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The Radiation-Induced Polymerization and Copolymerization of Butadiene in Emulsion

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ABSTRACT

The polymerization of butadiene in emulsion initiated by ^{60}Co gamma radiation has been studied in some detail. Similar studies with styrene and styrene-butadiene comonomer mixtures were also conducted. The rates of polymerization were found to be much lower than anticipated from the reported k_p values for butadiene and for the comonomer mixtures. Styrene, on the other hand, polymerizes at normal rates. A number of possible explanations for this behavior is discussed.

INTRODUCTION

In a previous paper the possible advantages of the use of high-energy radiation were discussed and some results obtained with styrene and vinyl acetate and its copolymers presented [1]. In general there has been comparatively little reported on the details

of radiation-initiated emulsion polymerizations. This paper will present some results obtained with butadiene and butadiene-styrene copolymer systems.

EXPERIMENTAL

Three kinds of butadiene were obtained from Matheson Company (99.0% C.P. grade) and from Phillips Company (99.6% S.P. grade and 99.9% Research grade). All three kinds of butadiene with different purities were purified and dried by passing successively through 5% aqueous potassium hydroxide solution and a calcium chloride column, and distilled before use. After purification no significant differences in rates could be observed between the three grades of butadiene used. Styrene was washed with aqueous potassium hydroxide solution and distilled water, dried over Drierite, and then distilled under vacuum prior to use. Sodium lauryl sulfate supplied by Fisher Scientific Company was used after recrystallization from ethanol.

Pyrex glass ampules containing a given amount of aqueous soap solution were degassed by four freeze-thaw cycles. After the monomers were distilled into the ampules they were sealed off under high vacuum and stored in a Dry Ice-acetone bath until irradiation. Irradiations were carried out by means of γ -rays from a ^{60}Co source mostly in the rotating wheel device shown in Fig. 1. A stream of water which is controlled at a constant temperature is passed through a narrow nozzle, which rotates the wheel on to which the ampules are held by the plates connected on the fringes of the wheel. In one series of experiments a magnetic stirring bar system was employed to examine the effect of agitation on the polymerization rate.

After irradiation the ampules were cooled in a Dry Ice-acetone bath, then opened, and the frozen latices were poured into saturated aqueous sodium chloride solution containing a small amount of hydroquinone. The coagulated polymers were filtered, washed thoroughly with water and methanol, dried under vacuum, and weighed.

Molecular weights of the polymers were measured by viscometry in toluene at 30°C, and calculated using the formula [2], $[\eta] = 2.94 \times 10^{-4} M_v^{0.753}$.

The particle diameters of latices were measured by electron microscopy. The bromination technique was used to harden the particles and to prevent them coalescing to each other [3]. The diluted latex was brominated in contact with gaseous bromine, and usually the addition of extra soap was essential to prevent the latex from agglomerating in the process of bromination. It has been

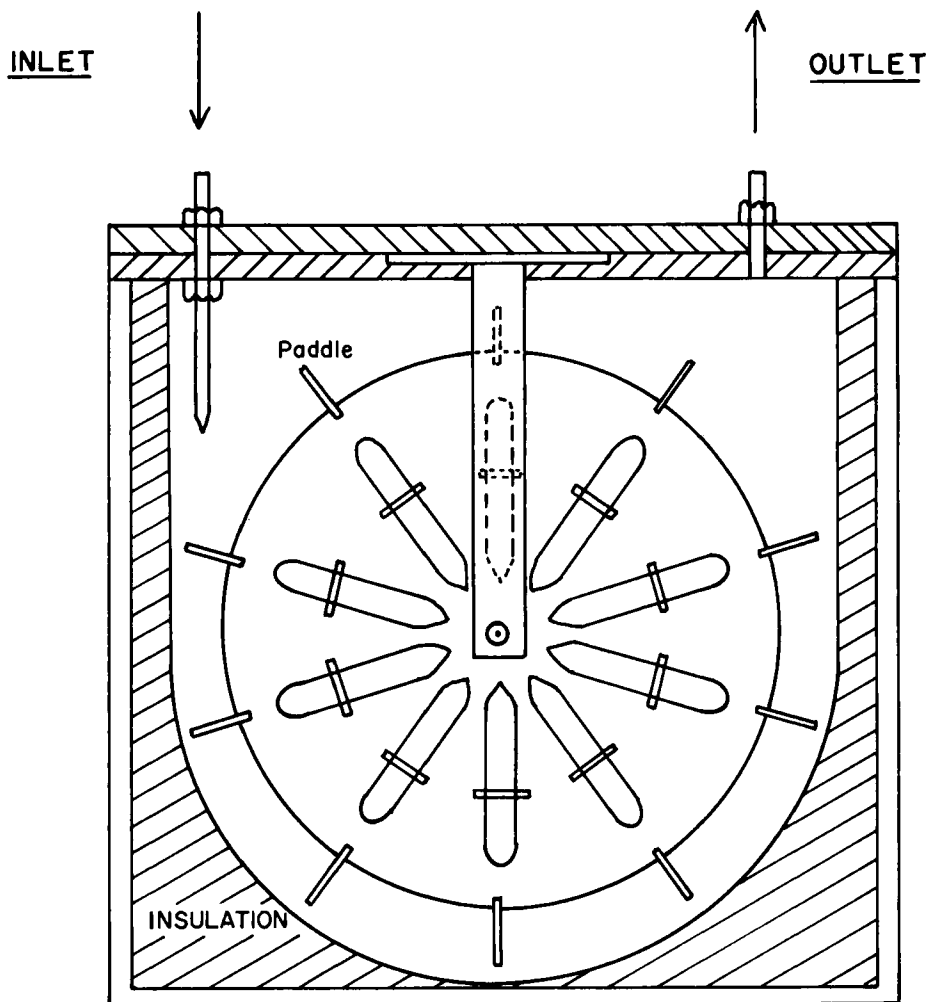


FIG. 1. Design of irradiation cannister.

reported that a correction is necessary because of the increase of diameter due to the swelling of the particles in the process of bromination. Recently Vanderhoff and Bradford [4] have reported that excellent agreement is obtained between the uncorrected bromination values and those measured by other independent methods, and they cast serious doubt on the bromination calibration factors.

