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The Radiation-Induced Copolymerization of Butadiene with Acrylonitrile in Emulsion Systems

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ABSTRACT

The copolymerization of butadiene and acrylonitrile in emulsion has been studied using gamma radiation for the initiation process. The polymerizations proceeded smoothly with good yields, G (monomer consumption) values ranging from 8,000 to 100,000. Some deviations from the standard Smith-Ewart Case II theory were observed, particularly with respect to the dependence of the rate on the soap concentration. A strong post-effect was observed showing a clear first-order radical termination process. The copolymer reactivity ratios were found to be normal.

INTRODUCTION

Ionizing radiation offers many advantages, in principle, over chemical methods for initiating polymerization in emulsion. The high yields

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of free radicals from the radiolysis of water combine with the high kinetic chain lengths associated with emulsion polymerization to reduce radiation costs to a minimum. In addition, the rate of initiation is independent of temperature. This makes it possible to conduct low-temperature polymerizations without difficulty and obviates the need to devise elaborate redox catalyst systems. Furthermore, the nature of radiation processing leads to considerable ease of control of the radical flux which can be monitored at will throughout the process. On the negative side, radiation interacts directly with every component of the emulsion recipe which could lead to excessive branching or gel formation or other problems.

These considerations have led to a series of studies of the kinetics and other features of radiation-induced emulsion polymerization. Previous papers have been concerned with vinyl acetate [1], styrene [1-3], including pilot plant studies [3] and with butadiene and butadiene-styrene systems [4] including the radiation-induced grafting of styrene to polybutadiene latex [5]. This paper presents the results of a study of the radiation-induced emulsion polymerization of the butadiene-acrylonitrile copolymer system.

EXPERIMENTAL

Acrylonitrile (Eastman Chemical Co.) was washed successively with 2% potassium hydroxide aqueous solution, with 5% sulfuric acid aqueous solution, and with distilled water, dried over calcium chloride, and then distilled prior to use. Butadiene was washed and dried by passing through 5% aqueous potassium hydroxide solution and through a calcium chloride column, and finally distilled into an ampule before use. Sodium lauryl sulfate supplied by Fisher Scientific Co. was purified by recrystallization from ethanol.

Irradiation was carried out by means of γ -rays from a ^{60}Co source in a rotating wheel device described in the following paper [4]. The dose rate was 0.12 Mrad/hr unless otherwise indicated.

The copolymer compositions were determined from elemental analyses. The particle diameters of the latices were measured by electron microscopy using a bromination hardening technique described previously [4].

RESULTS AND DISCUSSION

In Fig. 1 the time-conversion curves at various monomer compositions are shown. The shape of the conversion curve appears to depend on the monomer composition. The curves are convex to the time axis for the butadiene rich systems, while they are concave for

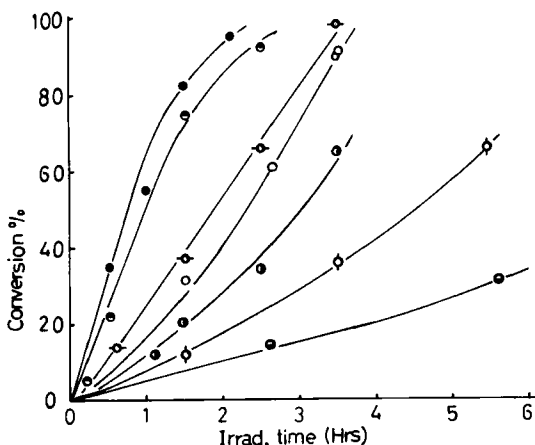


FIG. 1. The effect of monomer composition on copolymerization of butadiene with acrylonitrile in emulsion system: 25°C, 0.12 Mrad/hr, monomer/H₂O = 5/10 in volume, SLS 8.7×10^{-2} mole/liter: (●) AN, (◐) AN 90 mole %, (◑) AN 61 mole %, (○) AN 51 mole %, (◒) AN 41 mole %, (◓) AN 31 mole %, and (◔) AN 21 mole %.

the systems with extremely high acrylonitrile content. G values for the consumption of monomer varied from 8,000 to 80,000 according to the acrylonitrile content. Values for compositions in the nitrile rubber range were about 25,000. Radiation costs for the initiation process under these conditions would be in the 0.1 to 0.2 cents/lb range.

