Polymerization of Oil-in-Water Microemulsions: Polymerization of Styrene and Methyl Methacrylate

Intoduction

It has long been accepted that the monomer-swollen micelles are the principal loci for initiation of latex particles in emulsion polymerization. The emulsified monomer serves only a reservoir of the monomer supplying the radical-containing micelles and polymer particles by diffusion through the aqueous phase (1). Ugelstad, El Aasser, and Vanderhoff (2) suggested that if the monomer droplets could not compete with the micelles or primary latex particles because of their relatively small surface area, the dispersion of the monomer to a much smaller droplet size resulting in a drastically increased surface area should further the chances of droplet initiation. Indeed they demonstrated that such a hypothesis was valid in the emulsion polymerization of styrene using a combination of ionic emulsifier and long-chain fatty alcohols (3-5). Very vigorous agitation or high-pressure homogenization was used to produce the small-droplet emulsions.

Though microemulsions have been known for a long time (6,7), polymerization in such systems received little attention until recently (8-11). Microemulsions, unlike conventional emulsions, are not white; they are transparent or transluscent and do not separate into two phases on standing (12). They are formed spontaneously and do not require vigorous agitation or high-pressure homogenization. Such oil-in-water or water-in-oil microemulsions consist of droplets 100-600 Å in diameter (13). Polymerization of vinyl monomers incorporated as the continuous phase of the microemulsions showed essentially similar behavior as in solution polymerization (10,11). Leong and Candau (9) reported the polymerization of an inverse microemulsion of acrylamide where toluene forms the continuous phase. It was found to yield very small latex particles with very high molecular weight. However, the ratio of surfactant to monomer concentration used in their system was very high, of the order of 5. Such high surfactant concentrations are obviously undesirable in a polymerized latex. Polymerization of an oil-in-water-type microemulsion has not received much attention until recently. Atik and Thomas (14) reported the polymerization of styrene microemulsions using AIBN and a γ-ray source. Though the surfactant concentrations they use are not as high as that of Leong and Candau (surfactant styrene ≃ 1.5), it is debatable whether their system is truly a microemulsion since the system contained more than 95% water. The situation is not very different from that of a micellar solution where the oil is completely solubilized. Such micellar solution of monomers have been polymerized by Baxendale and co-workers (15-17) and was found to yield very small latex particles. Since polymerization of vinyl monomers in oil-in-water-type microemulsions is little understood, it was felt worthwhile to examine the polymerization of vinyl monomers in such systems. This article reports some of our data on the polymerization of styrene and methyl methacrylate microemulsions using oil-soluble initia-

TABLE I

Viscosity of Styrene Microemulsion Measured Using
a Brookfield Viscometer[a]

2% NaCl/styrene ratio	Viscosity (cp)
1.0	1.5
1.2	1.5
1.6	1.5
2.0	1.5
3.0	1.5

[a]Microemulsion recipe: Aerosol MA–80 = 4 g, Pluronic L–31 = 1 g,
styrene = 5 mL, 2% NaCl = 5-15 mL. Temperature = 60°C.

tors. The results obtained have been compared and contrasted with those re-
ported by previous workers.

Experimental

Styrene, methyl methacrylate, and benzoyl peroxide obtained from Fisher
Scientific Company were all reagent grade and were used without further puri-
fication. 2,2'-Azobisisobutyronitrile was an Eastman Kodak product. Aerosol
MA–80 of American Cyanamide and Pluronic L–31 obtained from BASF
Wyandotte were used for microemulsifying styrene. 2-Ethyl hexyl alcohol
ethoxylate with 3 mol of ethylene oxide (BASF Wyandotte) and sodium
dodecyl sulfate (ICN Pharmaceuticals, Inc.) were used for emulsifying methyl
methacrylate. Polymerization reactions were carried out in water-jacketed re-
action vessels with magnetic stirring in an atmosphere of nitrogen. A typical
microemulsion polymerization was conducted as follows: 30 mL of styrene, 60
mL of 2% NaCl, 24 g of Aerosol MA–80, 6 g of pluronic L–31, and 0.75 g of
Bz_2O_2 were introduced into the reaction vessel. Water at 70°C from a thermo-
stat was passed through the outer jacket and the contents were stirred magneti-
cally while nitrogen was bubbled through the solution. On stirring, the solution
immediately became clear. For rate determination, approximately 5 mL of the
reaction mixture was withdrawn at various time intervals into preweighed alumi-
num dishes, short-stopped with 2% hydroquinone in methanol, and evaporated
to dryness in vacuum at 60°C. Corrections were made for the amount of surfac-
tant remained in the residue while the percent conversion was calculated. Trans-
mission electron micrographs of the latex particles were obtained using a Carl
Zeiss EM 10 CA microscope in the usual way. A Brookfield viscometer was used
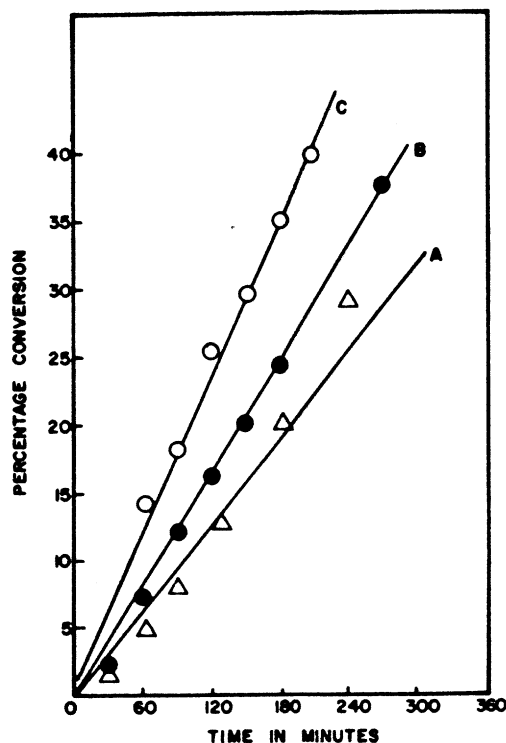to measure the viscosity of the microemulsions.

