Experiments with Soap-Free Polymerization of Styrene in the Presence of Alcohols

A. M. HOMOLA,* M. INOUE, and A. A. ROBERTSON, *Pulp and Paper Research Institute of Canada, Pointe Claire, Quebec, Canada H9R 3J9, and Department of Chemistry, McGill University, Montreal, Canada H3C 3G1*

Synopsis

Polystyrene latexes have been synthesized by a method based on that of Kotera et al.[4] The polymerization rates and yields have been improved by the addition of an alcohol (methanol) to the reactants. The effects of varying the methanol content and other process variables on the polymerization and on the properties of the latex are reported.

INTRODUCTION

The laboratory synthesis of polystyrene latexes has provided much of the experimental support for the Harkins-Smith-Ewart micellar theory of particle formation.

The theory describes the behavior of a system in which the monomer has limited solubility. An emulsifier, frequently a fatty acid soap, is added and has the treble functions of emulsifying the monomer, forming micelles that provide the loci for polymerization and stabilizing the latex particles after they are formed. The initiation reaction for the free-radical polymerization is usually provided by the decomposition of potassium persulfate.

The principles of the theory were advanced by Harkins, and the consequences were elaborated in kinetic terms by Smith and Ewart. Experimental support of the Smith-Ewart theories have been provided and are widely accepted.[1] However, a substantial number of contradictory experimental results, particularly relating to the initial stages of polymerization, have appeared recently. Fitch[2] has proposed an alternative approach.

Concurrently, it has been reported that stable polystyrene latexes can be prepared without soaps or indeed without any conventional emulsifier. The stability of the resulting latex is ascribed to the presence, on the surface of the latex particles, of ionizable carboxyl and sulfonate or sulfate groups resulting from the initiation reaction.

The development of emulsifier-free polystyrene latexes may be traced to Matsumoto and Ochi[3] who obtained a narrow particle-size distribution using only monomer and persulfate initiator in water. The role of temperature, monomer concentration, initiator concentration, and agitation on the particle

*Present address: Department of Chemistry, University of Melbourne, Parkville, Victoria, Australia.

size and uniformity was discussed. The strong acid group stabilization was reported to correspond to two acid groups per molecule, on the surface of the particle.

The investigation of these latexes has been pursued by Kotera,[4] Furusawa,[5] Ottewill,[6] and others. The range and number of polymerization variables affecting latex properties have been extended and now include electrolyte concentration and pH in addition to those already mentioned.

Much of the interest in emulsifier-free latexes derives from the possibilities for convenient preparation of simple, well-characterized model colloids. Preparations involving removal of soap from conventional latexes by dialysis or by ion exchange is a challenging task.[7,8] The limitations of the methods available for synthesis of emulsifier-free latex have been the low final solids concentrations, slow conversion rates, and often low attainable conversions. The purpose of this paper is to describe a procedure that overcomes these disadvantages.

The reported method resulted from the idea that the conversion rate could be speeded up by increasing the monomer solubility and thus increasing the availability of monomer at the polymerization sites. The addition of a solvent for the monomer to the emulsifier-free system was suggested as a suitable means of doing this. Of the solvents for styrene, methanol suggested itself because of its infinite miscibility with water and with styrene and its lack of solvency for the polymer. The possibility for easy removal after polymerization by stripping or by dialysis are also favorable factors. It should be noted that a similar use of methanol has been recorded,[9] although under somewhat different conditions and with different objectives.

EXPERIMENTAL

Materials. Styrene (Eastman) was distilled at 44.2°C/22 mm Hg; water was distilled in Pyrex glass; potassium persulfate and methanol were analytical grade and used as received. Nitrogen (Canadian Liquid Air) was purified by passage through a copper furnace.

