

# Emulsion Copolymerization of Alpha-Methylstyrene and Styrene

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## Synopsis

Fast copolymerizations of styrene and alpha-methylstyrene can be achieved in emulsion systems where free-radical reactions in the bulk or solution are inefficient. The Smith-Ewart-Gardon theory of emulsion polymerization was developed for homopolymerizations but should extend to this copolymerization since the particular comonomers meet the basic assumptions of this model. Sodium lauryl sulfate surfactant provided faster initial polymerization rates, but steady-state conversions were faster with potassium laurate, especially at higher alpha-methylstyrene contents. This is ascribed to acceleration of potassium persulfate decomposition by the former soap. Monomer concentration in the polymerizing particles was constant during steady reaction rates. The rate of volume growth of particles during this interval was generally as predicted by theory. The number of particles and particle sizes could be predicted well if allowance was made for initiator wastage reactions. The observed average number of radicals per particle appeared to be 0.5. Analysis of the composition of monomer droplets and proton NMR analyses of copolymer compositions provided independent confirmations that the present emulsion copolymerization was consistent with the terminal copolymerization model.

## INTRODUCTION

Alpha-methylstyrene is known to polymerize and copolymerize sluggishly in free-radical reactions and to yield low molecular weight products in such processes. This behavior has been variously ascribed to steric restrictions on the placement of successive monomer units (penultimate effect),<sup>1</sup> reversibility of alpha-methylstyrene polymerization,<sup>2,3</sup> degradative chain transfer to alpha-methylstyrene monomer,<sup>4</sup> and to kinetic factors.<sup>5</sup> Rates of chain transfer to styrene and alpha-methylstyrene have been reported in a related article<sup>6</sup> where it was shown that degradative chain transfer is not an important factor in the copolymerization of alpha-methylstyrene and styrene.

In earlier studies of the solution copolymerization of this system<sup>5,7</sup> it was concluded that the observed slow reaction rates and low molecular weights of the products probably resulted from the stability of the alpha-methylstyrene radical. In kinetic terms, this would be reflected in a normal termination rate constant and a low propagation rate constant for homopolymerization.

These conclusions suggest that fast copolymerization and high molecular weights could be achieved in an emulsion system, since termination processes are relatively less important under such conditions. Earlier work did indeed show that this expectation was realized.<sup>5</sup> Emulsion copolymerization<sup>8</sup> and homopolymerization<sup>9</sup> of alpha-methylstyrene have been reported by others, with few or no experimental details. Kenney and Patel<sup>10-13</sup> however have described the emulsion copolymerization of alpha-methylstyrene and methacrylonitrile.

In this article, the emulsion copolymerization of styrene and alpha-methylstyrene is examined with particular reference to the Smith-Ewart-Gardon<sup>14,15</sup> mechanism for emulsion polymerization of water-insoluble monomers. The literature on emulsion copolymerization exhibits considerable controversy,<sup>16</sup> and it was of value to study a system in which the basic scheme<sup>17-20</sup> advanced for styrene homopolymerization might be expected to extend directly to copolymerization. Styrene-butadiene copolymerizations have been reported to exhibit some discrepancies from the predicted behavior.<sup>21</sup> Most other copolymerizations of practical interest involve at least one monomer with appreciable water solubility and/or incomplete miscibility of the copolymer with the monomer feed. The styrene/alpha-methylstyrene system, on the other hand, meets all the basic assumptions of the theory for emulsion copolymerizations<sup>15</sup> in that the monomers are almost insoluble in water, both can be expected to have closely similar diffusion rates in aqueous media, and the copolymers and monomers are mutually soluble. It should be expected, then, that the "classical" emulsion polymerization theory which was not based on copolymerizations should extend to the present system. This article shows that the theory is indeed valid, by and large, in the styrene/alpha-methylstyrene case. A minor modification is suggested to allow for primary radical wastage reactions in some of the calculations.

This report also provides some additional, independent evidence that the copolymerization of interest here proceeds according to the simple copolymer model.<sup>7,22,23</sup> We have shown that emulsion copolymerization can be used to measure chain transfer rates to monomers and have reported these values elsewhere for styrene and alpha-methylstyrene and their radicals.<sup>6</sup>

The copolymers produced in this study are of practical interest, since they are essentially styrenic polymers with higher softening points than that of polystyrene. The molecular weights and physical properties of the copolymer products are described in an accompanying article.<sup>24</sup>

## EXPERIMENTAL

### Materials

Monomers were distilled under reduced pressure. Middle cut distillates were retained for copolymerization and were stored in a refrigerator until used. Storage periods never exceeded one week. The water was distilled and deionized. Analytical-grade potassium persulfate was used as supplied.

Potassium laurate and sodium lauryl sulfate soaps were recrystallized from methanol. The purified soaps were characterized by differential thermal analysis. Figure 1 records the thermogram of potassium laurate, with which most of our data were obtained. The small endothermic peak near 40°C probably reflects the melting of dodecanoic acid (mp 44°C at very slow heating rates). The peak near 96°C is attributed to a transition between an isotropic liquid mixture of potassium laurate and lauric acid and a suspension of the soap in a liquid.<sup>25</sup> Sodium lauryl sulfate exhibited a single exothermic peak at 119°C at a heating rate of 20°C/min.

Filtered analytical-grade methanol was used in the conversion-time measurements described below. The emulsions were broken with brine made up

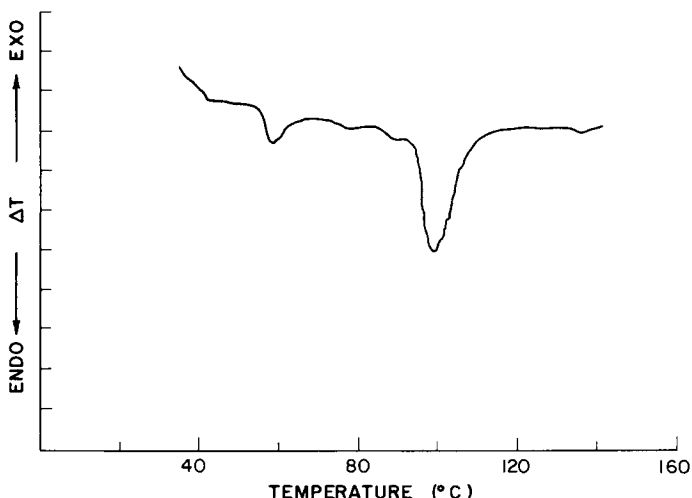


Fig. 1. Differential thermogram (20°C/min heating rate) of recrystallized potassium laurate.

from technical-grade sodium chloride. Filtered, reagent-grade benzene and methanol were used in polymer purifications.

### Polymerizations

Polymerizations were carried out in a 500-ml resin kettle fitted with a stirrer, thermometer, condenser, and a nitrogen inlet tube which dipped into the reaction mixture. Temperatures recorded are those of the reaction mixtures.

The recipe used was: water, 180 g; monomer(s), 100 g; initiator ( $K_2S_2O_8$ ), 0.853 g; soap, 0.012 moles (3.49 g sodium lauryl sulfate or 2.89 g potassium laurate).

All the soap was mixed with most of the water and charged into the kettle which was placed in a constant-temperature bath. The soap was dissolved by stirring and the reaction mixture was flushed with bubbling nitrogen for at least 30 min. Initiator was dissolved in the remainder of the water charge. Monomers were added, and after 5 min the initiator was added to the flask. The beginning of the reaction period was taken to be the time of initiator addition.

At appropriate intervals 2-ml samples were pipetted out of the reaction flask into chilled vials. The contents of these vials were emptied into tared aluminum weighing dishes. The vials were weighed before and after filling to determine the sample weight. Methanol was added to facilitate volatilization by reducing the mixture viscosity and hindering skin formation. Monomers, methanol, and water were driven off by air drying for about 12 hr, followed by a similar period in a vacuum oven at 40°C. Checks showed that this procedure brought the residue to constant weight. Other workers have followed similar procedures.<sup>26</sup>

The percentage of solids and the percent conversion were calculated from sample weights as follows. The percentage of solids is defined as (residue weight) (100)/(sample weight), and the fractional conversion is the difference between the percent solids and the percent nonpolymeric solids, all divided by the theoretical percent polymer solids for full conversion. The nonpolymeric solids here are surfactant and initiator residues.