In Fig. 2 the dependence of the copolymerization rate on the monomer composition is shown compared with that of bulk copolymerization. In the latter case the time-conversion curves were linear with time to considerably high conversion, and the initial slopes were taken as the copolymerization rate. In the emulsion systems, however, they are not linear as shown in Fig. 1 and the rates in Fig. 2 are the slopes of the curves at approximately 20 to 40% conversion. It is seen in Fig. 2 that in bulk systems the copolymerization rate decreases remarkably in the presence of a small amount of butadiene, while in emulsion it diminishes slowly with increasing butadiene concentration.

The composition of the copolymers obtained from emulsion system is plotted as a function of the composition of monomer charge in Fig. 3. Monomer reactivity ratios were calculated from the figure as follows: $r_{AN} = 0.02$ and $r_{BU} = 0.40$. It should be noted that there exists an apparent azeotropic point at approximately 35 mole % of acrylonitrile, where the copolymer composition is the same as that of the monomer

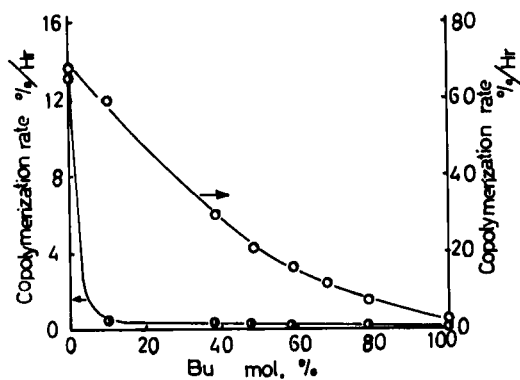


FIG. 2. The dependence of the copolymerization rate on the initial monomer charge ratio: 25°C, 0.12 Mrad/hr: (○) in emulsion, monomer/H₂O = 5/10 in volume, SLS 8.7×10^{-2} mole/liter; (●) in bulk.

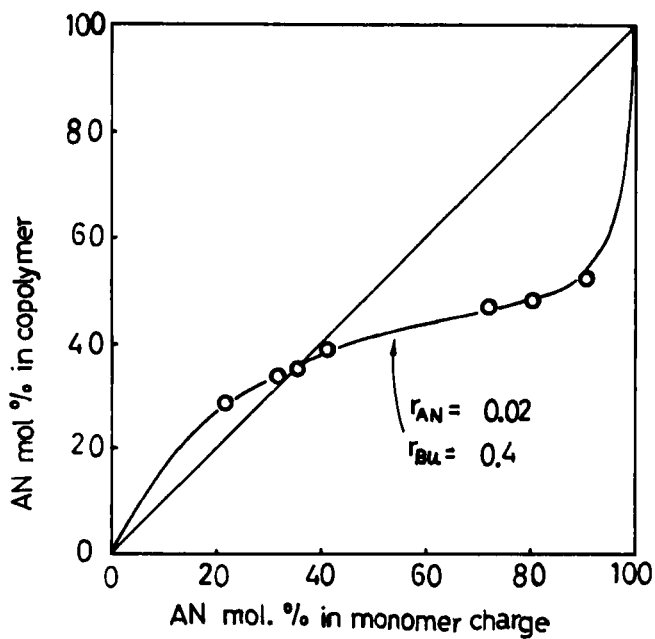


FIG. 3. Copolymer composition curve, 25°C, in emulsion.