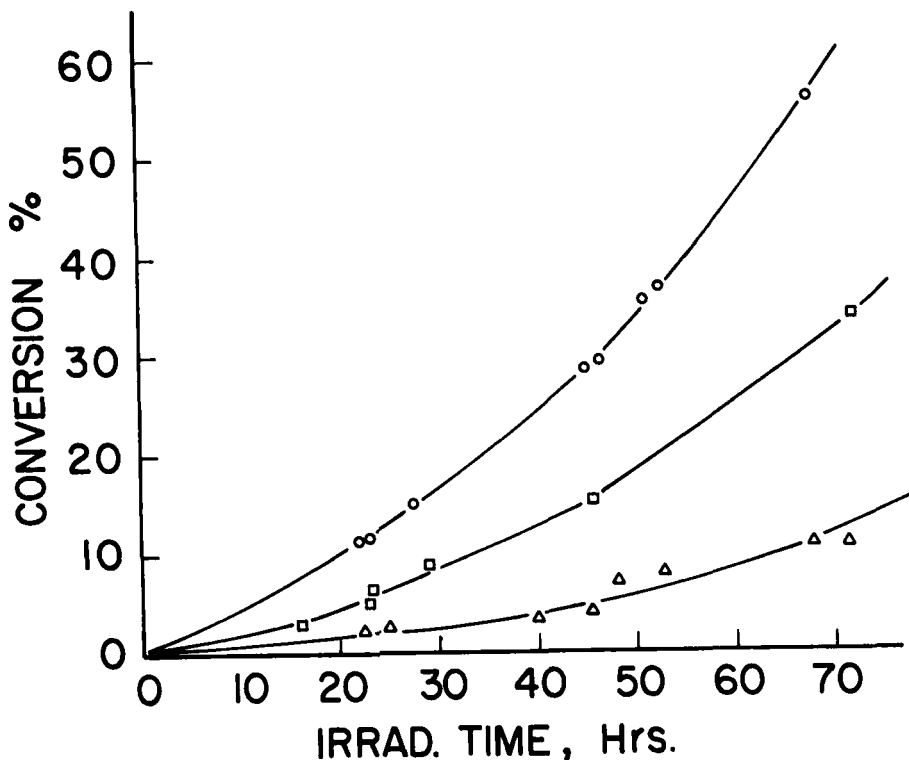


FIG. 2. Radiation-induced polymerization of butadiene at 25°C. Dose rate, 0.12 Mrad/hr. Monomer/water ratio, 1/2. (○) 8.7×10^{-2} M sodium lauryl sulfate; (□) 5.2×10^{-2} M sodium lauryl sulfate; and (△) 1.7×10^{-2} M sodium lauryl sulfate.

Therefore, in this work no correction was made for this factor, taking into account [5] the low concentration of the particles (usually below 70 ppm) in the bromination process.

RESULTS

In Figs. 2 and 3 some typical time-conversion curves are presented for the polymerization of butadiene at various soap concentrations. The polymerization proceeds very slowly in the initial stages, and thereafter the rate gradually increases. From the low rate at the initial stage the G-values of monomer consumption were calculated

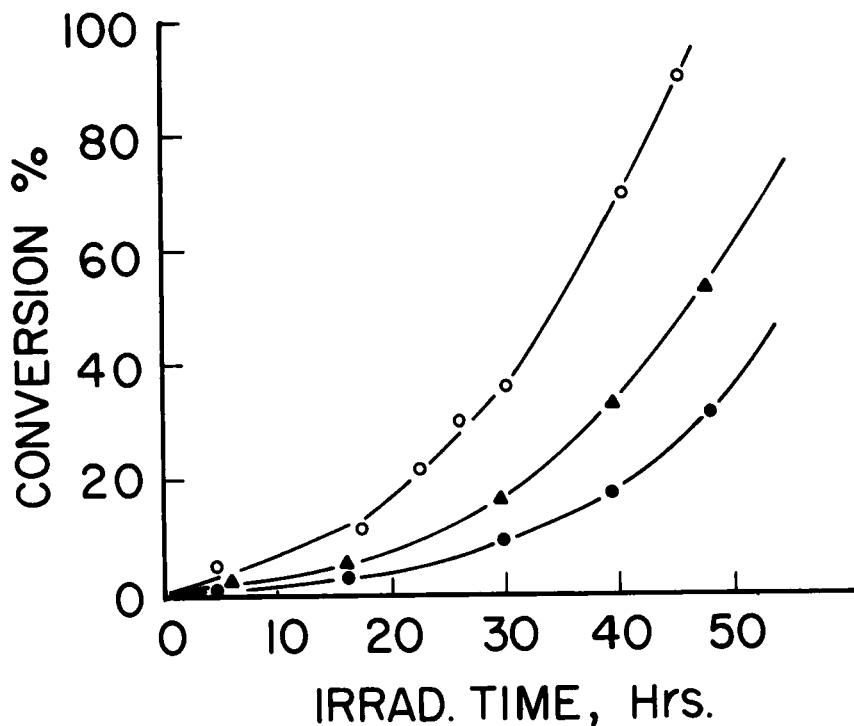


FIG. 3. Radiation-induced polymerization of butadiene at 40°C. Dose rate, 0.12 Mrad/hr. Monomer/water ratio, 1/2. (○) 8.7×10^{-2} M sodium lauryl sulfate; (▲) 1.7×10^{-2} M sodium lauryl sulfate; and (●) 0.9×10^{-2} M sodium lauryl sulfate.

as 710 (8.7×10^{-2} mole/liter soap, 25°C) and 994 (8.7×10^{-2} mole/liter soap, 40°C) on the basis of 100 eV absorbed by the monomer only. On the other hand, the slopes of the conversion curves after the slow initial stage corresponds to $G(-M)$ values of 1420 (25°C) and 3690 (40°C). Both were 8.72×10^{-2} mole/liter soap concentration.