Procedure. Polymerizations were conducted in narrow-mouth, 250-ml Pyrex bottles fitted with standard taper stoppers. Ingredients were weighed into the reaction bottles at room temperature to give a total reaction volume of about 170 ml, e.g., 144 g distilled water, 18 g distilled styrene, 18 g methanol, and 0.225 g potassium persulfate. Oxygen was purged from the bottle by bubbling purified nitrogen gas at 200 cm^3/min for 10 min. Multiple bottles were prepared, closed with silicone-greased stoppers and clamps, and attached to a rotor that tumbled them at 35 rpm in a water bath at 70°C (±0.1°).

Characterization. After the desired time of reaction, the sample bottle was removed. An aliquot was dried in the presence of 1% hydroquinone in an aluminum pan at 70°C to give the degree of conversion determined by the solid content. Particle sizes were determined from shadowgraph (Nikon) examination of transmission electron micrographs (JEM 6A). Latex samples were diluted to 1 ppm and a drop placed on carbon-coated electron microscope grids and dried. Averages and distributions of particle diameter were based on 100 particles.

RESULTS

Conversion Rates

Conversion curves obtained in this work conformed to a typical shape (Figs. 1 and 2) which suggests a short initial period, a rather linear conversion or constant conversion rate, followed by an accelerating conversion up to high conversion levels.
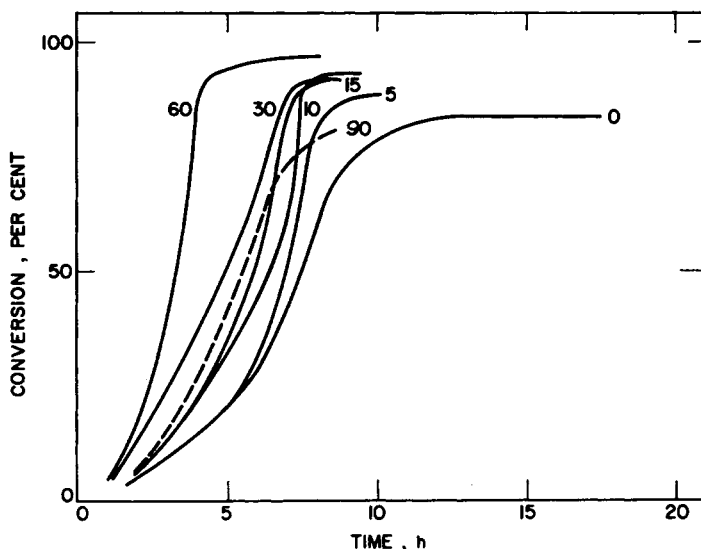

Fig. 1. Progress of polymerization, expressed as per cent monomer converted, at different methanol levels, expressed as per cent weight of reactor contents. Initial concentration of styrene, 10%; initiator, 0.125%.
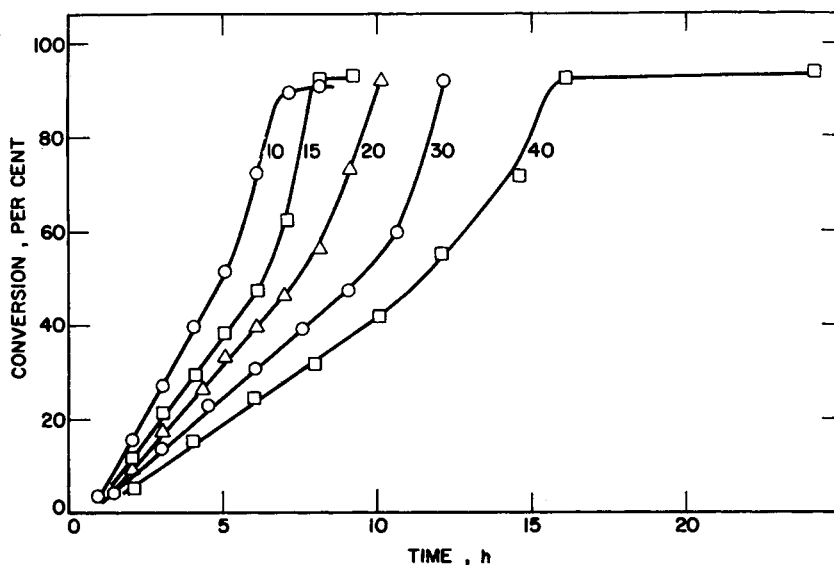