TABLE 1. The Effect of Conversion on Copolymer Composition at 25° C

Conversion (%)	AN (mole %) in copolymer
8.7	35.0
20.3	35.6
21.1	34.0
35.7	33.5
50.0	33.5
75.3	33.9

charge. Since 7.4 g of acrylonitrile dissolves in 100 g of water at 25° C and only 0.082 g of butadiene is soluble in 100 g of water under 1 atm [6], the monomer composition in the reaction loci might be different from the monomer charge ratio. If this difference is too large to be negligible, the real azeotropic point may be shifted from the apparent one, that is, about 35 mole % acrylonitrile. The compositions of the copolymers obtained at various conversions from the apparent azeotropic monomer mixtures are shown in Table 1. If the copolymerization is carried out exactly at the azeotropic point, the copolymer composition should remain constant and the same as the monomer composition irrespective of the conversion. The results in Table 1 show that the acrylonitrile content in the copolymer decreases only slightly (by approximately 1% at 75% conversion) as the copolymerization progresses, which means that the monomer composition in the reaction loci is a little richer in acrylonitrile than the real azeotropic point. However, the difference may be so small that the monomer composition in the reaction loci is considered to be approximately equal to that of the monomer charge.

Several authors have reported the monomer reactivity ratios for acrylonitrile-butadiene copolymerizations under various conditions. Mayo and Walling [7] and Ashikari [8] reported 0.00 ± 0.04 (r_{AN}) - 0.35 ± 0.08 (r_{BU}) and 0.04 ± 0.01 (r_{AN}) - 0.40 ± 0.02 (r_{BU}) in bulk copolymerization at 50° C, respectively. Embree et al. [9] have given 0.03 (r_{AN}) and 0.18 (r_{BU}) in bulk at 5° C. The comparison of the present result with those reported values seems to give support to the foregoing conclusion that the monomer ratio in the reaction loci is not greatly different from the monomer charge ratio despite the high solubility of acrylonitrile in water.

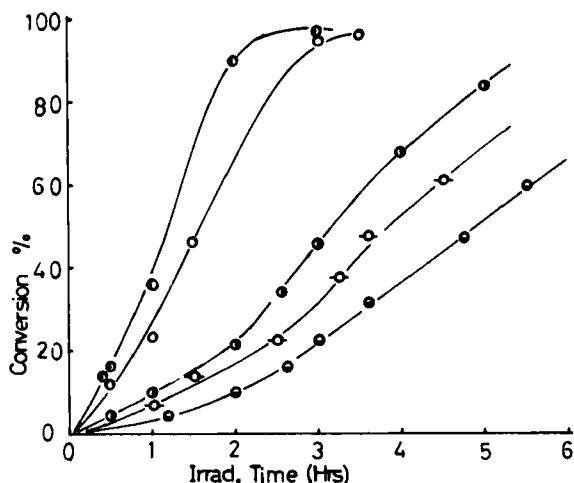


FIG. 4. Time-conversion curves of emulsion copolymerizations of butadiene with acrylonitrile under various conditions: 25°C, 0.12 Mrad/hr, monomer/H₂O = 3/10 in volume: (○) AN 68 mole %, SLS 1.7×10^{-2} mole/liter; (◐) AN 35 mole %, SLS 1.7×10^{-2} mole/liter; (◑) AN 35 mole %, SLS 1.0×10^{-2} mole/liter; (◒) AN 68 mole %, SLS 5.2×10^{-2} mole/liter; and (◓) AN 35 mole %, SLS 5.2×10^{-2} mole/liter.

In Figs. 4 and 5 the time-conversion curves at different soap concentrations are compared at two monomer charge ratios, one of which is taken to be the azeotropic mixture. It is seen that all the curves comprise three parts; the first one corresponds to a slow initial rate, the second is linear or a little accelerating, and in the third the rate levels off. These three stages of the reaction are more clearly seen at 40°C as indicated in Fig. 6. The initial stage is shorter in duration at 40°C and shorter in acrylonitrile rich systems. In this stage, radicals formed in aqueous phase react with the monomers in micelles or otherwise form into polymer particles, which provide isolated reaction loci. Since all the surface of a particle has to be covered by soap molecules for the particle to be stable, the total number of particles may be limited. Therefore, the initial stage is shorter in duration at higher temperatures or in acrylonitrile rich system because of the higher polymerization rates.