Fig. 1. Time-versus-percentage conversion plots for emulsion and microemulsion polymerization of styrene initiated by benzoyl peroxide. (A) In microemulsion, recipe: Aerosol MA−80 = 24 g, Pluronic L−31 = 6 g, styrene = 30 mL, 2% NaCl = 60 mL, Bz_2O_2 = 0.75 g, temperature = 70°C. (B) Aerosol MA−80 = 1.5 g, styrene = 30 mL, water = 60 mL, Bz_2O_2 = 0.75 g, temperature = 70°C. (C) Aerosol MA−80 = 1.5 g, Pluronic L−31 = 1.5 g, styrene = 30 mL, water = 60 mL, Bz_2O_2 = 0.75 g, temperature = 70°C.

Results and Discussion

Measurements of the viscosity of the styrene microemulsions with changes in brine/styrene ratio indicated that the microemulsion was of the oil-in-water type (Table I). Polymerization was initiated in deaerated systems using benzoyl peroxide as the catalyst at 70°C. The catalyst was dissolved in the styrene monomer prior to emulsification. The reaction rate in microemulsion was found to be less than that in a classical emulsion prepared with the same surfactant (Aerosol MA−80) or a mixture of the two (Aerosol MA−80 and Pluronic L−31) under identical conditions (Fig. 1). Introducing the oil-soluble initiator after effecting the emulsification resulted in lower rates. This is exemplified by the polymerization of methyl methacrylate initiated by AIBN in its microemulsion (Fig. 2).
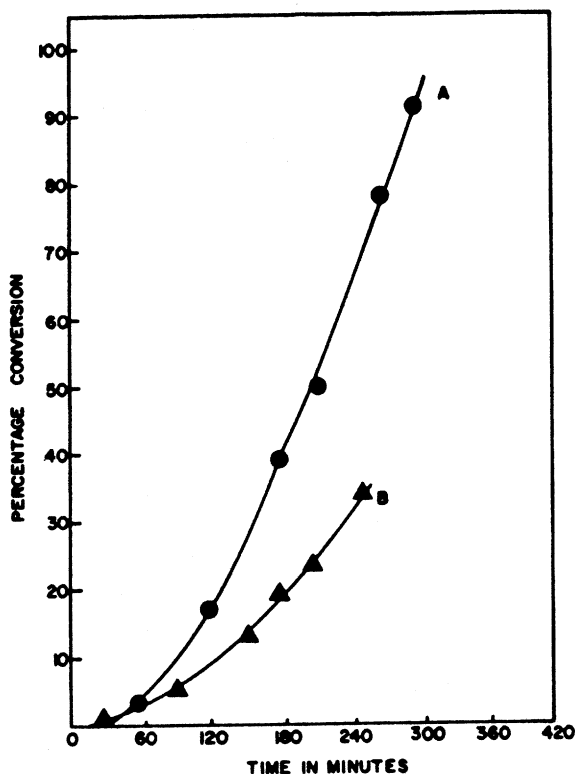
Fig. 2. Time-versus-percentage conversion plots for microemulsion polymerization of methyl methacrylate initiated by AIBN. Recipe: Sodium dodecyl sulfate = 3 g, 2-ethyl hexyl alcohol ethoxylate = 3 g, MMA = 9 mL, 2% NaCl = 27 mL, AIBN = 0.5 g, temperature = 50°C. (A) Initiator dissolved in monomer prior to emulsification. (B) Initiator added after emulsification.