It is interesting to note that the initial period at the low polymerization rate is longer with the system containing the lower soap concentration than with the higher soap concentration system.

The effect of the monomer-water ratio on the polymerization rate is indicated in Fig. 4. Two series of polymerizations at the higher monomer-water ratios give the same rate, except at the

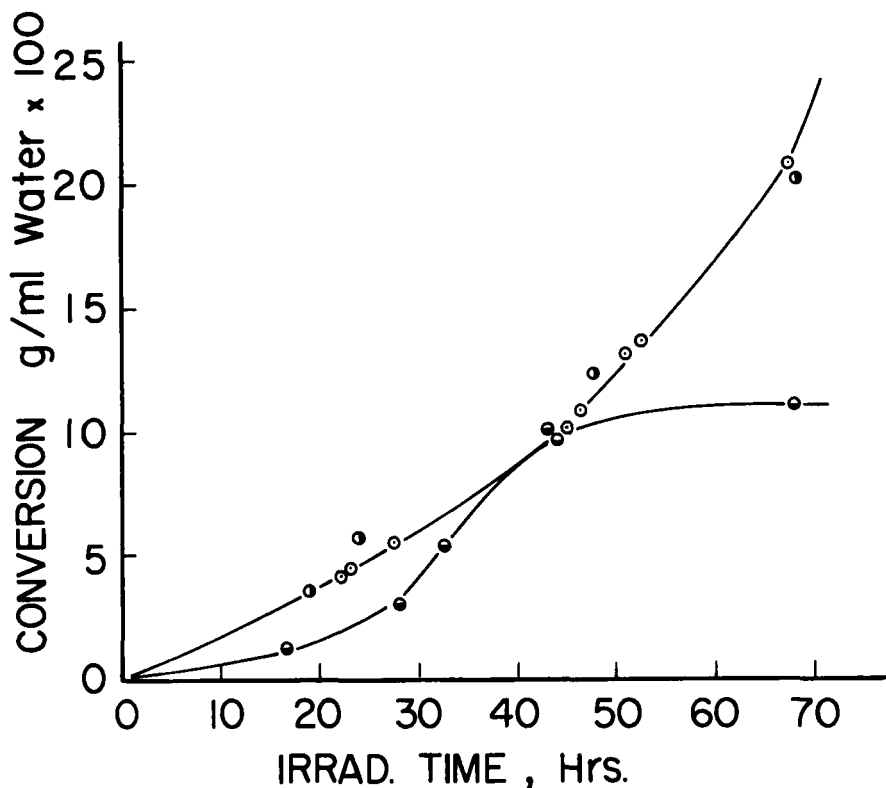


FIG. 4. Effect of monomer-water ratio on the radiation polymerization of butadiene at 25°C. Dose rate, 0.12 Mrad/hr. 8.7×10^{-2} M sodium lauryl sulfate. (○) Monomer/water ratio, 5/10; (●) Monomer/water ratio, 3/10; and (◐) Monomer/water ratio, 1.5/10.

very high conversion range, within the experimental errors, while in the run with the lowest monomer-water ratio the initial rate is remarkably low compared with the other two runs.

The above result suggests that the diffusion of monomer is an important factor, especially at the initial stage of polymerization. Consequently a different type of agitation with a magnetic stirring bar was used at a lower dose rate, for experimental reasons, to investigate the effect of the agitation on the polymerization. In Fig. 5 a time-conversion curve obtained from the strong agitation system using a stirring bar is compared with that from the usual agitation system. It is worthwhile to note that the conversion is higher with the powerful agitation system than with the usual system, even