Since the reaction mixture in our case contained 35.17% by weight of monomers the last equality is

$$\text{percent conversion} = \frac{\frac{\text{weight residue}}{\text{total weight}} - (A + B)}{35.17} \quad (1)$$

where  $A$  and  $B$  are the respective weights of surfactant and initiator in 100 g reaction mixture.

In an alternative method, the samples were weighted directly into tared, chilled aluminum weighing dishes which contained some hydroquinone. The samples were dried as described above and reweighed. Both methods gave results which coincided to within 1% or 2% conversion. A separate brief investigation revealed that the measured extent of conversion was not affected by the use of hydroquinone to quench polymerization in samples which had been removed from the reactor.

### Equilibrium Monomer Concentration

The equilibrium monomer concentration in a monomer-swollen particle  $C_M$  is related to the monomer volume fraction  $\phi_M$  in the particle by

$$C_M = \frac{d_m \phi_M}{M_0} \times 10^3 \quad (\text{moles/l.}) \quad (2)$$

where  $M_0$  is the formula weight of the monomer (g/mole) and  $d_m$  is the monomer density (g/cm<sup>3</sup>). The monomer volume fraction can be expressed as

$$\phi_M = \frac{W_M d_p}{d_m + W_M d_p} \quad (3)$$

where  $W_M$  is the ratio of the weights of monomer and polymer in the particle and  $d_p$  is the polymer density. With eq. (2),  $C_M$  can be evaluated from

$$C_M = \frac{W_M d_p d_m \times 10^3}{M_0 (d_m + W_M d_p)} \quad (4)$$

The only experimental parameter in eq. (4) is the monomer/polymer weight ratio  $W_M$ . This was measured as follows: Precision bore centrifuge tubes about 7.5 cm long and with 4 mm diameter were used in the measurements of  $W_M$ . Hydroquinone powder was coated onto the inner walls of the tubes by revolving the tubes. The additive was effectively at about 8 wt % on the reaction mixture in the tubes. Hydroquinone was used as a chain stopper in preference to more common materials like sodium dimethyldithiocarbamate because it has appreciable solubility in water. The efficiency of hydroquinone was checked by adding 3 wt % of this material to an emulsion polymerizing at 70°C. Conversions were measured at intervals and it was established that the reaction ceased after addition of the chain stopper.

Samples were taken from the reaction mixture at appropriate intervals and added to chilled, tared centrifuge tubes. The tubes were reweighed to determine the sample weight  $W_s$  and were stored in ice until they were spun.

Centrifugation was at 23,000  $g$  for 30 min. This served to separate the monomers in droplets but did not extract monomer from the polymerizing par-

ticles. The height of the monomer layer was measured with a cathetometer, and this datum was converted to monomer weight. Thus, 100 g polymerizing mixture would contain an amount  $W_d$  of monomers in droplets, where

$$W_d = \frac{\pi r^2 H d_m}{W_s} \times 100 \quad (5)$$

with  $r$  being the tube radius,  $H$  the height of the monomer layer, and the effective density  $d_m$  of the monomer mixture being given by

$$d_m = \left( \frac{S}{0.909} + \frac{1-S}{0.9165} \right)^{-1} \quad (6)$$

where  $S$  is the weight fraction of styrene in the monomer feed and 0.909 and 0.9165 g/cm<sup>3</sup> are the respective densities of styrene and alpha-methylstyrene.

From the feed recipe it is known that 100 g reaction mixture contains 35.17 g monomers initially. Thus, the total weight of unreacted monomers (in droplets and particles)  $W_u$  at a certain fractional conversion  $p$  will be

$$W_u = 35.17 - 35.17p \quad (7)$$

and the amount of polymer  $W_p$  would be

$$W_p = 35.17p \quad (8)$$

The ratio of the weights of monomer and polymer in the polymerizing particles,  $W_M$ , is

$$W_M = \frac{W_u - W_d}{W_p} \quad (9)$$

or

$$W_M = \frac{35.17 - 35.17p - (100\pi r^2 H d_m / W_s)}{35.17p} \quad (10)$$

Insertion of this value in eq. (4) provides the equilibrium monomer concentration  $C_M$ .

### Number of Particles

The number of particles can be calculated from a knowledge of the fractional conversion  $p$  and the corresponding weight (or volume) of an average particle. A spherical particle with diameter  $D$  has a volume of  $\pi D^3/6$  and contains a volume  $V_p$  of polymer, where

$$V_p = (1 - \phi_M)(\pi D^3/6) \quad (11)$$

It will be recalled that  $\phi_M$  is the equilibrium volume fraction of monomer in the particles during steady-rate polymerization. The weight of polymer  $W_p$  in a single particle is

$$W_p = (1 - \phi_M)(\pi D^3/6)d_p \quad (12)$$

The feed recipe contains 35.17 g monomer per 63.5 g water. Thus, the number of particles per cm<sup>3</sup> of aqueous phase,  $N$ , is given by the ratio of the total weight of polymer produced at a fractional conversion  $p$  divided by the weight of polymer in the average particle. From eqs. (8) and (12),

$$N = \frac{35.17p}{(\pi D^3/6)(1 - \phi_M)d_p(63.5)} \quad (13)$$

where the density of water is implicitly taken to be 1 g/cm<sup>3</sup>. All parameters in eq. (13) except  $D$  are available as described earlier.

Particle diameters were measured by liquid exclusion chromatography (LEC) as described by Hamielec and Singh.<sup>27</sup> The latex sample is very highly diluted (500:1) before injection into the LEC columns. This high dilution results in an almost complete extraction of the monomer from the polymer particles. The measured particle diameter  $D^*$  is then less than that of the original monomer-swollen particle. In the monomer-free particle, the weight of polymer  $W_p$  has the same magnitude as given by eq. (12), but its relation to  $D^*$  is now

$$W_p = \pi(D^*)^3 d_p / 6 \quad (14)$$

Thus, in terms of experimentally observable parameters, eq. (13) should be corrected to read

$$N = \frac{35.17p}{[\pi(D^*)^3/6](d_p)63.5} \quad (15)$$

The LEC columns were packed with 37–74 mesh porous glass beads with a maximum pore diameter of 3000 Å. The carrier liquid was water containing 1 g/l. Aerosol OT surfactant (di-2-ethylhexyl sodium sulfosuccinate) to prevent adsorption of the lyophobic emulsion particles. Potassium nitrate at 1 g/l. concentration was also added to the carrier medium to suppress the size of the electrical double layer and permit the latex particles to enter the pores. A flow rate of 7.6 cm<sup>3</sup>/min was employed. The detector was an ultraviolet spectrophotometer operating at 254 nm with a cell of 10 mm path length. The carrier fluid flow rate was monitored with a 5-cm<sup>3</sup> siphon. Dow polystyrene latex standards were used to establish the calibration curve in terms of particle diameter and retention volume.

Axial dispersion and peak broadening are severe in liquid exclusion chromatography.<sup>27</sup> As a result, the apparent size dispersity of the standard polystyrene samples was not appreciably smaller than that of our samples. It was therefore not possible to characterize the size distributions of our samples nor to calculate average diameters from the experimental data. The diameter at the peak height for each sample was taken as characteristic of the specimen, without attempting axial dispersion corrections.

Reaction mixture samples for particle size measurements were removed from the polymerization kettle at appropriate intervals and stored under refrigeration until the liquid exclusion chromatography measurements were made.

#### Average Number of Radicals per Particle

The concentration of monomer-ended radicals  $[M\cdot]$  is given for a homopolymerizing system by

$$[M\cdot] = \frac{R_p}{K_p[M]} \quad (\text{moles/l.}) \quad (16)$$

If there are  $N$  particles in 1 liter of the reaction mixture, the average number of radicals per particle,  $\bar{n}$ , is

$$\bar{n} = \frac{[M\cdot]}{N} N_A = \frac{N_A R_p}{K_p [M] N} \quad (17)$$

where  $N_A$  is Avogadro's number.

If a copolymerizing system follows Smith-Ewart kinetics<sup>14,15,28</sup> and fits the simple copolymer model,<sup>22,23,29</sup> the corresponding expression is

$$\bar{n} = \frac{N_A R_p [K_{p2} r_1 f_1 + K_{p1} r_2 f_2]}{N[M] K_{p1} K_{p2} [r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2]} \quad (18)$$

where  $K_{p_i}$  is the rate of propagation for homopolymerization of monomer  $i$  at the reaction temperature,  $f_i$  is the mole fraction of the designated monomer in the feed,  $r_1$  and  $r_2$  are copolymerization reactivity ratios, and styrene is indexed as monomer 1 in this case.