This points out the fact that the microemulsion droplets are covered with a firm interphase layer of surfactants which prevents the diffusion of radicals into their core. Unlike the polymerization of acrylamide microemulsion, as reported by Leong and Candau, styrene as well as methyl methacrylate microemulsions were no longer transparent and stable during the polymerization process. Though these authors have reported that the polymerization was very rapid and total conversions were attained in less than 30 min, styrene and methyl methacrylate microemulsions polymerize less rapidly than classical emulsion prepared with the same surfactants. Though increase in concentrations of the surfactant results in an increased rate of polymerization in classical systems, in microemulsions, the large amount of the surfactant present was found to have an adverse effect. While Leong and Candau used quasielastic light scattering for determining the size of the latex particles of polyacrylamide, no visual evidence was there to ascertain whether the particles were really spherical or not. Atik and Thomas'

electron microscope studies show that the radiation-polymerized styrene micro-
emulsion latex particles are not spherical. (The latex appears to have a "cell-
type structure" though the authors claim that they are monodisperse latex par-
ticles of 350 ± 30- or 200 ± 20-Å diameters.) There is a tremendous difference
between the product obtained in microemulsion polymerization and the latex
one usually produced by conventional emulsion polymerization. First, the latex
is not stable and cannot be diluted as in the case of classical latexes. The insta-
bility of the latex is observed regardless of whether the system contained an
electrolyte such as NaCl. The use of 2% NaCl in the polymerization recipe was
to increase the monomer solubilization capacity of the microemulsions. It has
been demonstrated that increase in the salinity of an ionic surfactant system
resulted in an increase in its lipophilic character, thereby favoring increased oil
solubility (18). While the presence of electrolyte in the system could be
considered as responsible for the instability of the latex by inducing coagulation,
even in the absence of any electrolyte present, polymerization of styrene micro-
emulsion did not give rise to any stable latex. A styrene microemulsion was
prepared with Aerosol MA−80, 2-ethyl hexyl alcohol ethoxylate, and water
(with a 20/80 volume ratio of monomer/water) and was polymerized using
Bz_2O_2 at 70°C. The resulting latex was found to be unstable and the electron
micrographs did not show any latex particles. Transmission electron micro-
graphs of the polystyrene latex produced using Aerosol MA−80, mixed emulsi-
fier, and the microemulsion are shown in Figure 3. Using a mixture of Aerosol
MA−80 and Pluronic L−31, the particle distribution becomes narrow. As can
be seen, the polystyrene latex produced in the microemulsion has extremely
small particle size but is not spherical in shape. We repeated the experiment of
Atik and Thomas on the polymerization of styrene microemulsion without in-
corporating the cosurfactant n-hexanol in the recipe. The resulting latex when
examined in the transmission electron microscope showed spherical particles
unlike the cell-type structure observed by them when n-hexanol was present in
the system (Fig. 4). This suggests that short-chain alcohols in addition to func-
tioning as potential chain transfer agents also act as destabilizers for the latex by
desorbing the surfactant from the surface of the polymer−monomer particles
(19). This was further checked as follows: A microemulsion of styrene was
prepared by magnetically stirring 1.5 g of Aerosol MA−80, 8 mL of water, 3 mL
of styrene, and 4 mL of n-butanol. The microemulsion was transparent and
clear up to 60°C. Polymerization was initiated by benzoyl peroxide. Even pro-
longed reaction periods failed to produce a latex as in the case of classical emul-
sion polymerization, instead an oily polymer was obtained.