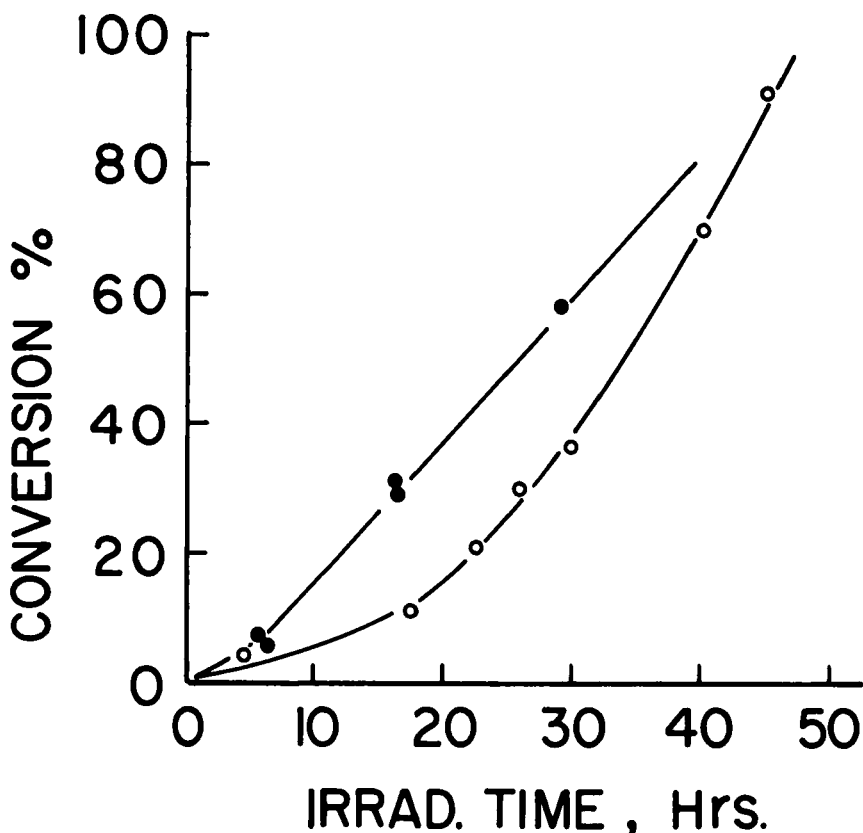


FIG. 5. Effect of agitation rate on the radiation polymerization of butadiene at 40°C. Monomer/water ratio, 1/2. 8.7×10^{-2} M sodium lauryl sulfate. (●) Strong agitation with stirrer bar, 0.02 Mrad/hr; and (○) Normal end-to-end rotation, 0.12 Mrad/hr.

though the dose rate is lower, and that the period of the slow initial stage seems to be shorter with the strong agitation. The polymerization rate after the initial stage, however, is higher with the usual higher dose rate system.

It is well known that the addition of a small amount of mercaptan gives rise to the higher rate in the chemically initiated polymerization of butadiene in emulsion. In Table 1 the effects of the several additives, including inorganic ions, are summarized. The addition of mercaptan evidently increases the conversion by 20 to 30%, while the other inorganic ions reduce the polymerization rate.

TABLE 1. The Effect of Additives on Polymerization^a

| Additives | Amount added ^b | Relative rate, R/R ₀ |
|---|---------------------------|---------------------------------|
| n-Dodecyl mercaptan | 0.44 | 1.2 |
| | 0.66 | 1.3 |
| | 2.2 | 1.3 |
| | 2.3 | 1.2 |
| CCl ₄ | 2.9 | 0.5 |
| Fe ²⁺ [FeSO ₄ NH ₄ SO ₄] | 0.15 | 0.4 |
| | 0.30 | 0.4 |
| Ag ⁺ [AgNO ₃] | 1.4 | 0.7 |
| Co ²⁺ [CoCl ₂] | 5.9 | 0.4 |
| Pd ²⁺ [PdCl ₂] | 3.5 | 0.3 |

^a25°C, 0.12 Mrad/hr, monomer:water = 1/2.

^bWeight % on the basis of monomer.

If the diffusion of monomer plays an important role in this system as mentioned above, then the solubilization of monomer in the soap solution is presumed to also be an important process. Thus the polymerizations were carried out using different soaps. As shown in Fig. 6, the reaction rates are rather low in all cases, and no significant difference was observed among the different soaps used.

The soap concentration dependence of the polymerization rates appears to be rather different at two temperatures as shown in Figs. 7 and 8, but there is one feature common for both temperatures; this is the tendency for the reaction rate to be proportional to the higher exponent of the soap concentration at the initial stage than at the middle stage of the polymerization. According to the Smith-Ewart theory [6] and to Gardon's [7] extension, the polymerization rate should be proportional to the 3/5th power of the soap concentration during Interval II, while the rate is supposed to be dependent on the soap concentration during Interval I. This suggests that the situation is rather complicated in the present system, and the simple Smith-Ewart model may not be applicable to this system.

The particle diameters of several latices obtained are listed in Table 2. The volume-average diameter (D_v) was calculated from the electron microscope picture according to

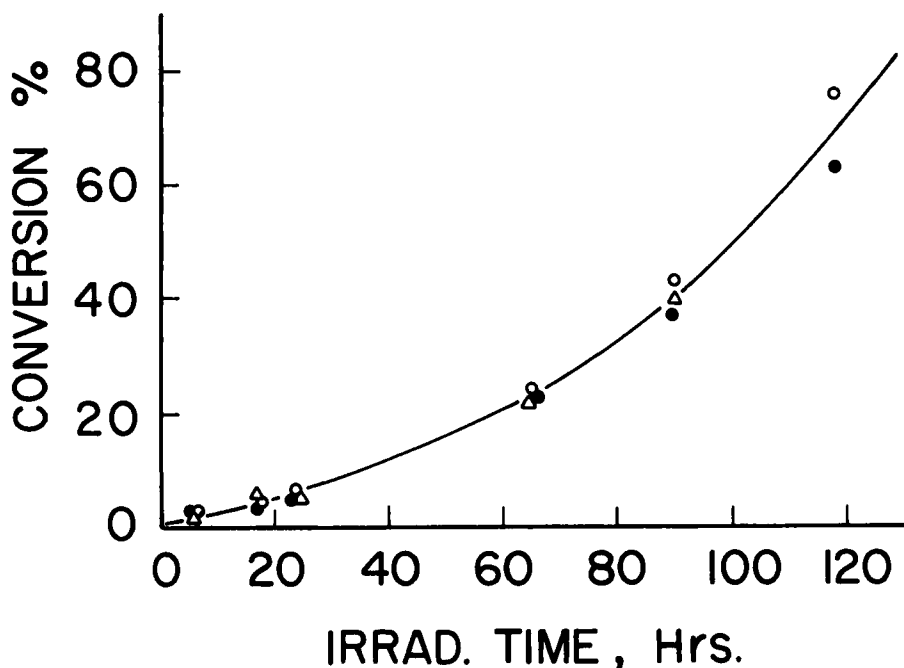


FIG. 6. Effect of type of emulsifier on the radiation polymerization of butadiene at 25°C. Dose rate, 0.18 Mrad/hr. Monomer/water ratio, 11/25. 5.2 M emulsifier content $\times 10^{-2}$. (Δ) Sodium dodecyl benzene sulfonate; (\odot) Sodium di-isooamyl sulfosuccinate; and (\circ) Sodium dioctyl sulfosuccinate.

$$\bar{D}_v = \left(\frac{\sum n D_n^3}{\sum n} \right)^{1/3}$$

where n is the number of the particles with the diameter D_n .