The average number of radicals per particle is available from eq. (18) once  $[M]$ ,  $N$ , and  $R_p$  have been measured. In this case, the reactivity ratios were taken as  $r_1 = 1.124$  and  $r_2 = 0.627$ .<sup>30</sup> The propagation rate constants  $K_{p1}$  and  $K_{p2}$  were taken to be<sup>31,32</sup> 176 and 26 l./mole-sec at 60°C following application of these values to solution copolymerization by Rudin and Chiang.<sup>5</sup> The activation energies for the propagation rate constants for both monomers were set equal to 7.4 kcal/mole. This is the value given by Morton and co-workers for emulsion polymerization of styrene.<sup>33</sup> It has been used also to estimate rates of chain transfer to monomer in the styrene/alpha-methylstyrene system.<sup>6</sup>

## POLYMERIZATION RESULTS

The rate data obtained at 60°C with potassium laurate and sodium lauryl sulfate surfactants are summarized in Table I. Conversion rates are given for the steady reaction period, which is called interval 2 in the Smith-Ewart model.<sup>14,28</sup> Sodium lauryl sulfate generally provided faster polymerization rates initially (in interval 1), but the conversion tended to be faster with potassium laurate in interval 2, especially at higher alpha-methylstyrene feed contents. These trends are shown in Figures 2-4.

The following hypothesis may account for the observed apparent interaction between surfactant type and feed composition. It is relevant to note that the surface area per molecule of sodium lauryl sulfate is<sup>34</sup>  $61 \times 10^{-20}$  m<sup>2</sup>, while that of potassium laurate<sup>35</sup> is  $48 \times 10^{-20}$  m<sup>2</sup> and that the two soaps were used here in equimolar quantities. In the Smith-Ewart-Gardon<sup>15</sup> model, the number of particles  $N$  nucleated in interval 1 is related to the soap concentration by

$$N = 0.37(a_s S)^{0.6} (R/\mu)^{0.4} \quad (19)$$

where  $a_s$  is the area occupied by unit weight of emulsifier,  $S$  is the weight concentration of surfactant,  $R$  is the rate of radical generation, and  $\mu$  is the rate of volume growth of a particle (assumed linear with time). The parameter  $\mu$  is a function of the monomer feed composition and temperature.  $R$ , the rate of radical production, also depends on temperature, but may be influenced by the soap, if this affects initiator decomposition rates. Ignoring this possibility for the moment, we note that

$$a_s S = N_A A_S [S] \quad (20)$$

where  $N_A$  is Avogadro's number,  $A_S$  is the surface area per surfactant molecule, and  $[S]$  is the soap concentration in moles per unit volume. (To be absolutely correct,  $[S]$  in eq. (20) should be the difference between the actual soap con-

Table I  
Effect of Soap Type on Rate Data at 60°C

Styrene	Feed composition, mole fraction	Interval 2 conversion, %/hr		Polym. rate $\times 10^3$ , moles/l. aq. phase/sec		Final conversion, %		Total reaction time, hr	
		Potassium laurate	Sodium lauryl sulfate	Potassium laurate	Sodium lauryl sulfate	Potassium laurate	Sodium lauryl sulfate	Potassium laurate	Sodium lauryl sulfate
1	0.0	123.3	150.0	1.82	2.22	97.5	100	2.75	1.75
0.911	0.089	76.9	77.5	1.12	1.13	94.5	97	3.75	3.95
0.819	0.181	46.7	34.6	0.67	0.67	92.5	85.0	5.75	4.0
0.726	0.274	27.9	20.5	0.40	0.29	92.5	80.0	7.0	6.0
0.63	0.37	16.8	15.3	0.24	0.21	86.0	82.5	9.0	9.0
0.532	0.468	9.5	8.3	0.13	0.11	75.0	72.0	11	12.0



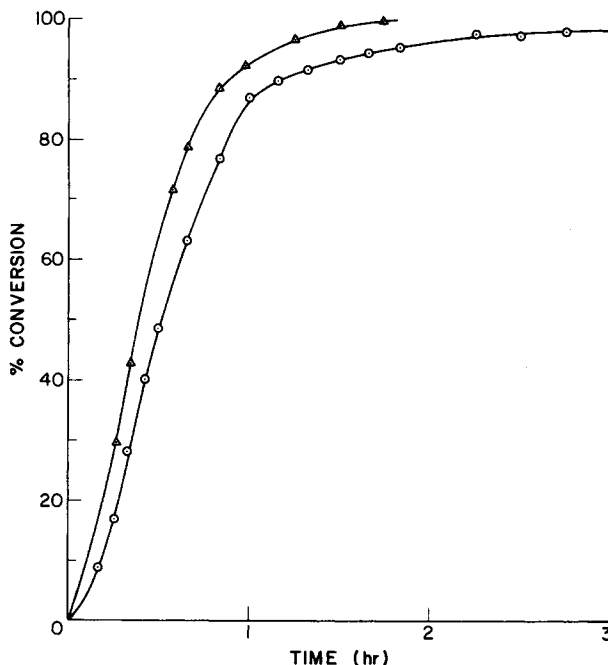


Fig. 2. Comparison of rate curves for polystyrene polymerization at 60°C: ( $\Delta$ ) sodium lauryl sulfate; ( $\odot$ ) potassium laurate.

centration and the critical micelle concentration (*CMC*). This can be neglected, however, because  $[S] \gg [CMC]$ .

Since the same molar concentrations were used, eqs. (19) and (20) indicate that the ratio of particles in the sodium lauryl sulfate and potassium laurate reactions should be equal to  $(61/48)^{0.6} = 1.2$ . The rate of polymerization depends on  $N$  directly, and the observed ratios for styrene homopolymerizations in Table I is in fact 1.2.

This order is reversed when the feed contains alpha-methylstyrene. It is possible that this inversion reflects a greater acceleration of potassium persulfate decomposition by sodium alkyl sulfates than by potassium laurate. The half-life of this initiator is about 33 hr at 60°C if its decomposition is not influenced by other substances in the reaction mixture.<sup>36,37</sup> Since the overall reaction time is increased by the addition of alpha-methylstyrene to the feed, the apparent anomalous effect of monomers on reaction rate could reveal the faster depletion of the initiator in the presence of the sulfate soap.

Potassium laurate was used exclusively for further studies at different temperatures because it has the lower Krafft point of the two surfactants.<sup>38</sup> (Not all the emulsifier is available for use in emulsion polymerizations if the temperature is below the Krafft point.)

The various copolymerizations with potassium laurate soap are summarized in Table II. Figure 5 contains conversion-time plots for polystyrene at 69°, 60°, and 40.7°C. Figure 6 shows the rate of conversion at 70°C for various comonomer feed compositions. Figures 7 and 8 depict similar plots at 60° and 40°C, respectively. Interval 2 conversion rates are plotted as functions of temperature and styrene content in the feed in Figure 9. It is clear from these results that

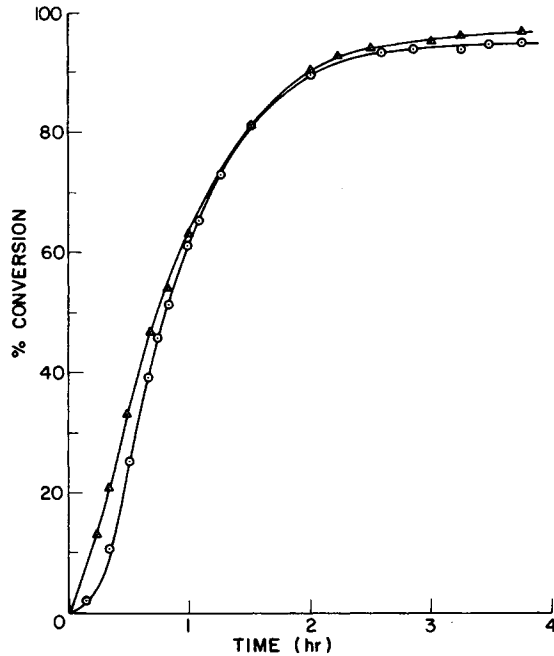


Fig. 3. Rate curves for 60°C copolymerization of feed containing 91.1 mol % styrene: ( $\Delta$ ) sodium lauryl sulfate; ( $\odot$ ) potassium laurate.