Gan et al. (20) recently reported on the influence of nonpolar polymers on
the stability of microemulsions. Using the dimer of styrene in styrene micro-
emulsions, they demonstrated that other than conformational factors, more
subtle molecular interactions could be operative in determining the stability of
microemulsions, since the styrene dimer could produce no space restriction
effect. The nature of these interactions is not known yet, but the fact that in-
stability problems due to polymer solubility are not confined to excluded vol-
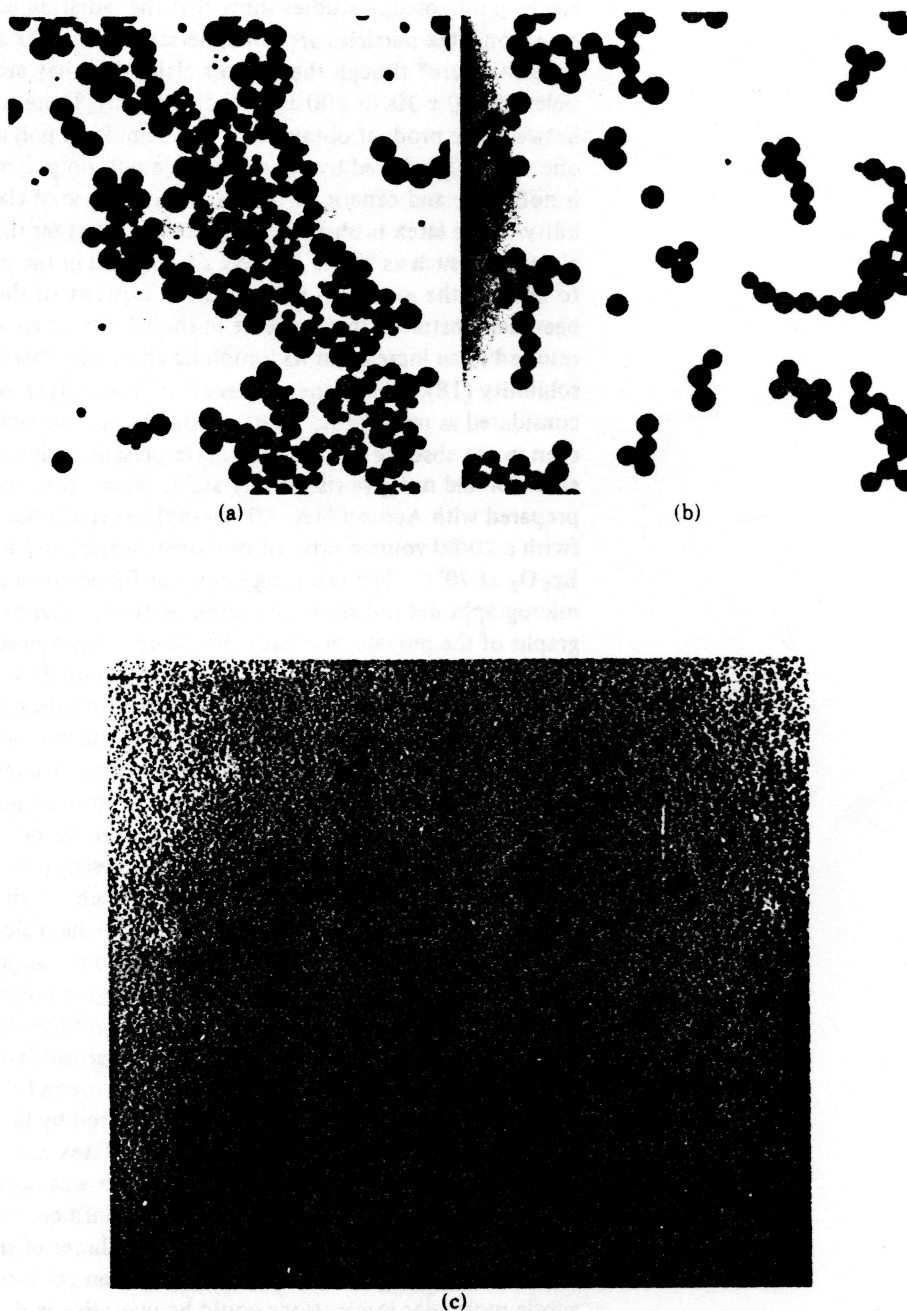ume and accompanying entropy effects makes it further complicated.

Fig. 3. Transmission electron micrographs of polystyrene latexes, (a) prepared by Aerosol MA−80 alone, (b) using a combination of Aerosol MA−80 and Pluronic L−31 in a 1:1 ratio and (c) obtained in microemulsion. Magnification 40,000X. (Polymerization recipe corresponds to that of lines B, C, and A of Fig. 1.)
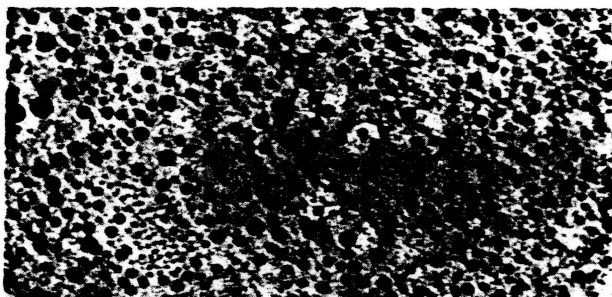
Fig. 4. Electron micrograph of polystyrene latex prepared using the recipe of Atik and Thomas without incorporating n-hexanol. Recipe: Cetyltrimethyl ammonium bromide = 1 g, styrene = 1 g, water = 50 mL, AIBN = 1.0×10^{-6} mol/dm^3 at 60°C.

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