In Table 2 the volume-average particle diameters and the particle number of the latices prepared under various conditions are presented. The particle diameter increases with conversion as a matter of course, and increases with decreasing soap concentration, with

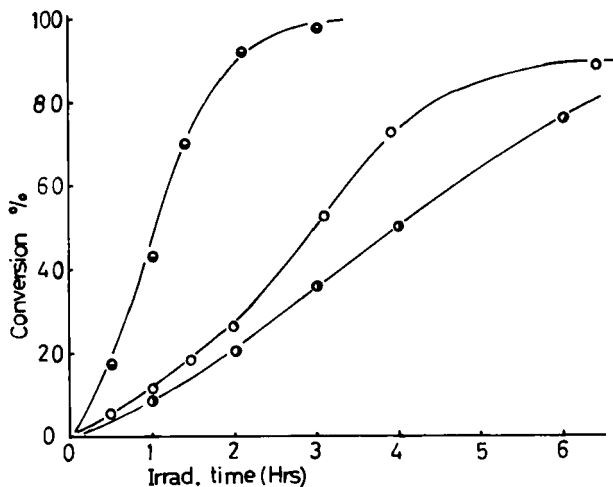


FIG. 5. Time-conversion curves of emulsion copolymerizations of butadiene with acrylonitrile under various conditions: 25°C, monomer/H₂O = 3/10 in volume, SLS 8.7×10^{-2} mole/liter: (●) AN 68 mole %, 0.12 Mrad/hr; (○) AN 35 mole %, 0.12 Mrad/hr; and (◐) AN 35 mole %, 0.052 Mrad/hr.

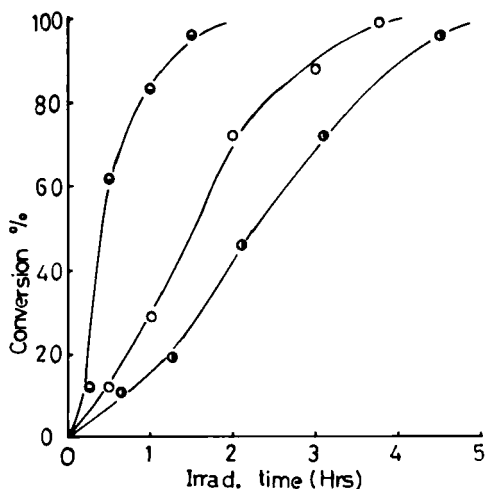


FIG. 6. Time-conversion curves of emulsion copolymerizations of butadiene with acrylonitrile under various conditions: 40°C, 0.12 Mrad/hr, monomer/H₂O = 3/10 in volume: (●) AN 68 mole %, SLS 8.7×10^{-2} mole/liter; (○) AN 35 mole %, SLS 8.7×10^{-2} mole/liter; and (◐) AN 35 mole %, SLS 1.7×10^{-2} mole/liter.

TABLE 2. Particle Diameters of Lattices Prepared Under Various Conditions

Polymerization condition				\bar{D}_v (Å)	Particle number (10^{16} /ml H ₂ O)	
AN (mole %)	Temp. (°C)	Soap (10^{-2} mole/liter)	Conversion (%)		Obs	Calc
35	25	8.7	80	290	1.5	1.7
35	25	5.2	84	326	1.2	1.3
35	25	1.7	60	298	1.1	0.68
35	40	8.7	72	369	1.1	1.2
35	40	8.7	100	322	1.4	1.2
35	40	5.2	96	370	0.95	0.93
35	40	1.7	95	409	0.67	0.49
68	25	1.7	95	413	0.68	0.57
68	40	8.7	92	341	1.1	1.0
68	40	1.7	97	459	0.51	0.40

increasing acrylonitrile concentration and with temperature. This is qualitatively in line with the Smith-Ewart theory. It seems interesting to consider the kinetics of emulsion copolymerization in connection with the Smith-Ewart theory.