Fig. 2. Progress of polymerization, expressed as per cent monomer converted, at different initial monomer levels, expressed as per cent weight of reactor contents. Concentration of methanol, 30%; initiator, 0.125%.
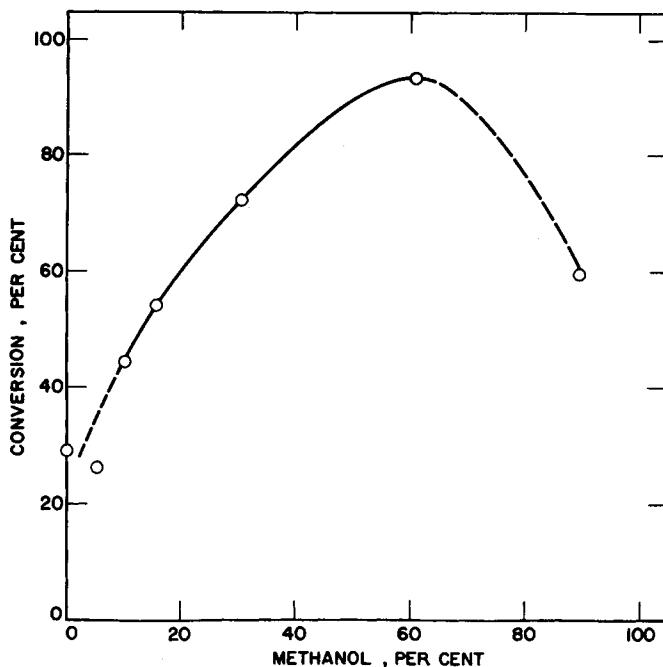
Fig. 3. Polymerization, expressed as per cent monomer converted at 6 hr of reaction time, as a function of methanol level. As in Fig. 1.

The change in conversion rate as a function of methanol content is shown in Figure 1. The same trend is shown more clearly in Figure 3, which shows the conversion achieved after 6 hr at different methanol levels. The comparison here is made at low (10%) styrene contents to permit inclusion of comparative methanol-free polymerization data.

The change in conversion rate expressed in per cent is shown in Figure 2 when the monomer concentration is progressively changed at a methanol concentration of 30%. Replotting on the basis of amount, rather than per cent conversion (Fig. 4), however, shows a polymerization rate which increases modestly with monomer content.

The rates indicated by the linear part (0–55%) of the conversion curves also increase linearly with the initiator (potassium persulfate) concentration (Fig. 5).

Particle Size

The purpose of the synthesis is frequently to obtain monodisperse latexes of a particular particle size. The size obtained is also a function of the various variables described and some control over the final particle size is therefore possible.

