becomes wider with a decrease in N .

In Fig. 13, the effect of dose rate is shown. There is no remarkable difference in the rate through the whole monomer concentration

TABLE 4. k_p of Polymerization of Styrene in the PBD Latex with Initiation by $K_2S_2O_8$

Monomer concentration (mole/liter)	k_p		Corresponding activation energy (kcal/mole)
	40°C	50°C	
2.1	44	-	-
3.4	58	125	9.5
5.4	37	79	9.4
6.7	39	-	-
7.5	41	54	3.4

range. There should be some difference in the rate between these two runs according to the model. The reaction rate at low dose rates are obtained from the conversion at four hours reaction time. In this case, it is supposed that time-conversion curves may be concave. Therefore, the average rate estimated from only one conversion may be low comparing with the real values. This may be one of the reasons for this discrepancy from the model. The G values for the grafting reactions have been calculated, and the results are summarized in Table 2. The values range from about 10^3 to 10^5 . At low monomer concentrations a considerably higher G value is obtained. These values are important as they determine the doses needed to effect the polymerizations and therefore both the time to complete the reaction and the economics of the process. G values above 10^4 may be considered to be economically competitive with corresponding chemically initiated reactions.

Considering now the case of chemical initiation, the k_p values have been calculated with the assumption that the Smith-Ewart theory is applicable, and the results are summarized in Table 4.

The values obtained at low monomer concentrations are considerably lower than those calculated in the case of γ -ray initiation. On the other hand, the k_p values at high monomer concentrations were slightly higher than those obtained in radiation initiation. This tendency is more clearly shown in Fig. 14: R_p (the reaction rate per milliliter of water) for both systems are plotted against the monomer concentrations. At high concentrations, both systems show a very similar tendency and the differences in R_p is relatively small. However, at low monomer concentrations, the γ -ray initiation systems show very high R_p values compared with the chemical systems. One of the reasons may be the difference in the radical formation rate

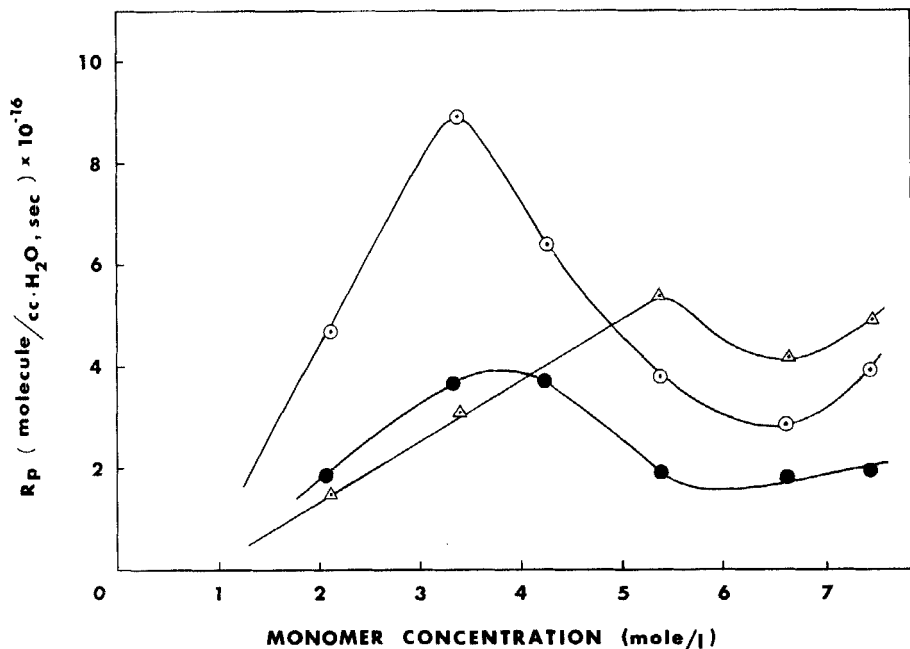


FIG. 14. Comparison of polymerization rates between chemical and radiation initiation, $N = 3.2 \times 10^{14}$: (○) radiation, dose rate 0.12 Mrad/hr, 40°C; (●) radiation, dose rate 0.12 Mrad/hr, at 25°C; (Δ) chemical, $K_2S_2O_8 = 0.06$ mole/liter, at 40°C.

which is considerably higher with radiation than with the chemical systems, therefore, the gel effect seems to be more predominant in the radiation system.