The particle number of polystyrene latex prepared under similar condition is given for comparison in the last line of Table 2.

In Fig. 9 the particle number (N) is plotted vs the soap concentration. It is found that the particle number is proportional to the 0.8th power of the soap concentration. This exponent is a little higher than expected from the Smith-Ewart theory.

The polybutadienes obtained at 25°C are usually soluble in such solvents as benzene, chloroform, or toluene, but the polymers

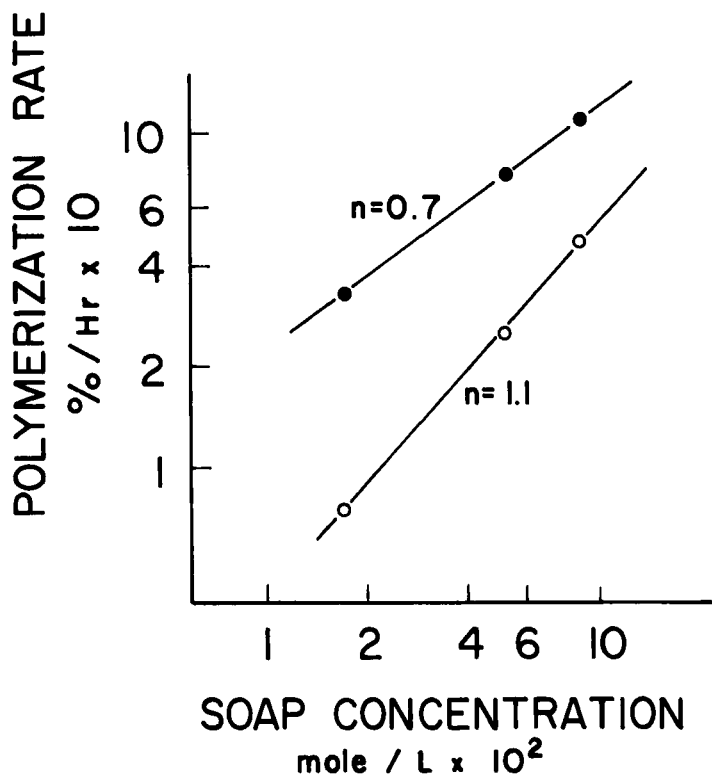


FIG. 7. Dependence of rate of emulsifier content at 25°C. Dose rate, 0.12 Mrad/hr. Monomer/water ratio, 1/2. Emulsifier, sodium lauryl sulfate; (●) initial rates; and (○) rates at 40% conversion.

obtained at 40°C contain insoluble gels except for those obtained at low conversions. In Fig. 10 the molecular weights of the polymers obtained under several conditions at 25°C are plotted vs the conversions. In all cases the molecular weights of the polymers increase with increasing conversion. It has been reported that in the emulsion polymerization of divinyl monomers such as butadiene [8] or isoprene [9] the molecular weight of the polymer initially increases with the conversion and after the gel point it decreases with increasing conversion. Under the present experimental conditions, gel formation was not observed at 25°C, and the above results also show that under these conditions the polymerization progresses very slowly without reaching the gel point even at the higher conversion.

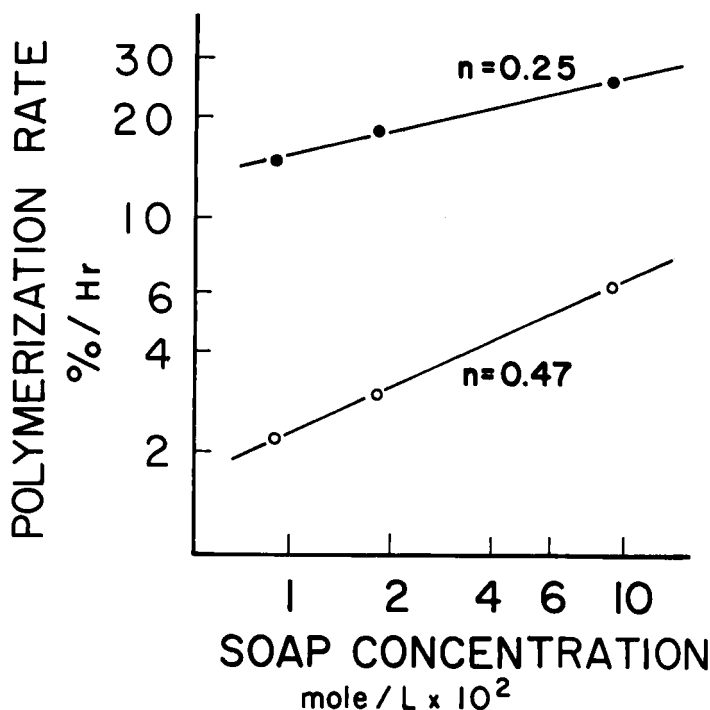


FIG. 8. Dependence of rate of emulsifier content at 40°C. Dose rate, 0.12 Mrad/hr. Monomer/water ratio, 1/2. Emulsifier, sodium lauryl sulfate; (●) initial rates; and (○) rates at 40% conversion.

It is interesting to note that the molecular weight is more dependent on the monomer-water ratio than on the soap concentration.