comonomer compositions containing at least 50% alpha-methylstyrene can be polymerized at reasonable rates at reaction temperatures which are equal to or higher than the ceiling temperature of the alpha-methylstyrene homopolymer. It is also evident that the rate of copolymerization decreases with increasing alpha-methylstyrene content in the feed and with decreasing reaction temper-

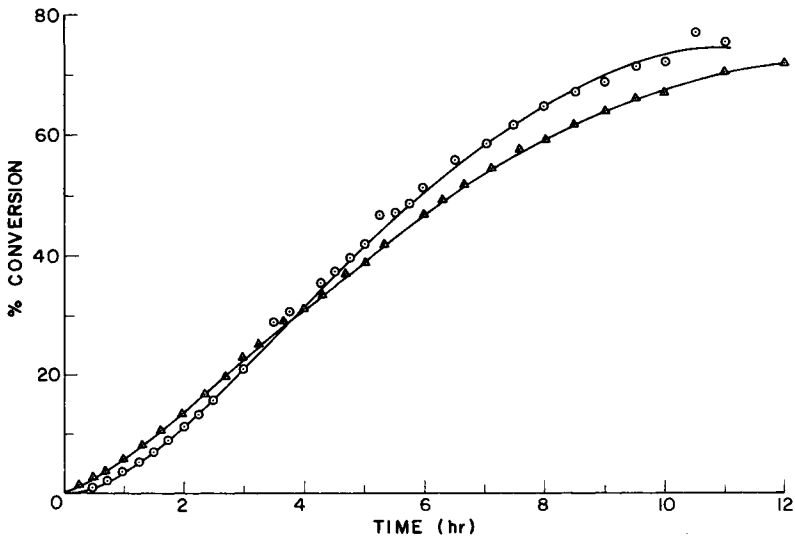


Fig. 4. Rate curves for 60°C copolymerization of feed containing 53 mol % styrene: ( $\Delta$ ) sodium lauryl sulfate; ( $\odot$ ) potassium laurate.

Table II  
Rate Data at Different Temperatures

Polymerization temperature, °C	Code	Feed composition, mole fraction		Interval 2 conversion, %/hr	Interval 1 polym. rate $\times 10^3$ , moles/l. aq. phase/sec	Final conversion, %	Total reaction time, hr
		Styrene	$\alpha$ -Methylstyrene				
69 $\pm$ 1	1C	1	0.0	218.2	3.23	~100.0	1.00
	2C	0.911	0.089	120.0	1.75	93.0	2.25
	3C	0.819	0.181	80.8	1.16	95.0	3.00
	4C	0.726	0.274	52.6	0.75	90.0	4.00
	5C	0.630	0.37	30.6	0.43	87.0	6.00
	6C	0.532	0.468	17.1	0.24	79.0	9.00
60 $\pm$ 1	1B	1	0.0	123.3	1.82	97.5	2.75
	2B	0.911	0.089	76.9	1.12	94.5	3.75
	3B	0.819	0.181	46.7	0.67	92.5	4.75
	4B	0.726	0.274	27.9	0.40	92.5	7.00
	5B	0.630	0.370	16.8	0.24	86.0	9.00
	6B	0.532	0.468	9.5	0.13	75.0	11.00
40.7 $\pm$ 1	1A	1	0.0	25.0	0.37	90.0	5.07
	2A	0.911	0.089	13.3	0.19	82.0	8.00
	3A	0.819	0.181	8.6	0.12	70.0	10.00
	4A	0.726	0.274	3.2	0.05	60.0	19.00

ature. Data presented in a separate article<sup>24</sup> show that the polymers made have sufficiently high molecular weights to be mechanically useful and have higher softening points than polystyrene.

While no particular attempt was made to determine the limiting conversions accurately, it is clear from Table II that the ultimate conversion decreases with increasing alpha-methylstyrene content and with decreasing temperature. This is as expected since both variations increase the difference between the polymerization temperature and the main glass transition temperature of the copolymer. Polymerization probably ceases when the glass temperature of the monomer-polymer mixture in the particle equals the reaction temperature.

The monomer volume fraction  $\phi_M$  in the particles during interval 2 polymerizations is recorded in Table III. There seems to be no significant dependence of  $\phi_M$  on feed composition. This is as expected since the two monomers have such similar structures. The equilibrium monomer concentration for styrene was found to be 4.7M. This is very close to the figures reported by van der Hoff.<sup>28,39</sup> These data are consistent with the theoretical prediction that monomer concentration in the particles is constant during interval 2 polymerizations.

Measurements of particle diameters in samples withdrawn at various times during the polymerization provided data on rates of particle growth. Figure 10 is such a plot. It will be noted that the values recorded are those of monomer-free particles. The active particles would have been swollen with monomer. Thus, the measured diameters of monomer-free particles recorded in Figure 11 show no decrease with conversion after about 60% reaction, whereas the particles in the actual polymerizing system probably started to shrink somewhat in this region as their monomer content progressively decreased.

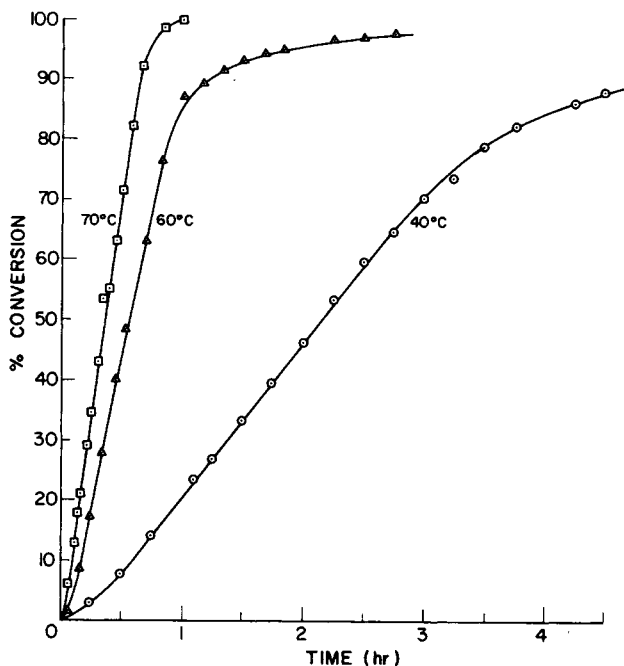


Fig. 5. Effect of temperature on polymerization rate of styrene with potassium laurate emulsifier.

The rate of volume growth of particles during interval 2 polymerization is recorded in Table IV. The measured values obtained on monomer-free particles were adjusted by dividing by  $1 - \phi_M$ . Gardon<sup>40</sup> has derived the following expression for the rate of volume increase  $\mu$  of particles during steady-rate emulsion homopolymerization:

$$\mu = \left( \frac{3}{4\pi} \right) \frac{K_p}{N_A} \left( \frac{d_m}{d_p} \right) \frac{\phi_M}{1 - \phi_M} \quad (21)$$

With  $d_m$  from eq. (6),  $d_p = 1.04 \text{ g/cm}^3$ ,  $K_p = 176 \times 10^3 \text{ cm}^3/\text{mole-sec}$ , and  $\phi_M$  as recorded in Table IV, the calculated rate for styrene homopolymerization at 60°C is  $7.5 \times 10^{-20} \text{ cm}^3/\text{sec}$ . The analogous term for the copolymerization would be

$$\mu = \left( \frac{3}{4\pi} \right) \left( \frac{d_m}{d_p} \right) \frac{\phi_M}{N_A(1 - \phi_M)} \left( \frac{K_{p1}K_{p2}(r_1f_1^2 + 2f_1f_2 + r_2f_2^2)}{K_{p2}r_1f_1 + K_{p1}r_2f_2} \right) \quad (22)$$

Entries in Table IV compare experimental and predicted values of  $\mu$ . It can be seen that the agreement is reasonably good, considering the experimental uncertainty and theoretical difficulties involved.