The particle size increases with the amount of potassium persulfate (KPS) (Fig. 6). The effect of increased KPS is not only that of increased initiation but presumably also of electrolyte concentration. It had been anticipated that additional initiator would lead to more particles of smaller size, but this result was not obtained unless the comparison was made at constant total electrolyte concentration. When this was done by appropriate addition of
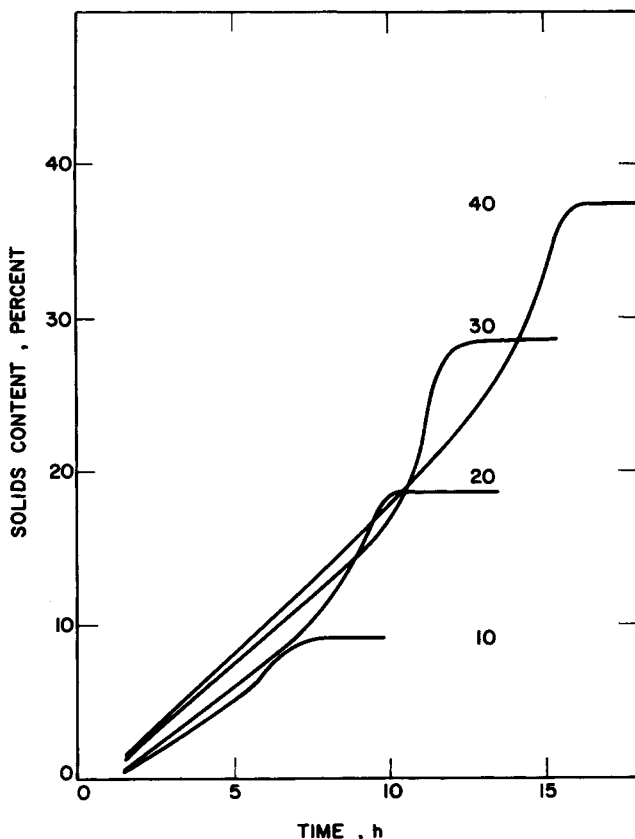
Fig. 4. Progress of polymerization, expressed as amount of monomer converted to polymer, at different initial monomer levels expressed as per cent weight of reactor contents. As in Fig. 2.

NaCl, increasing KPS resulted in decreasing final particle size (Fig. 7). A further control over particle size is thus indicated by control of electrolyte concentration, larger particles being attained with more electrolyte present (Fig. 8). The behavior is similar to that found by Ottewill et al.[6] Limits are set by the slowing of polymerization rates and decreasing stability of the latexes.

Increased monomer concentration leads to increasing particle size (Fig. 9) as anticipated under the conditions of the experiment, while increases in methanol concentration reduced the particle size with correspondingly increased particle number (Fig. 10).

Conversion rate studies were conducted by interrupting polymerization at various times by the addition of hydroquinone and removal of the samples from the bath. However, when the latex samples were examined after some weeks storage, it was found that the particles were all of similar size (Fig. 11). It is presumed that polymerization within the latex particles had continued even though solution polymerization had been short-stopped by the conventional means.

It must be admitted that not all emulsion polymerizations within the experimental limits resulted in monodisperse stable latexes. However, samples
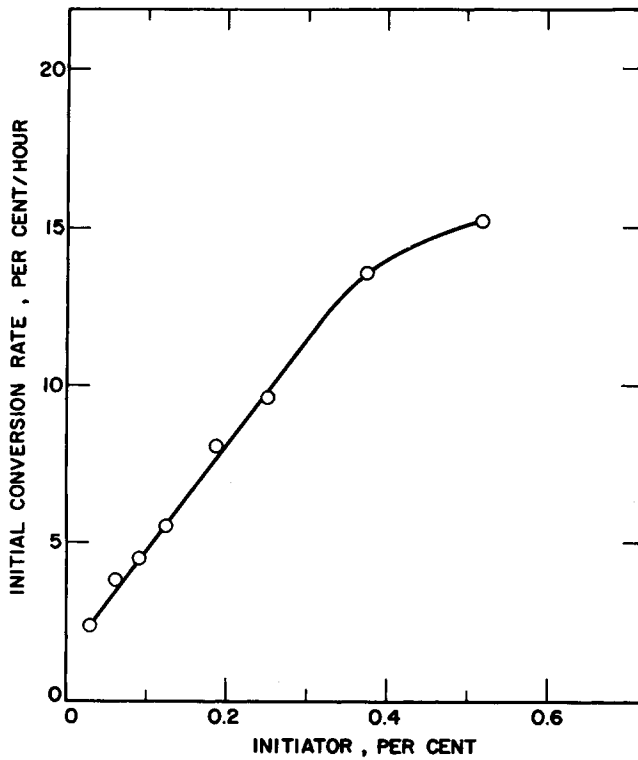
Fig. 5. Polymerization rate as a function of initiator concentration. Concentration of styrene, 30%; methanol, 30%.
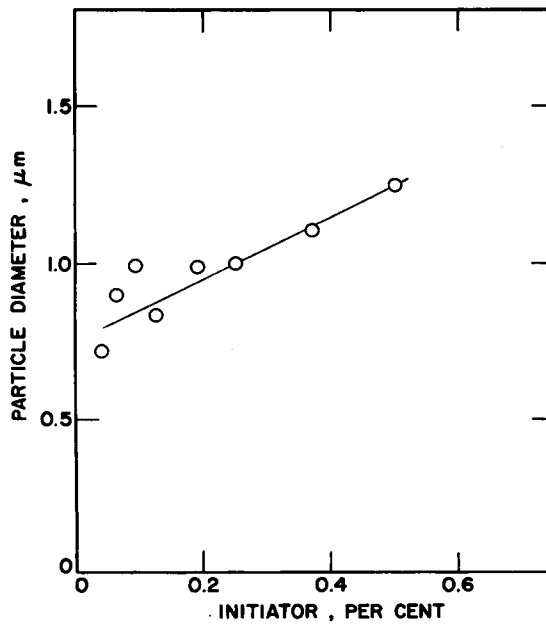