The overall rate of the propagation steps, which are composed of the four reactions shown in Eqs. (1) to (4), is given in Eq. (5).



$$-\frac{d[(A) + (B)]}{dt} = \{ [k_{BA}(A)_p + k_{BB}(B)_p](B\cdot)_p + [k_{AB}(B)_p + k_{AA}(A)_p](A\cdot)_p \} v_p \quad (5)$$

where A and B refer to acrylonitrile and butadiene, respectively, the brackets with subscript p indicate the concentrations of the relevant species in polymer particles, and V_p is the particle number per unit volume of aqueous phase. If Eq. (6) is assumed as in usual copolymerizations, and $[M]$ and $[R]$ are defined as in Eqs. (7) and (8), the copolymerization rate is given by Eq. (9) using the mole fraction of acrylonitrile, M_A .

$$(B\cdot)(A)_p = (A\cdot)(B)_p \tag{6}$$

$$(M)_p = (A)_p + (B)_p \tag{7}$$

$$(R)_p = (A\cdot)_p + (B\cdot)_p \tag{8}$$

$$-\frac{d[(A) + (B)]}{dt} = k_{BB} \frac{1 + 2(1/r_B - 1)M_A + (1 - 2/r_B + r_A/r_B)M_A^2}{1 + (\delta - 1)M_A} (M)_p (R)_p V_p$$

$$= K(M)_p (R)_p V_p \tag{9}$$

where K, γ_A, γ_B and δ are given by

$$K = k_{BB} \frac{1 + 2(1/r_B - 1)M_A + (1 - 2/r_B + \gamma_A/\gamma_B)M_A^2}{1 + (\delta - 1)M_A} \tag{10}$$

$$r_A = k_{AA}/k_{AB} \tag{11}$$

$$r_B = k_{BB}/k_{BA} \tag{12}$$

and

$$\delta = k_{BA}/k_{AB} = (r_A/r_B) (k_{BB}/k_{AA}) \tag{13}$$

If the Smith-Ewart theory (Case 2) is assumed to be applicable to the present system, the total radical number is equal to one-half of the particle number N and Eq. (9) reduces to

$$-\frac{d[(A) + (B)]}{dt} = K(M)_p N/2 \tag{14}$$

Here K is considered to be an average rate constant of the propagation reactions, being dependent on the monomer composition.

According to the Smith-Ewart theory, the particle number N is given by

$$N = kI(\rho/\mu)^{2/3} (A_s S)^{3/5} \quad (15)$$

where k is a constant between 0.37 and 0.53, ρ is the rate of formation of free radicals per cubic centimeter of water phase, μ is the rate of increase in volume of a particle, and S and A_s refer to the total amount of soap in 1 cc of aqueous phase and the interfacial area occupied by a gram of soap. Of these only μ depends upon K , being proportional to K . Thus, if the dependence of $(M)_p$ on the monomer composition is neglected, the dependence of the copolymerization rate on the monomer composition is evaluated from Eqs. (14) and (15), using the values of r_A and r_B measured and those of k_{AA} and k_{BB} in literature [7].

In Fig. 7 the dependences of the copolymerization rate and k as derived above are shown. As k increases with increasing acrylonitrile concentration in the monomer mixture, the particle diameter increases and, consequently, the particle number decreases with increasing acrylonitrile concentration on the basis of the Smith-Ewart theory. In Table 2 the particle number N estimated according to Gardon's equation [11] using

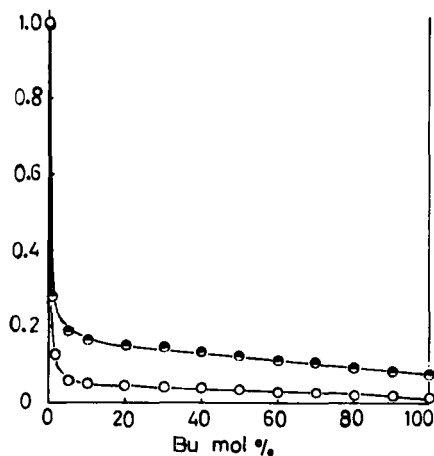


FIG. 7. Theoretical dependences of copolymerization rate and K on monomer composition: (●) copolymerization rate, and (○) K .

k instead of k_p is compared with experimental values. The agreement seems to be very reasonable considering the relatively large errors involved in the measurement of the particle diameters.