In Fig. 11 typical time-conversion curves are shown for the emulsion copolymerization of butadiene with styrene compared with the homopolymerization of each monomer. The $G(-M)$ values are calculated as 87,000 for styrene, 3,800 for the 60 mole % styrene system and 1,000 for the 21.5 mole % styrene system.

DISCUSSION

According to the generally accepted theory of the mechanism of emulsion polymerization, the monomer exists partly as an emulsified phase in the micelles and partly as oil droplets before

TABLE 2. Particle Diameters of the Lattices

| Sample No. | Polymerization conditions | | | | | | | \bar{D}_v (Å) | Particle number measured ($10^{16}/\text{ml H}_2\text{O}$) | Particle number calculated ($10^6/\text{ml H}_2\text{O}$) ^a |
|--------------|---------------------------|---------------------|-----------------------------------|----------------|-----------------------------------|----------------|-----------------------------------|-----------------|--|--|
| | Temp (°C) | Dose rate (Mrad/hr) | Soap conc (10^{-2} mole/liter) | Conversion (%) | Soap conc (10^{-2} mole/liter) | Conversion (%) | Soap conc (10^{-2} mole/liter) | | | |
| 13-24 | 25 | 0.12 | 8.7 | 36 | 8.7 | 36 | 122 | 15 | 2.6 | |
| 17-38 | 40 | 0.12 | 8.7 | 91 | 8.7 | 91 | 418 | 0.94 | 1.8 | |
| 17-21 | 40 | 0.02 | 8.7 | 38 | 8.7 | 38 | 280 | 0.85 | 0.87 | |
| 20-1 | 40 | 0.02 | 8.7 | 39 | 8.7 | 39 | 304 | 0.68 | 0.87 | |
| 28-13 | 40 | 0.12 | 1.7 | 17 | 1.7 | 17 | 373 | 0.25 | 0.93 | |
| 32-30 | 40 | 0.12 | 1.7 | 55 | 1.7 | 55 | 537 | 0.27 | 0.93 | |
| 28-14 | 40 | 0.12 | 1.1 | 10 | 1.1 | 10 | 375 | 0.15 | | |
| Poly-styrene | 25 | 0.12 | 8.7 | 37 | 8.7 | 37 | 252 | 1.1 | 1.2 | |

^aParticle number was calculated according to Gardon's equation [7] using the reported values of k_p .

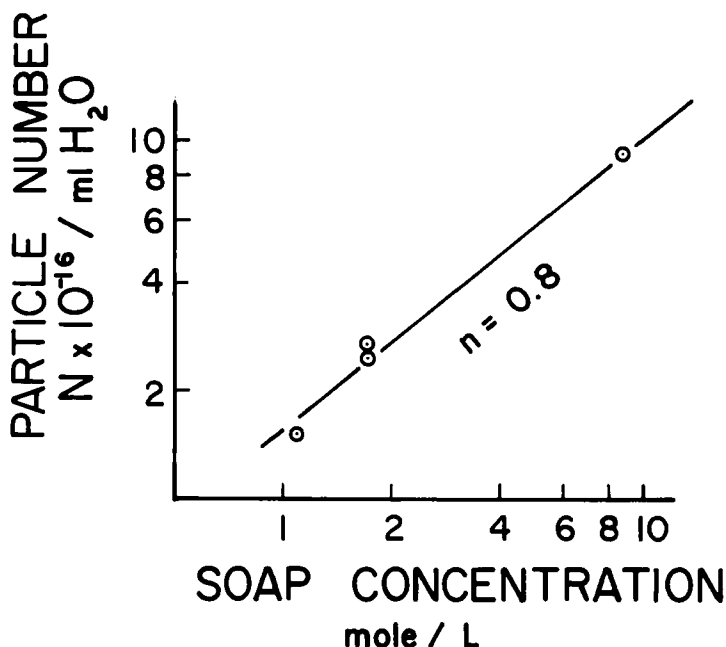


FIG. 9. Effect of emulsifier content on the number of particles at 25°C. Dose rate, 0.12 Mrad/hr. Emulsifier, sodium lauryl sulfate. Monomer/water ratio, 1/2.

the polymerization starts. Ionizing radiation interacts directly with water and monomer molecules, producing radicals in both the aqueous and oil phases. These radicals react with monomer either in the micelles or in the monomer droplets, and grow to be macromolecular radicals. This step may take place in both the aqueous and oil phases. The reactions in oil phases, however, are negligibly slow, due to the remarkably higher G-value of radical formation in the aqueous phase and the very low polymerization rate of butadiene in bulk systems. The macromolecular radicals may absorb soap on their surfaces to become polymer particles and present the isolated reaction loci, which thereafter afford high rates and high molecular weights. The initial stages with slow rates always observed under the present recipe are considered to correspond to this period, often called Interval I, during which time the reaction loci are being formed. The critical conversion at which the particle nucleation stops was calculated for each case according to Gardon's Eq. (1) [6].