Fig. 6. Particle diameter vs. initiator concentration. Concentration of styrene, 30%; methanol, 30%.
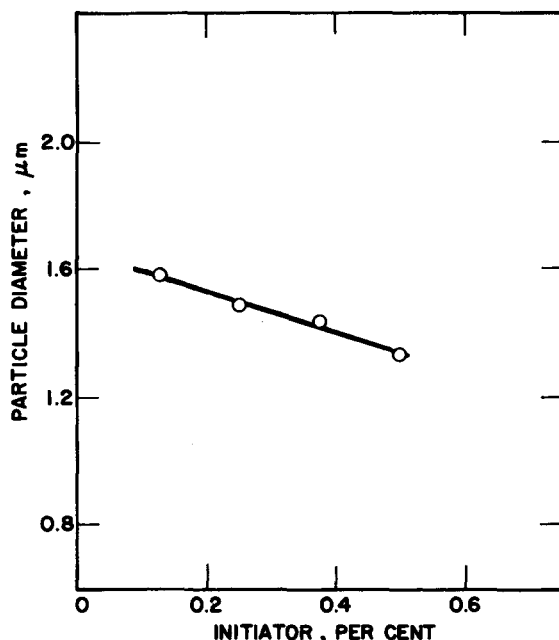
Fig. 7. Particle diameter vs. initiator concentration at constant electrolyte level. NaCl added.

corresponding to >80% conversion normally showed standard deviations of less than 2.5% of their mean diameter although the heterogeneity is often greater at lower conversions. As an example, the standard deviations expressed as percentages of the particle diameters shown in Figure 11 are respectively 5.1, 4.6, 3.8, 7.3, 4.7, 3.8, 2.6, and 2.5. Figure 11 also shows the ir-
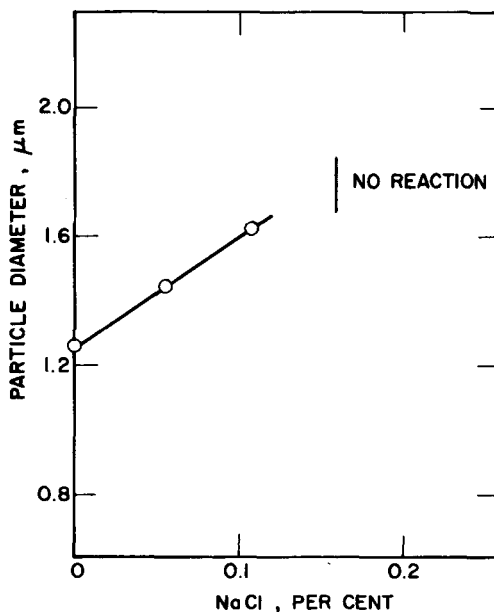