The numbers of particles per unit volume of aqueous phase,  $N$ , are recorded in Table IV. These values were obtained from the peak elution diameters in liquid exclusion chromatography as explained above in connection with eq. (15). The mean volume diameter is a more appropriate parameter to use in this connection, but this average could not be obtained for reasons given above. Any uncertainty in measurements of particle diameter is magnified in the subsequent calculation of particle volume and hence of  $N$ . The values recorded in Table

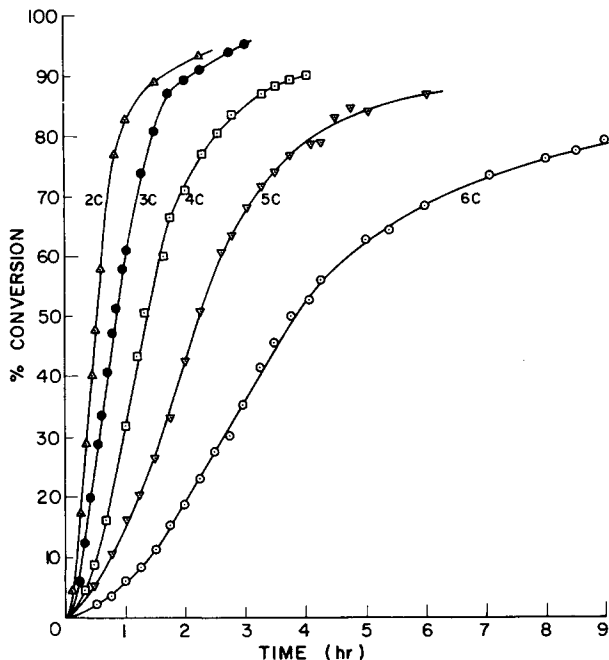


Fig. 6. Polymerization rate curves at 60°C for various comonomer feed ratios. The feed compositions corresponding to the labels on the curves are given in Table II.

IV cannot be claimed to be very accurate, although their uncertainty is typical of all experimental measurements of this parameter.<sup>41</sup>

The number of particles per unit volume of aqueous phase,  $N$ , can be calculated from eq. (18). The estimated values tended to be some three- to fivefold greater than the measured quantities. However, fairly good agreement was obtained if experimental values of  $R$  and  $\mu$  were used in this equation. The two sets of numbers are compared in Table IV. The major reason for the discrepancy between experimental and theoretical quantity is probably in the expression for  $R$ , which is given theoretically<sup>15</sup> as

$$R = 2N_A k_d [I] \quad (23)$$

in which  $k_d$  is the first-order rate constant for decomposition of the initiator which is present at concentration  $[I]$ . No allowance is made in eq. (23) for initiator wastage, which is appreciable in this system.<sup>6</sup> When the right-hand side of eq. (23) is modified to include the experimental values of  $f$ , the initiator efficiency, the agreement between calculated and estimated values of  $N$  is reasonable, as shown in Table IV.

Gardon's formula<sup>15</sup> for calculating particle diameter  $r$  is

$$r = 1.05 \left( \frac{m}{w} \right)^{0.33} \left( \frac{dw}{d_p} \right)^{0.33} S^{-0.2} \left( \frac{\mu}{R} \right)^{0.133} \quad (24)$$

where  $m$  and  $w$  are the respective masses of monomers and water,  $d_w$  is the density of water, and the other parameters have been defined earlier. Agreement between the measured and estimated values of  $r$  is again good when the experimental  $R$  and  $\mu$  figures are used, as shown also in Table IV.

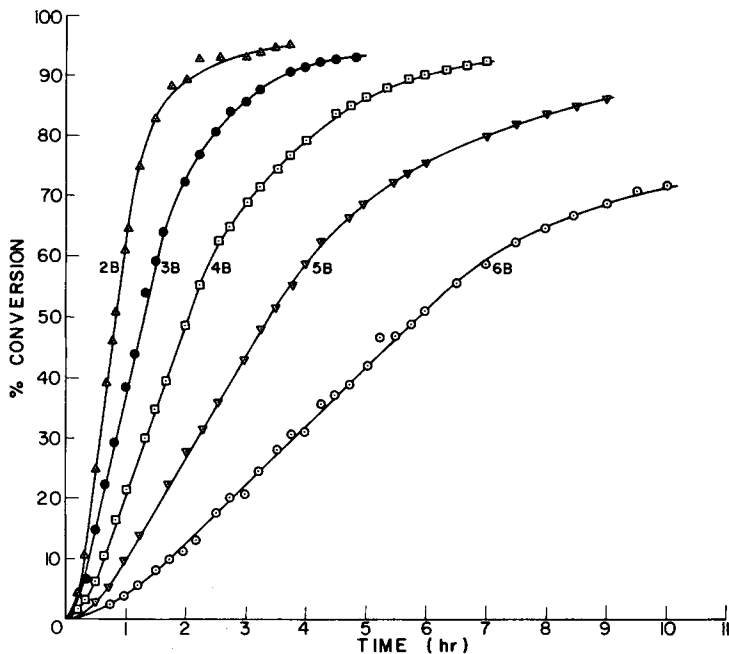


Fig. 7. Polymerization rates at 60°C. The monomer feed compositions corresponding to the labels on the curves are given in Table II.

The average numbers of radicals per particle, calculated from eq. (18), are also listed in Table IV. The values depend on  $N$  and on the  $K_p$  figures assumed for this calculation. The data are not sufficiently certain to encourage speculation about the effects of monomer feed composition on  $\bar{n}$ .

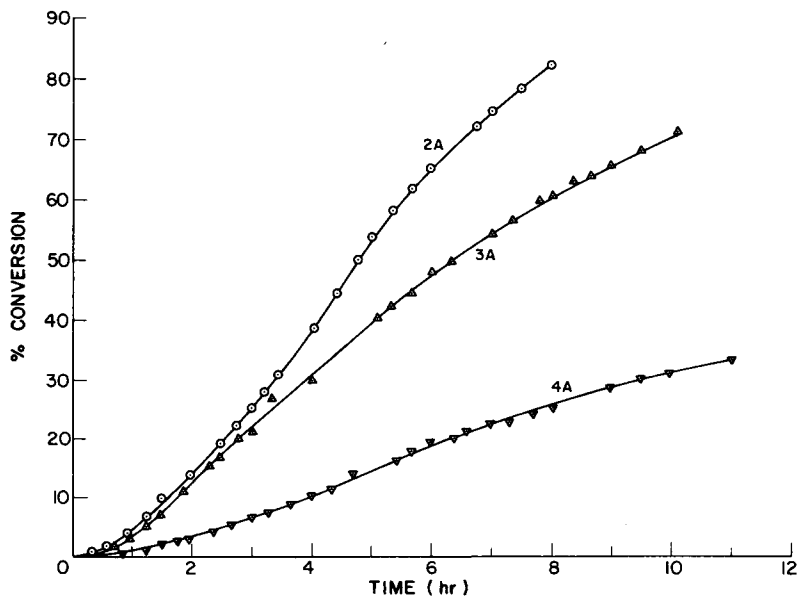


Fig. 8. Polymerization rates at 40°C. The monomer feed compositions corresponding to the labels on the curves are given in Table II.

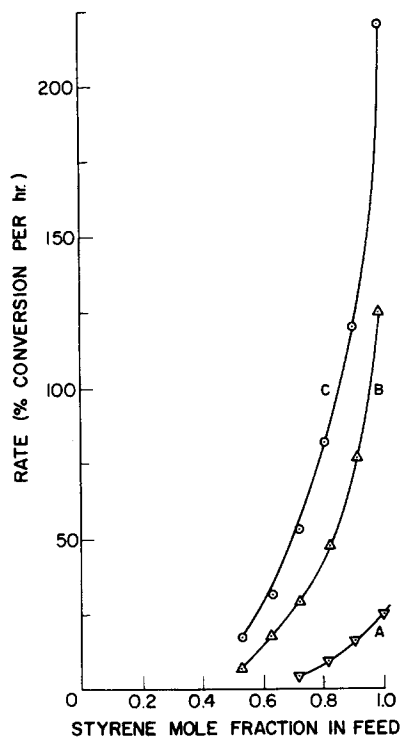


Fig. 9. Effect of feed composition on polymerization rate at different temperatures: (A) 40.7°C; (B) 60°C; (C) 69°C.