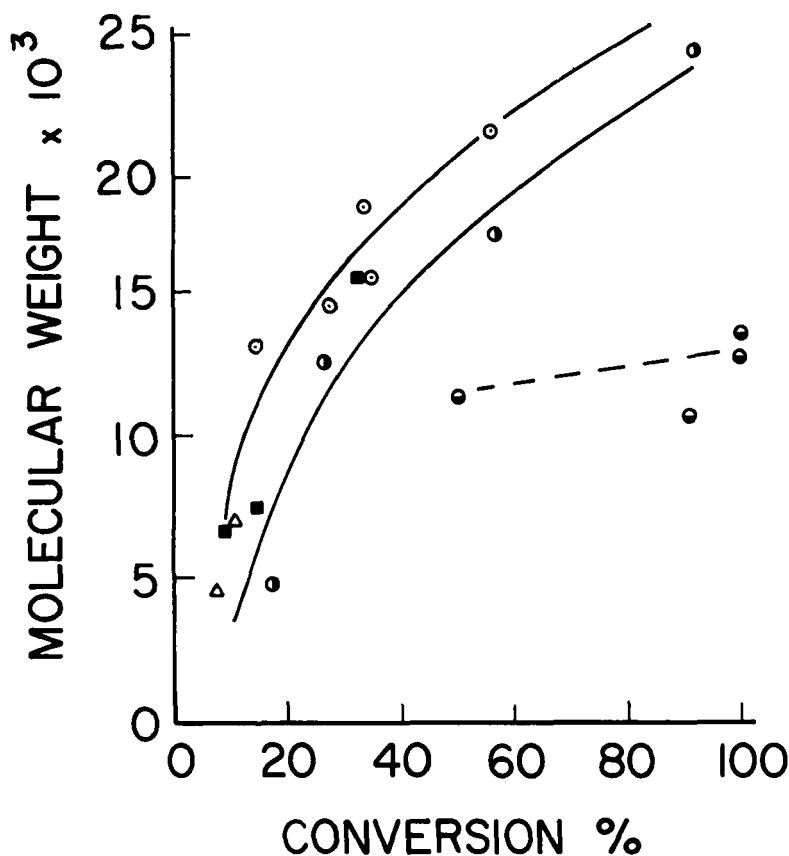


FIG. 10. Molecular weight vs conversion relationships at 25°C. Dose rate, 0.12 Mrad/hr. Emulsifier, sodium lauryl sulfate $\times 10^{-2}$: (○) 8.7 M, monomer/water ratio, 5/10; (●) 8.7 M, monomer/water ratio, 3/10; (◐) 8.7 M, monomer/water ratio, 1.5/10; (■) 5.2 M, monomer/water ratio, 5/10; and (△) 1.7 M, monomer/water ratio, 1.5/10.

$$P_{cr} = 0.209 S^{1.2} (K/R)^{0.2} (1 - \phi m) \quad (1)$$

where S stands for the square centimeters surface area of soap molecules present in 1 ml of water, R is the number of radicals produced in 1 ml of water per second, and K is defined by

$$K = (3/4 \pi) (k_p/N_A) (dm/dp) \phi m (1 - \phi m) \quad (2)$$

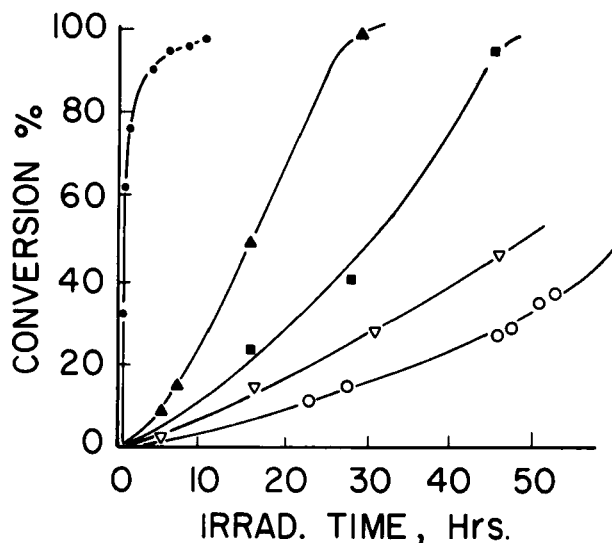


FIG. 11. The radiation-induced copolymerization of butadiene with styrene at 25°C. 0.12 Mrad/hr. Monomer/water ratio, 5/10. 8.7 M sodium lauryl sulfate $\times 10^{-2}$: (\circ) pure butadiene; (∇) butadiene 78.5-styrene 21.5 mole %; (\blacksquare) butadiene 60.9-styrene 39.1 mole %; (\blacktriangle) butadiene 40.0-styrene 60.0 mole %; and (\bullet) pure styrene.

where k_p is a propagation constant, N_A is Avogadro's number, ϕ_m is the monomer volume fraction in the polymer particle, and d_m and d_p are the densities of the monomer and polymer, respectively. The values are listed in Table 3, where the critical conversions are converted to the percent values, though P_{cr} stands for the absolute value (cc polymer/ml H_2O) in Eq. (1).

If it is assumed that the Smith-Ewart theory is applicable, the particle number is supposed to be constant after the initial stage of the particle nucleation, and the conversion should be linear with time according to Eq. (3), if the rate of the monomer diffusion is large enough.

$$R_p = \frac{N}{2} k_p [M] \quad (3)$$

where N refers to the number of the polymer particles and $[M]$ to the monomer concentration. In Figs. 2 through 7 the kinetic curves

TABLE 3. Calculated Critical Conversion and k_p Measured from Kinetic Data on the Basis of the Smith-Ewart Assumption

| Temp (°C) | Polymerization condition | | | | | k_p (liter/mole)(sec) |
|--------------|--------------------------------------|------------------------|--------------------------------|-------------------------------|-----------------|----------------------------|
| | Soap Conc (10^{-2} mole/liter) | Dose rate (Mrad/hr) | Monomer/ water in volume | Critical conversion (%) | | |
| 40 | 8.7 | 0.12 | 5/10 | 16.5 | 1.0 | |
| 40 | 8.7 | 0.02 | 5/10 | 23.9 | 1.2 | |
| 40 | 1.7 | 0.12 | 5/10 | 2.6 | 2.9 | |
| 25 | 8.7 | 0.12 | 5/10 | 13.8 | 0.05 | |
| 25 | 8.7 | 0.12 | 3/10 | 23.1 | | |
| 25 | 8.7 | 0.12 | 1.5/10 | 46.1 | | |
| 25 | 5.2 | 0.12 | 5/10 | 7.2 | | |
| 25 | 1.7 | 0.12 | 5/10 | 2.2 | | |
| 25 | 8.7 | 0.12 | 5/10 | | 32 ^a | |