Fig. 8. Particle diameter vs. electrolyte (NaCl) level. Concentration of styrene, 30%; methanol, 30%; persulfate, 0.25%; 60°C.

regularity sometimes observed of a bimodal distribution of particle sizes in which the two components are more or less monodisperse. These bimodal populations have not yet been shown to be systematically dependent on ex-
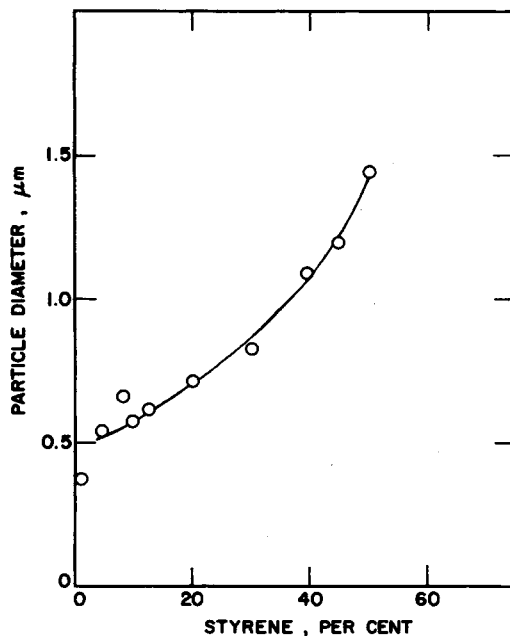

Fig. 9. Particle diameter vs. initial monomer concentration expressed as per cent weight of reactor contents. Concentration of methanol, 30%; persulfate, 0.125%.
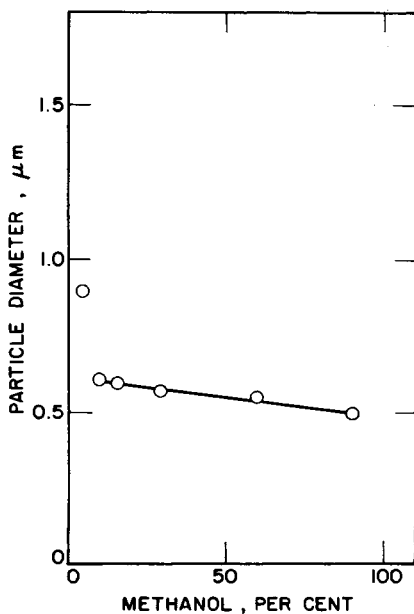

Fig. 10. Particle diameter vs. methanol concentration expressed as per cent weight of reactor contents. Concentration of styrene, 10%; persulfate, 0.125%.
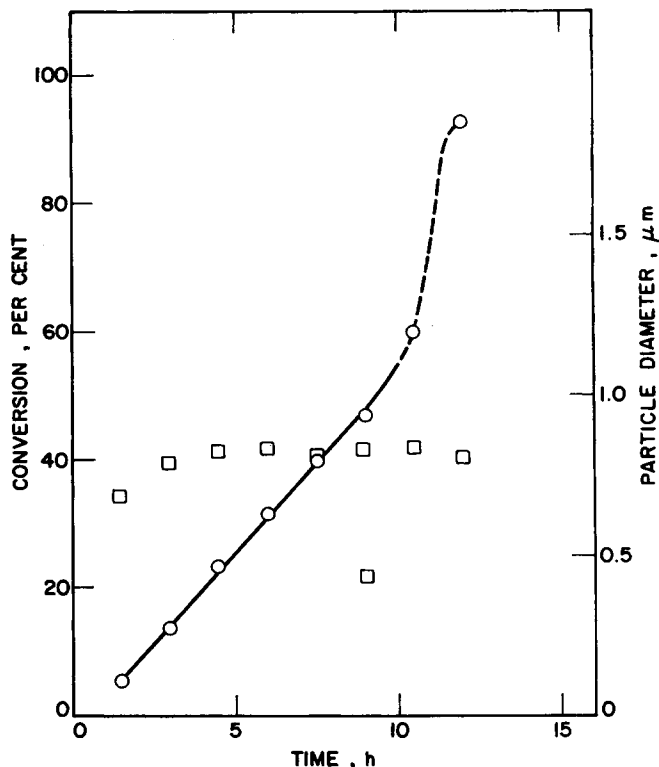
Fig. 11. Progress of polymerization expressed as per cent monomer converted. Square points record the particle diameters measured after extended sample storage. Concentration of styrene, 30%; methanol, 30% persulfate, 0.125%.