Figure 15 shows the effect of initiator concentration on the reaction rate. The rates were calculated from the conversion after 2 or 3 hr reactions. In the case of chemical initiation, the radical formation rate in the aqueous phase was controlled by changing the initiator concentration, and the reaction temperature. In Table 5, the radical production rates in some cases are given. At first, no maximum was observed, but with an increase of the initiator concentration, a maximum occurred. There was a tendency for the monomer concentration where the maximum occurs to move lower with an increase in the radical formation rate.

Concerning the comparison between the graft efficiency by radiation and chemical initiation it would have been expected that higher values for G_R would be found for the radiation system because the PBD radicals formed by direct interaction of the γ -rays should promote the graft reaction. The reason for the somewhat lower G_R values

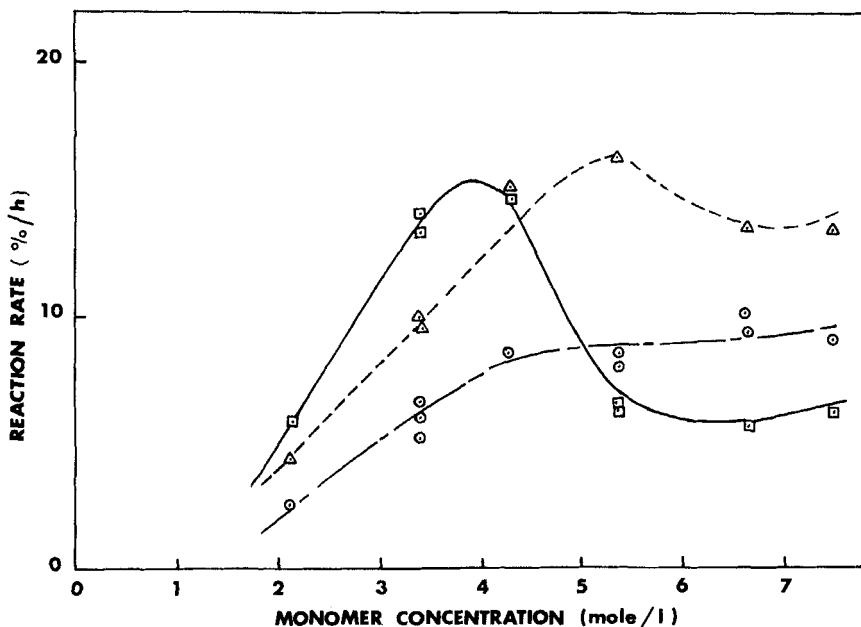


FIG. 15. Effect of initiator concentration on the rate of polymerization at 40°C , $N = 3.2 \times 10^{14}$: (\square) $K_2S_2O_8 = 0.12$ mole/liter; (\triangle) $K_2S_2O_8 = 0.06$ mole/liter; (\circ) $K_2S_2O_8 = 0.015$ mole/liter.

of the radiation system may be attributed to a difference in the radical formation rate. According to the theory presented in the earlier paper, the graft efficiency is mainly affected by the chain length; i. e., the molecular weight. The low chain lengths observed in γ -ray initiation systems may cause the lower graft efficiency. However, the situation is very complicated, and can only be partially explained by theory. In addition, the experimental results show a great deal of scatter due to experimental error.