On comparison of Fig. 7 with Fig. 2 it is noted, however, that the monomer composition dependence of the copolymerization rate theoretically derived is rather different from the experimental one, even if the variation of the monomer composition with the progress of the reaction is taken into account. This deviation may arise from both or either of two sources. First, $(M)_p$ may depend upon the monomer composition in that the solubilities of the monomers in copolymer are dependent upon the copolymer composition as well as the monomer composition. Hence, it might not be reasonable to take no account of the dependence of $(M)_p$ on the monomer composition.

Second, the derivation of the above equations are based on the Smith-Ewart Case 2 theory, which may not be applicable to the present system.

The dependence of the copolymerization rate and the particle number on the soap concentration are shown in Fig. 8. The linear rate of the copolymerization after the initial stage and the particle number N are seen to be approximately proportional to the 0.2 to 0.3 power and 0.4 power of the soap concentration, respectively, while if the Smith-Ewart theory is applied, both should be proportional to the 0.6 power of the soap concentration. This deviation might arise from the situation that in systems where the monomer has high solubility in the aqueous phase, such as the present, the radicals formed in the aqueous phase have the possibility of reacting with a large number of the monomer molecules to grow into new polymer particles before entering micelles or preexisting polymer particles. In this case the particle number may not reach the constant value of Eq. (15) which is assumed in the Smith-Ewart theory, increasing, probably, with polymerization time, and thus the exponent for the soap concentration dependence is smaller than 0.6. In Table 2, N is seen to actually increase with increasing conversion (4th and 5th lines), though this is only one example.

It was found that the post-irradiation effect is very remarkable in the present system. In Fig. 9 the time-conversion curves are indicated for the post-irradiation polymerization. It is surprising that the post-effect continues to occur for more than 10 hr. This suggests that each radical is isolated in the polymer particle and hardly transfers out of the particles.

If the radicals existing at the end of irradiation decay according to a unimolecular reaction, the rate is given by

$$-dR/dt = k_1 R \quad (16)$$

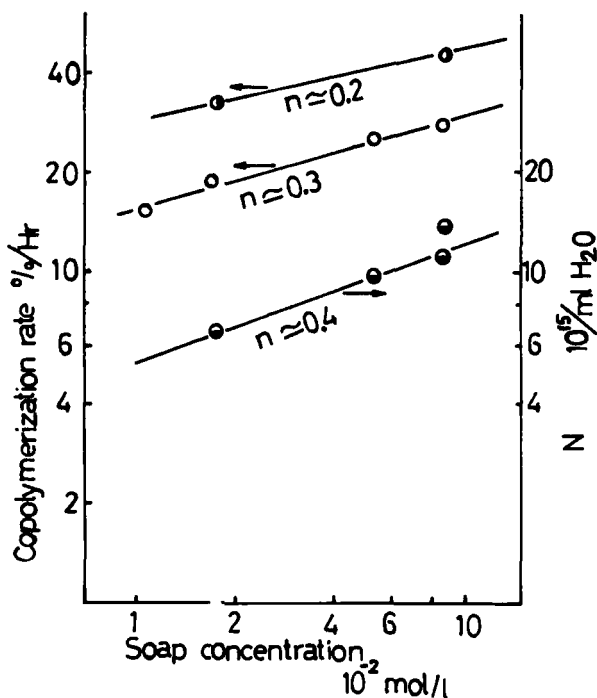


FIG. 8. Dependences of copolymerization rates and particle number on soap concentration: 0.12 Mrad/hr, AN 35 mole %, monomer/H₂O = 3/10 (○) rate at 25°C, (●) rate at 40°C, and (●) particle number at 40°C.

where R is the number of radicals in the system. The integration of Eq. (16) with $R = R_0$ at $t = 0$ gives

$$R = R_0 \exp(-k_1 t) \quad (17)$$

The conversion in the postpolymerization is given by

$$dY/dt = \gamma K(M)_p r \quad (18)$$

where γ is a constant for the adjustment of the dimensions and Y is the conversion. The total monomer concentration $(M)_p$ may be considered to be constant as long as the monomer droplets exist. The substitution