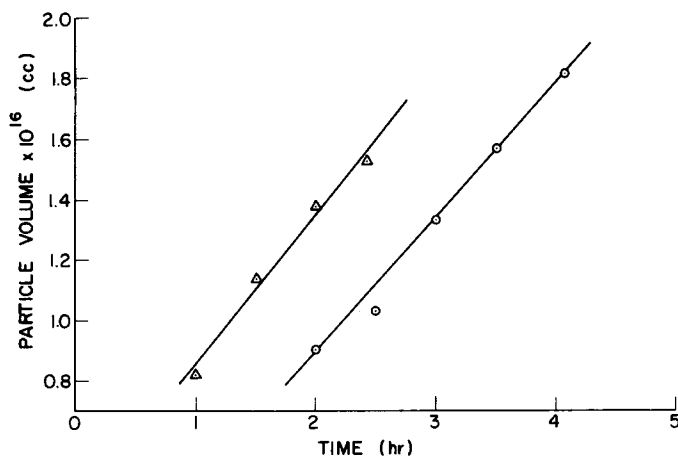


Fig. 10. Time dependence of particle volume for 69°C polymerization: ( $\Delta$ ) 5C 0.630 mole fraction styrene in feed; (O) 6C 0.532 mole fraction styrene in feed.

We note that the calculations of rate of volume growth, which are in reasonable agreement with experiment, are based on the assumption<sup>27</sup> that  $\bar{n}$  is 0.5 and conclude that the weight of evidence here does not show any significant departure from this expectation.

As a further check, the rate of polymerization in interval 2 was calculated using eq. (18) with experimental values of  $N$  and  $[M]$  and with  $\bar{n}$  set equal to 0.5. The

Table III  
Monomer Volume Fraction in Latex Particles

Polymerization temperature, °C	Code	Feed composition, mole fraction styrene	Conversion, %	Monomer volume fraction $\phi_M$ , [eq. (3)]	Equilibrium monomer conc. in particles $C_M$ moles/l. [eq. (4)]
69 ± 1	1C	1.0	15	0.56	4.6
			21	0.55	
			29	0.51	
			35	0.52	
			43	0.45	
	2C	0.911	18	0.60	4.6
			29	0.57	
			40	0.49	
			42	0.53	
	3C	0.819	34	0.56	4.5
42			0.53		
4C	0.726	32	0.55	4.5	
		43	0.48		
60 ± 1	3B	0.819	22	0.55	4.8
			29	0.55	
			38	0.51	
	4B	0.726	30	0.55	4.8
	5B	0.630	29	0.55	4.7
60 ± 1	6B	0.532	16	0.57	4.7
			20	0.57	
			26	0.57	
			31	0.52	

calculated and observed values are compared in Table V, where it can be seen that the agreement is reasonable, considering the possible uncertainties in the various parameters in this equation.

### VERIFICATION OF THE SIMPLE COPOLYMER MECHANISM

Earlier work from this laboratory<sup>5,7</sup> led to the conclusion that alpha-methylstyrene copolymerizes with styrene according to simple copolymer model kinetics.<sup>22,23</sup> This conclusion was based on experimental measurements of unreacted monomer composition by gas-liquid chromatography (GLC). The reactivity ratios calculated on this basis<sup>30</sup> have been used to estimate copolymer compositions in this work.

In this section we report the use of two additional experimental techniques to verify the aforementioned reactivity ratios and the applicability of the simple copolymer model to the emulsion copolymerization of styrene and alpha-methylstyrene. These methods involve analysis of the composition of monomer droplets during the emulsion reaction and proton NMR analysis of copolymer compositions.

#### Monomer Feed Composition During Emulsion Copolymerization

The structures and molecular weights of the two monomers used in this study are so similar that it is highly likely that their water solubilities and diffusion rates will not differ significantly. The ratio of monomer concentrations in the



Table IV  
Rate of Volume Growth, Particle Size, and Number of Particles

Polym. temp., °C	Code	Feed composition, mole fraction styrene, $f_1$	Volume fraction monomers in particles, $\phi_M$	Monomer conc. in particles moles/l.	Conversion $p$ , %	Rate of volume growth $\mu$ (cm <sup>3</sup> /sec) $\times 10^{20}$		Rate of initiation (moles/cm <sup>3</sup> aqueous phase) $\times 10^{10}$ <sup>a</sup>	Particle diameter, $A^\circ$		Number of particles/cm <sup>3</sup> H <sub>2</sub> O $N \times 10^{-15}$		Number of radicals per particle $\bar{N}$
						Expt.	Calc. [eq. (21)]		Expt.	Calc. [eq. (23)]	Expt.	Calc. <sup>b</sup> [eq. (18)]	
69 ± 1	1C	1.0	0.53	4.6	35	—	—	0.54	700	700	2.0	—	0.9
	2C	0.911	0.53	4.6	45	12.5	6.3	—	790	680	0.9	1.1	1.3
	3C	0.819	0.53	4.5	47	6.6	5.2	—	790	620	1.2	1.5	0.9
	4C	0.726	0.53	4.5	32	3.1	4.5	—	620	560	1.3	2.0	0.6
	6C	0.532	0.53	4.4	36	2.6	3.7	—	630	550	1.4	2.1	0.7
	60 ± 1	3B	0.819	0.55	4.8	54	—	—	0.16	810	—	1.0	—
4B		0.726	0.55	4.8	31	—	—	—	660	—	1.0	—	0.5
5B		0.630	0.55	4.7	29	—	—	—	670	—	1.0	—	0.4
6B		0.532	0.57	4.7	21	2.0	2.8	—	580	460	1.0	1.4	0.3

<sup>a</sup> Data from ref. (6).

<sup>b</sup> Calculated from eq. (18) with experimental values of  $\mu$  and  $R$ .

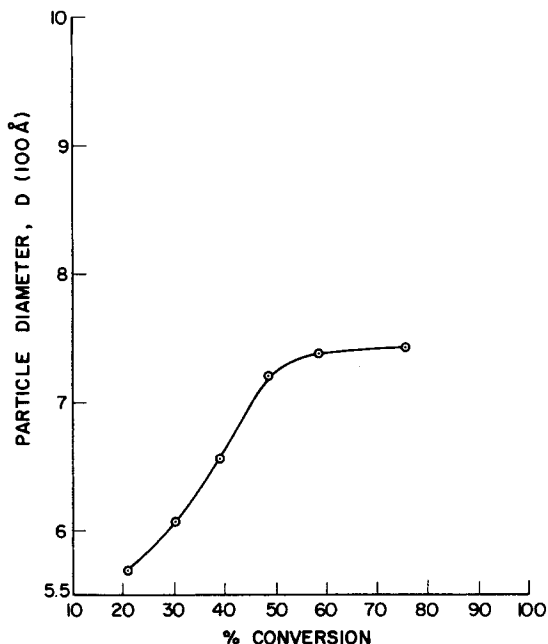


Fig. 11. Dependence of particle diameter on conversion for 60°C polymerization; 0.532 mole fraction styrene in feed.

polymerizing particles at any time should be the same as that in the monomer droplets in the system. In these experiments the monomer droplets were sampled and analyzed by GLC.

The monomer droplets lose their protective surfactant layers during the second phase of an emulsion polymerization, and a separate organic layer is formed in the absence of agitation. It is possible, however, to produce such a layer at will during the polymerization by centrifuging an aliquot of the reaction mixture. This is what was done in this work.

The ratio of monomers in the feed will change continuously as the reaction proceeds, unless both reactivity ratios are unity or the initial feed is an azeotrope.