G_R values of the chemical systems increased gradually with decreasing initiator concentration, similarly the radiation grafting system was more efficient at lower dose rates. In both cases this could again be reasonably attributed to the longer chain lengths of the grafted side chains obtained at lower initiation rates. The scatter in the data is too great to show clearly the effect of N and temperature on the efficiencies, but these variables do not appear to change the results greatly. In both the chemical and the radiation-initiated systems grafting efficiencies of 60-80% seem to be readily attainable.

TABLE 5. Radical Production Rates in the Aqueous Phase

Reaction temperature (°C)	Type of initiation	Initiator concn (mole/liter or dose rate (Mrad/hr)	Radical formation rate (radicals/sec-ml aqueous phase)
40	Chemical (K ₂ S ₂ O ₈)	0.015	4.6 × 10 ¹²
40	Chemical (K ₂ S ₂ O ₈)	0.06	1.8 × 10 ¹³
40	Chemical (K ₂ S ₂ O ₈)	0.12	3.7 × 10 ¹³
50	Chemical (K ₂ S ₂ O ₈)	0.06	9.2 × 10 ¹³
-	Radiation	0.12	1.3 × 10 ¹⁴

Molecular Weights

Considering the molecular weights of the extracted polystyrene the data are presented graphically in Fig. 6 for the radiation and in Fig. 10 for the potassium persulfate polymerizations. In the case of radiation, there was comparatively little change in the molecular weight with the initial monomer concentration except at the low dose rate experiment, where a distinct maximum was seen. This was presumably due to the gel effect (discussed earlier) and is not uncommon in grafting reactions. The increase in molecular weight with increasing particle numbers is expected as the average life time of the radicals in the particles will increase, as also discussed earlier in this paper. In the case of the potassium persulfate-initiated polymerizations, only one particle number was examined. The results are summarized in Fig. 10. At low initial monomer concentrations there appeared to be little influence of the initial persulfate concentration. At higher monomer concentrations, however, there were distinct differences. The molecular weights increased progressively with decreasing initiator concentration, in agreement with theory. A maximum occurred, however, only at the highest initiation rate. The system is highly complex, and it is not possible to offer an explanation for this behavior at this time. It is clear on comparing the data in Figs. 6 and 10 that, in general, the molecular weights are lower in the case of the radiation initiated samples. This was also noted in the previous paper and ascribed to the higher radical fluxes obtained with radiation. This important observation means that, at a given level of grafting, there are more but shorter grafted side chains in the case of radiation initiation. The technological importance of this structural difference is not known but is certainly worthy of further study.

Finally, it should be emphasized that in both papers the molecular weight of the extracted polystyrene has been tacitly assumed to be

TABLE 4. Molecular Weights of Extracted Homopolymer and of the Corresponding Grafted Side Chains

	Sample 1	Sample 2	Sample 3	Sample 4
Polybutadiene latex	γ -synthesized	γ -synthesized	Firestone 2004	Firestone 2004
Method of initiation	γ	$K_2S_2O_8$	γ	$K_2S_2O_8$
Conversion	54.9	37.0	59.0	64.0
Grafting efficiency	61.7	47.3	62.8	56.5
\bar{M}_v (extracted homopoly-styrene)	9.03×10^5	7.61×10^5	2.33×10^5	4.05×10^5
\bar{M}_w (isolated grafted side chains)	9.39×10^5	8.46×10^5	2.77×10^5	3.58×10^5
\bar{M}_n (isolated grafted side chains)	1.86×10^5	1.73×10^5	0.79×10^5	1.14×10^5

similar to that of the grafted side chains. To check this assumption, four samples were subjected, after extraction of the polystyrene homopolymer, to oxidative destruction of the polybutadiene backbone, and the molecular weights of the grafted side chains were determined by GPC. These results, which were kindly obtained by the Monsanto Company, are summarized in Table 6 together with the extracted homopolymer molecular weights. It can be seen that there is good agreement between the molecular weights of the extracted homopolymer and the isolated polystyrene side chains of the grafted polybutadiene.

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