^aThe value was calculated for the polymerization of styrene from the data in Fig. 2 and Table 2.

evidently show the lower rates at the initial stage and the higher rates at the latter stage. However, it does not seem easy to determine unambiguously the critical conversions from these curves. The approximate rates at Interval II were calculated from the slopes of these curves in the range of about 30 to 60% conversion, and the values of k_p were estimated on the basis of Eq. (3) using these rates, the particle numbers as measured, and the literature value [9] of $[M]$. As shown in Table 2, these are unusually small compared with those reported by Morton et al. [9], 49 (40°C) and 20 (25°C) liter/mole sec, in contrast with the reasonable value found for styrene. Thus it may be concluded that the Smith-Ewart theory (Case 2) is not applicable to the present system, and the polymerization rate is much lower than expected from theory.

It is interesting to compare the low rates obtained under the present recipe with the reported values. Morton et al. have reported in two series of papers on the emulsion polymerization by chemical initiators. In the latter one [9] the polymerization was conducted using an initiator of the hydroperoxide-polyamine type, and it was possible to calculate the absolute propagation rates according to the Smith-Ewart theory, as already cited above. However, when potassium persulfate was employed as an initiator [10, 11], it was found that the Smith-Ewart theory is not applicable to this system, and the polymerization rates were quite low compared with those obtained from the other initiator system, though no explanation was given for this difference by the authors. For instance they reported 5.5 to 10.8×10^{-22} g/sec (40°C) as the value of the polymerization rate per particle in the potassium persulfate system. This value is comparable to the value obtained in the present paper, 2.8×10^{-22} g/sec, and is smaller by a factor of about 20 than that expected from the reported value of k_p .

It is assumed in the Smith-Ewart theory that the radicals are formed only in the aqueous phase, but in the case of the initiation by radiation, the radicals are produced in all phases, including the polymer and the monomer absorbed in the particles.

If the rates of radical formation in the aqueous phase, the polymer, and the monomer are defined as R_w , R_p , and R_m , respectively, then they are calculated in the case of the dose rate of 0.12 Mrad/hr as follows:

$$R_w = 1.3 \times 10^{14} / \text{ml H}_{20} \text{ sec} \quad (G_w = 6 [12])$$

$$R_p = 4.2 \times 10^{13} / \text{g poly-Bu sec} \quad (G_p = 2 [13])$$

$$R_m = 1.1 \times 10^{13} / \text{g Bu sec} \quad (G_m = 0.5)$$

The assumed G-values of the radical formation in each phase are shown in parentheses. Thus the rate of the radical entrance into a particle (ζ) is estimated using the value of N at 40°C.

$$\zeta = \frac{1.3 \times 10^{14}}{9.4 \times 10^{15}} = 1.4 \times 10^{-2}/\text{sec}$$

If a polybutadiene particle of 300 Å diameter saturated with the monomer is considered, the rates of radical formation in the polymer (ζ_p) and the monomer (ζ_m) present in the particle are calculated as

$$\zeta_p = 5.4 \times 10^{-4}/\text{sec}$$

$$\zeta_m = 1.2 \times 10^{-4}/\text{sec}$$

$$\frac{\zeta_p + \zeta_m}{\zeta} \approx 0.05$$

Thus the number of radicals formed in the polymer and monomer in the particle is only 5% of the number of radicals entering the particle from the aqueous phase. Therefore it does not seem reasonable to attribute the deviation of the kinetic features from the Smith-Ewart theory to the effect of radicals formed directly in the particle.

It was already suggested that the diffusion of the monomer might be a rate-determining process in the present system, especially at the initial stage. It is generally accepted that the diffusion current of monomer to a particle (I) is equal to $4\pi rDC$, where r is the particle radius (about 300 Å in the present system), D is the diffusion coefficient of the monomer (about 10^{-5} cm² sec⁻¹), and C is the concentration of monomer in the aqueous phase. On the other hand, the polymerization rate in a particle (v) can be calculated for the polymerization at 40°C using the values of k_p and $[M]$.

$$v = k_p [M] = 40 \times 6.2 = 250/\text{sec}$$

Hence the monomer concentration which is necessary to maintain the above polymerization rate may be calculated as follows:

$$4\pi rDC = 4 \times 3.14 \times 150 \times 10^{-8} \times 10^{-5} \times C = 250$$

$$C = 1.3 \times 10^{12} \text{ molecules/cm}^3$$

The solubility of butadiene is reported to be much higher (9.1×10^{18} molecules/cm³) than this value. Therefore as far as the above expression for the current I holds, the diffusion rate of the monomer to a particle is high enough to keep the system chemically controlled.

The foregoing discussion, however, is concerned with the diffusion of monomer from the aqueous phase to the particle. There is one more important diffusion process which has not been discussed by other workers. This is the diffusion of monomer from the monomer droplets to the aqueous phase, which may play a more important role in the system containing a large number of particles like the present one. If this process is not fast enough, it reduces the rate of the monomer diffusion from the aqueous phase to the particles and finally decreases the rate of polymerization in the particles. Such factors as the mechanical agitation and the monomer-to-water ratio may have a considerable effect on this process.

In summary, the rates found with the radiation-initiated emulsion polymerization of butadiene were very low compared with those estimated from the known values of the propagation rate constant. They were comparable, however, with the corresponding potassium persulfate initiated systems. The number of particles was much larger than was found with other systems which could lead to a diffusion controlled process. It is not possible, however, at this time, to adequately explain the slow rates found with butadiene. Styrene has been found to behave normally with similar systems both with potassium persulfate [14] and with radiation initiation [15].

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