Table V  
Rates of Polymerization

Polymerization temperature, °C	Feed composition, mole fraction styrene	[M], moles/l.	$N \times 10^{-15}$ , per cm <sup>3</sup> water	$K_{p1}$ , l./mole s	$K_{p2}$ , l./mole s	Interval 2 $R_p \times 10^3$ , moles/l. aq. phase/sec	
						Expt.	Calc. [eq. (18)]
69 ± 1	0.911	4.6	0.9	236	35	1.75	1.40
	0.819	4.5	1.2			1.16	0.50
	0.726	4.5	1.3			0.75	0.60
	0.532	4.4	1.4			0.24	0.45
60 ± 1	0.819	4.8	1.0	176	26	0.67	0.44
	0.726	4.8	1.0			0.40	0.37
	0.630	4.7	1.0			0.24	0.30
	0.532	4.7	1.0			0.13	0.25

The relation between degree of conversion  $p$  and monomer concentration is given by<sup>42</sup>

$$p = 1 - \left( \frac{f_1}{f_{10}} \right)^\alpha \left[ \frac{f_2}{f_{20}} \right]^\beta \left[ \frac{f_{10} - \delta}{f_1 - \delta} \right]^\gamma \quad (25)$$

where

$$\alpha = \frac{r_2}{1 - r_2}$$

$$\beta = \frac{r_1}{1 - r_1}$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}$$

and

$$\delta = \frac{1 - r_2}{1 - r_1 - r_2}$$

In this case  $f_i$  is the mole fraction of monomer  $i$  in the feed, and the subscript zero denotes the initial value. Since

$$f_{20} = 1 - f_{10} \quad (26)$$

and

$$f_2 = 1 - f_1 \quad (27)$$

eq. (25) can be written as

$$p = 1 - \left[ \frac{f_1}{f_{10}} \right]^\alpha \left[ \frac{1 - f_1}{1 - f_{10}} \right]^\beta \left[ \frac{f_{10} - \delta}{f_1 - \delta} \right]^\gamma \quad (28)$$

Equation (28) can be used with known values of  $r_1$ ,  $r_2$ , and  $f_{10}$  to calculate  $f_1$  and  $f_2$  at any value of  $p$ . These estimated figures can be compared with experimental values of  $f_1$  and  $f_2$  derived as described below. If the copolymerization model and reactivity ratios are valid, the calculated and experimental feed compositions should coincide.

The conversion  $p$  was determined gravimetrically as described earlier.

To determine the feed composition, samples were taken directly from the polymerizing system into chilled centrifuge tubes. Each tube was first coated with a powder layer of chain stopper (hydroquinone) by rotating the tube with the hydroquinone inside. The reaction mixture was centrifuged for 30 min at 12,000 rpm to develop a supernatant monomer layer.

The monomer layer was analyzed with a Carle Model 9000 gas chromatograph using a hydrogen flame detector. The column packing was 8% dinonyl phthalate on Anakron ABS. The flow rate of helium plus hydrogen was 15–18 ml/min, and the column temperature was  $133^\circ \pm 2^\circ\text{C}$ . The column contained a glass wool plug in its first inch of length to trap the stopping agent and any other nonvolatile substances which might have been present in the sample. The volume injected was approximately 1  $\mu\text{l}$ . Standard monomer mixtures were analyzed under the same experimental conditions to provide a calibration line in terms of monomer concentrations and GLC peak areas. Each sample was measured at least twice. The discrepancy between replicate measurements was

usually 0.4–0.8% of the mean measured mole fraction. Peak areas were measured with the help of a planimeter. The recorder used was equipped with a disc-type integrator, but this was not accurate enough for present purposes because the errors caused by baseline drift could not be compensated accurately.

Table VI compares calculated and observed mole ratios of styrene/alpha-methylstyrene in the feed at various conversions. The agreement is evidently very good. It will be noted that all experiments were at 60° and 69°C where any reversibility of alpha-methylstyrene polymerization might be expected to be accentuated.

### Analysis of Copolymer Composition by NMR

Ordinary spectroscopic methods for determining polymer composition do not always yield satisfactory results in the case of styrene/alpha-methylstyrene copolymers. Chemical analysis is not attractive because the two structural units differ only in the alpha position. Braun and co-workers<sup>43</sup> have reported that ultraviolet spectral analysis using extinction coefficients at 269 m $\mu$  was an unsatisfactory method. Good agreement was found, however, between the results of infrared analysis (CCl<sub>4</sub> solutions and band intensities at 2850 and 2910 cm<sup>-1</sup>)

Table VI  
Calculated and Measured Monomer Feed Compositions

Polymerization temperature, °C	Initial feed composition, styrene mole fraction, $f_{10}$	Degree of conversion $p$ , %	Mole ratio $\alpha$ -methylstyrene/styrene $f_2/f_1$	
			Observed	Calc. <sup>a</sup>
69	0.726	1.1	0.38	0.38
		4.6	0.38	0.38
		9.3	0.38	0.39
		16.1	0.39	0.39
		24.5	0.40	0.40
		31.8	0.41	0.41
		43.4	0.47	0.42
60	0.630	2.7	0.59	0.59
		9.1	0.60	0.60
		18.3	0.61	0.61
		28.6	0.63	0.63
		35.6	0.66	0.65
69	0.630	0.9	0.58	0.59
		4.4	0.60	0.59
		8.0	0.61	0.60
		14.0	0.61	0.61
		20.0	0.61	0.62
		26.3	0.64	0.62
		32.9	0.66	0.64
69	0.532	5.8	0.90	0.90
		10.8	0.90	0.91
		18.6	0.93	0.93
		27.1	0.95	0.96
		35.6	1.01	0.99

<sup>a</sup> With  $r_1 = 1.124$ ,  $r_2 = 0.627$ .<sup>30</sup>

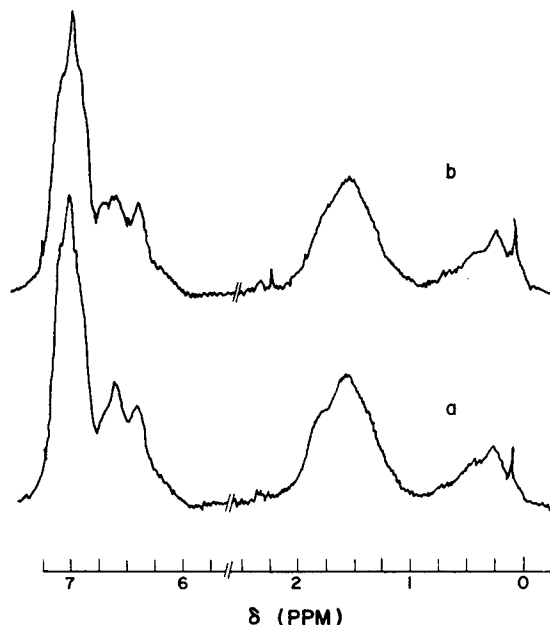


Fig. 12. 220 MHz NMR spectra of copolymers polymerized at 60°C: (a) 0.32 mole fraction alpha-methylstyrene in copolymer; (b) 0.41 mole fraction alpha-methylstyrene in copolymer.

and NMR (200 g/l. in hexachlorobutadiene solutions, 170°C, 56.4 MHz spectra). The free-radical reactivity ratios reported by these authors are slightly outside the joint confidence loops reported for this pair by Rudin et al.,<sup>30</sup> but Braun and co-workers estimated their reactivity ratios with a computational method which is now known to be unreliable.<sup>45</sup>

NMR spectral analysis was used in this case to determine the copolymer composition. In polystyrene spectra the methine and methylene groups show resolved peaks, but these two groups are present as one broad band in the case of copolymers. Methyls have a separate peak in copolymers.

If the methyl peak area is  $x$  and the combined methine and methylene peak area is  $z$ , then

$$x \propto 3F_2 \quad (29)$$

$$z \propto 3(1 - F_2) + 2F_2 \quad (30)$$

or

$$z \propto (3 - F_2) \quad (31)$$

where  $F_2$  is the mole fraction of alpha-methylstyrene in the copolymer. The proportionality constants implied in eq. (30) and (31) are sensitivity factors. Since styrene and alpha-methylstyrene are similar in nature, it seems unlikely that the proton resonances of equivalent groups in the two moieties would differ significantly. We have therefore combined eq. (29) and (31) to give

$$\frac{z}{x} = \frac{3 - F_2}{3F_2} \quad (32)$$

or

$$F_2 = \frac{3x}{3z + x} \quad (32')$$

Table VII  
Essential Features of 220 MHz Proton NMR Spectra Peak Positions (in ppm)

Polymerization temperature, °C	Code	Aromatic peak		Shoulder on	Methine group	Methylene group	Methyl group		Remarks
		Meta and para protons	Ortho protons				Peak	Shoulder	
60 ± 1	1B	7.00	6.57	6.47 peak is prominent	1.90	1.52	—	—	
	2B	7.03	6.59	6.48 peak is prominent	1.89	1.50	1.50	0.45	methine peak prominent
	3B	7.00	6.57	6.45 is prominent	1.86	1.52	0.46	—	methine peak prominent
	4B	6.97	6.56	6.36 peak is prominent	1.81	1.52	0.43	0.27	methine peak is shoulder on methylene peak
40.7 ± 1	5B	6.93	6.55	6.36 peak is prominent	1.80	1.58	0.27	0.43	methine peak is small shoulder on methylene peak
	6B	6.93	6.53	6.34 peak is prominent	1.80	1.56	0.27	0.45	
	3A	7.01	6.59	6.45 is prominent	1.84	1.50	0.45	—	
60 ± 1	3B	7.00	6.57	6.45	1.86	1.52	0.46	—	methine peak prominent
	3C	7.00	6.57	6.47 peak is prominent	1.90	1.52	—	—	