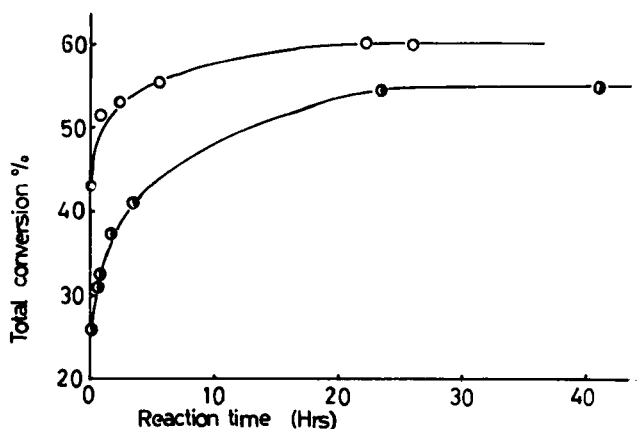


FIG. 9. Conversion of postpolymerization vs time: 25°C, monomer/H₂O = 3/10 in volume, SLS 8.7×10^{-2} mole/liter: (●) AN 35 mole %, 0.12 Mrad/hr, 2 hr irradiation; and (○) AN 68 mole %, 0.12 Mrad/hr, 1 hr irradiation.

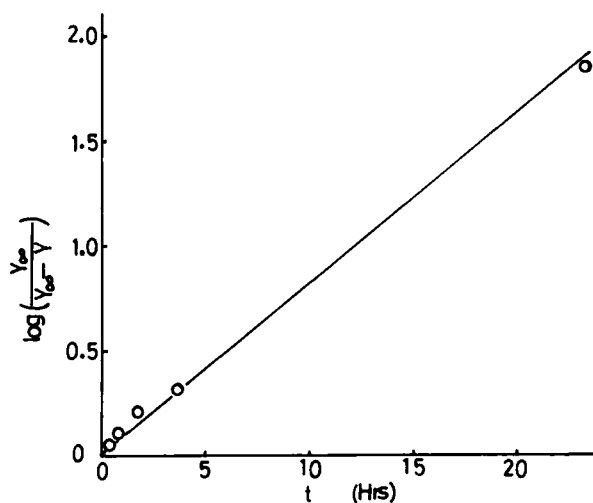


FIG. 10. A plot of $\log [Y_{\infty}/(Y_{\infty} - Y)]$ vs t : AN 35 mole %, 25°C, monomer/H₂O = 3/10 in volume, SLS 8.7×10^{-2} mole/liter, 0.12 Mrad, 2 hr irradiation.

of Eq. (17) into Eq. (18) and the subsequent integration give

$$Y = \gamma k(M)_p / k_1 r_0 (1 - \exp(-k_1 t)) \quad (19)$$

This equation indicates that after a long time the conversion approaches a limiting value Y_∞ , which is given by

$$Y_\infty = \frac{\gamma k(M)_p R_0}{k_1} \quad (20)$$

Equation (19) leads to

$$\log\left(\frac{Y_\infty}{Y_\infty - Y}\right) = k_1 t \log e \quad (21)$$

In Fig. 10 the values of $\log [Y_\infty / (Y_\infty - Y)]$ calculated using the observed value of Y_∞ are plotted as a function of time and a rather good linear relationship is obtained.

On the other hand, if the radicals decay according to bimolecular reactions, the decay rate is given by Eq. (22), and the same procedure as before gives Eq. (23) finally.

$$-dR/dt = k_2 R^2 \quad (22)$$

$$Y = \frac{\gamma K(M)_p}{k_t} \ln(k_2 R_0 t + 1) \quad (23)$$

In this expression Y does not show any limiting value at infinite time t .

Thus it may be concluded that the radicals decay according to unimolecular reactions rather than bimolecular reactions. This would correspond to the situation where the radicals, which are isolated, are forced to continue the reaction with the monomer in the particles. They eventually transfer out of there and either terminate with each other in the aqueous phase or reenter another particle with an alternative possibility of instantaneous termination or commencement of polymerization. In all these processes the step of transferring out of the particle is inferred to be rate-determining for the termination.

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