perimental conditions but may indicate the possibility of secondary nucleation when primary particles reach some limiting size.

DISCUSSION

The formation of particles may occur in the following way:

1. Solution polymerization of styrene is initiated by thermal decomposition of the potassium persulfate to form active oligomers.

2. The oligomers, which are visualized as having surfactant properties, grow until (a) they terminate by recombination while still soluble, or (b) with growth of styrene chains, they aggregate and precipitate or micellize into particles or nuclei.

3. The particles grow by further aggregation[2,6] and by continued polymerization. They are now able to take up monomer from solution and to become swollen.

4. The site of polymerization shifts from the solution to the particles. It is noted that the initiator is organophobic and initiation occurs in the water–methanol phase and is propagated in the particle by active oligomer particles which diffuse to and into the particles. A sufficient monomer concentration is also maintained in the particle by diffusion.

Up to 50% conversion, the rate of conversion is typically constant after an initial period during which the particles are initiated and the number of par-

ticles is determined. This constant rate period is characterized by only modest increases of rate with monomer content (Fig. 4), but the increases are substantial with KPS concentration (Fig. 5) or methanol concentration (Figs. 1 and 2). That is, the rate is determined by the rate of initiation and availability or solution concentration of monomer at the initiation sites and the ability of the monomer to reach the propagation sites.

The continued growth of particles after attempts at short-stopping (Fig. 11), perhaps similar to the experience of Glenn et al.,[10] is explained by the inaccessibility to the inhibitor (hydroquinone) of the propagation sites within the particles while accessibility to monomer is maintained.

The increase in conversion rate after reaching 50% conversion is not so readily explained. It is assumed that there are multiple oligomeric or polymeric free radicals in the particles. Their termination by recombination becomes less as the molecular weight increases, i.e., monomer can diffuse to propagation sites, but free radicals attached to growing polymer chains become less mobile. This is a realization of the Trommsdorff effect[11]; increases in rate at higher conversions, observed in a number of polymerization systems, have been similarly explained.

The presence of methanol may have several effects: (a) solubilization of the monomer and oligomer; (b) modification of the aggregation of oligomers by affecting their lyophobic-lyophilic characteristics with respect to the bulk medium; (c) increasing the rate of initiator reaction; (d) possible participation of methanol in free-radical reactions to modify the products; (e) changes in the dielectric constant, density, surface tension, and viscosity of the bulk medium and the effect of these on diffusion and stability.

No attempt has yet been made to evaluate the significance of each of these possible effects. The purpose of this paper is to describe the phenomena observed when methanol is added to the system and to show that the behavior is consistent with the suggestions made by others in explanation of emulsifier-free latexes in particular and, to some extent, of emulsion polymerization generally.

Possibilities are evident for the use of this system for the investigation of the mechanisms and kinetics of latex formation. Limited trials show that the use of alcohols other than methanol and monomers other than styrene can show similar behaviour and result in stable and relatively uniform latexes.

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