Table VIII  
NMR Data of Various Copolymers

Polymerization temperature, °C	Designation	$\alpha$ -Methylstyrene mole fraction in copolymer					
		NMR peak areas, arbitrary units			Calculated [eq. (31)]	Experimental	
		Phenyl	Methyl	Methine + methylene		Phenyl/ methyl [eq. (30)]	Methine + methylene/methyl [eq. (29a)]
60 $\pm$ 1	1B	10.0	0.0	6.0	0	0	0
	2B	10.7	0.5	6.2	0.68	0.78	0.79
	3B	10.6	0.85	5.3	0.16	0.13	0.15
	4B	10.1	1.4	5.2	0.24	0.23	0.25
	5B	10.6	1.9	5.4	0.32	0.30	0.32
	6B	9.7	2.3	5.2	0.41	0.40	0.39
40.7 $\pm$ 1	3A	10.2	0.8	5.3	0.16	0.13	0.14
	3B	10.6	0.85	5.3	0.16	0.13	0.15
	3C	10.4	0.95	5.8	0.16	0.16	0.16

Similarly, the phenyl and methyl peak areas yield

$$F_2 = 5x/3y \quad (33)$$

where  $y$  is the phenyl peak area. The copolymer composition can be calculated from Eq. (32') or from eq. (33).

The NMR spectra were measured at 220 MHz and 20°C. Solutions were at about 5% (w/v) in tetrachloroethylene with methylene chloride as the internal reference. Response areas were obtained from NMR spectrometer integration.

Typical spectra are shown in Figure 12. Table VII lists the essential features of such spectra. The peak near 7 ppm arises from meta and para aromatic hydrogens, while that at 6.5 ppm represents ortho protons. The latter band is resolved into two peaks in polystyrene spectra but appears as mildly resolved peaks or a shoulder in the case of copolymers. Methine and methylene responses provide separate peaks in polystyrene spectra but are not so well resolved in copolymers. As the alpha-methylstyrene content increases, the methine peak becomes a shoulder on the methylene peak. In copolymers, the methyl peak is shifted upfield and the methine peak downfield, so that the two resonances eventually overlap.

Table VIII compares copolymer compositions calculated from experimental results and eqs. (30a) and (31) as well as from

$$F_2 = 1 - F_1 = \frac{r_2 f_2^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (34)$$

with the reactivity ratios cited earlier. Equation (34) is one form of the simple copolymer equation. It can be seen that the NMR analyses agree with the simple copolymer model predictions generally to within about 5%. This is the uncertainty in NMR measurements of this type.

These experiments confirm the validity of the simple copolymer model and the reactivity ratios produced in studies of solution copolymerizations of this monomer pair.<sup>30</sup>

## CONCLUSIONS

The emulsion copolymerization of styrene and alpha-methylstyrene appears to follow Smith-Ewart-Gardon kinetics if allowance is made for initiator wastage. This minor correction to the basic theory should also be applied to homopolymerizations.

The present copolymerization is consistent with the terminal copolymerization model. Emulsion polymerization yields high molecular weight copolymers at fast rates because the normal bimolecular termination reactions are relatively suppressed in emulsion systems.

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## References

1. G. Ham, *J. Polym. Sci.*, **45**, 169, 183 (1960).
2. G. G. Lowrey, *J. Polym. Sci.*, **47**, 463 (1960).
3. P. Wittmer, *ACS Polym. Prepr.*, **11**(1), 367 (1970).
4. G. Smets and L. DeHaes, *Bull. Soc. Chim. Belges*, **59**, 13 (1950).



5. A. Rudin and S. S. M. Chiang, *J. Polym. Sci. Chem. Ed.*, **12**, 2235 (1974).
6. A. Rudin, M. C. Samanta, and B. M. E. van der Hoff, *J. Polym. Sci. Chem. Ed.*, **17**, 493 (1979).
7. H. K. Johnston and A. Rudin, *J. Paint Technol.*, **42**, 435 (1970).
8. A. V. Golubeva, A. F. Usmanova, and A. A. Vansheidt, *J. Polym. Sci.*, **52**, 63 (1961).
9. W. G. Barb, *J. Polym. Sci.*, **37**, 515 (1959).
10. J. F. Kenney and P. J. Patel, *J. Appl. Polym. Sci.*, **20**, 449 (1976).
11. J. F. Kenney and P. J. Patel, *J. Appl. Polym. Sci.*, **20**, 457 (1976).
12. J. F. Kenney and P. J. Patel, *J. Polym. Sci. Chem. Ed.*, **20**, 449 (1976).
13. J. F. Kenney, *J. Polym. Sci. Chem. Ed.*, **20**, 457 (1976).
14. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
15. J. L. Gardon, *Rubber Chem. Technol.*, **43**, 74 (1970).
16. W. F. Fowler, Jr., in *Vinyl Polymerization*, Part II, G. E. Ham, Ed., Marcel Dekker, New York, 1969.
17. W. D. Harkins, R. W. Mattoon, and M. L. Corrin, *J. Am. Chem. Soc.*, **68**, 220 (1946).
18. W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).
19. W. D. Harkins, S. W. Herzfeld, A. Roginsky, and M. L. Corrin, *J. Polym. Sci.*, **5**, 207 (1950).
20. W. D. Harkins, *J. Polym. Sci.*, **5**, 217 (1950).
21. F. A. Bovey, I. M. Kolthoff, A. I. Medalia, and E. I. Meehan, in *Emulsion Polymerization*, High Polymer Series, Vol. IX, Wiley-Interscience, New York, 1955.
22. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
23. T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).
24. A. Rudin and M. C. Samanta, *J. Appl. Polym. Sci.*, to appear.
25. J. W. McBain and M. C. Field, *J. Phys. Chem.*, **37**, 675 (1933).
26. P. M. Hay, J. C. Light, L. Marker, R. W. Murray, A. T. Santonicola, O. J. Sweeting, and J. G. Wepsic, *J. Appl. Polym. Sci.*, **5**, 23 (1961).
27. A. E. Hamielec and S. S. Singh, *J. Appl. Polym. Sci.*, **22**, 577 (1978).
28. B. M. E. van der Hoff, *ACS Adv. Chem. Ser.*, **34**, 6 (1962).
29. F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).
30. A. Rudin, S. S. M. Chiang, H. K. Johnston, and P. D. Paulin, *Can. J. Chem.*, **50**, 1757 (1972).
31. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951).
32. B. K. Kang, K. F. O'Driscoll, and J. A. Howell, *J. Polym. Sci. A-1*, **10**, 2349 (1972).
33. M. Morton, P. P. Salatiello, and H. Landfield, *J. Polym. Sci.*, **8**, 279 (1952).
34. J. G. Brodnyan and G. L. Brown, *J. Colloid Sci.*, **15**, 76 (1960).
35. Z. Pelzbauer, V. Hynkova, M. Bezdek, and F. Hrabak, *J. Polym. Sci. C*, **16**, 503 (1967).
36. E. Hakoila, as quoted by D. C. Blackley, *Emulsion Polymerization*, Applied Science Publishers, London, 1975, pp. 163 and 165.
37. C. E. M. Morris and A. G. Parts, *Makromol. Chem.*, **119**, 112 (1968).
38. K. Krafft and B. H. Wiglau, *Ber.*, **28**, 2566 (1895).
39. B. M. E. van der Hoff, *J. Polym. Sci.*, **44**, 241 (1960).
40. J. L. Gardon, *J. Polym. Sci. A-1*, **6**, 643 (1968).
41. J. W. Vanderhoff, in *Vinyl Polymerization*, Part II, G. E. Ham, Ed., Marcel Dekker, New York, 1969, p. 103.
42. I. Skeist, *J. Am. Chem. Soc.*, **68**, 1781 (1946).
43. D. Braun, G. Heufer, V. Johansen, and K. Kolbe, *Kolloid-Z.*, **195**, 134 (1964).
44. P. W. Tidwell and G. A. Mortimer, *J. Macromol. Sci. Rev.*, **C4**, 281 (1970).

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