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Microemulsion polymerization of styrene

L. M. Gan[1],*, C. H. Chew[1], I. Lye[1], and T. Imae[2]

[1]Department of Chemistry, National University of Singapore, Republic of Singapore
[2]Department of Chemistry, Nagoya University, Nagoya 464, Japan

Summary

Microemulsion polymerization of styrene initiated by water-soluble potassium persulphate produced microlatexes which are stable at room temperature even after a year of preparation. The effects of initiator concentration, polymerization temperature, as well as monomer concentration on the polymerization kinetics and molecular weight distribution were investigated. The microemulsion polymerization rate shows only two reaction intervals as a function of monomer conversion. It increased to a maximum at about 20% conversion and then decreased on further polymerization. The final latexes obtained are characterized by high molecular weight of polystyrene ($\bar{M}_w$: $5\text{-}10\times10^6$) and small particle diameter (D: 20-40 nm). It is calculated that each latex consists of two to four polystyrene chains.

Introduction

Microemulsions are thermodynamically stable, transparent or translucent dispersions consisting of very small droplets with radius of the order of 5-50 nm. When oil and water (brine) are mixed with relatively large amounts of surfactant and cosurfactant (usually a medium chain length alcohol), microemulsions are formed spontaneously either in the form of oil-in-water (o/w) , or water-in-oil (w/o), or bicontinuous structure in which aqueous and oily domians are interconnected.

Since 1980, methyl methacrylate (MMA) or styrene has been unsuccessfully polymerized in the oil continuous phase of w/o microemulsions due to phase separation during polymerization [1-3]. But the polymerizations of water-soluble acrylamide in w/o microemulsions [4,5] produce stable microlatexes ($d \sim 40$ nm) of high molecular weights (10^6-10^7). As for polymerization of styrene or MMA in o/w microemulsions, the formed microlatexes are stable only when the concentration of the monomer is limited to a few percent (2-6 wt%). These polymerized o/w microemulsions are characterized by small latex diameter (20-30 nm) and high molecular weights (10^5-10^6) of the polymer produced. The reported recipes for those o/w microemulsions consist of various compositions of sodium dodecyl sulphate (SDS), pentanol, styrene/MMA, water and initiator [6-9]. It is only very recently that polymerization of styrene has also been successfully carried out in o/w microemulsions stabilized only by dodecyltrimethyl ammonium bromide

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*To whom offprint requests should be sent without using a cosurfactant [10].

The polymerization of styrene in the stable o/w microemulsions using a cationic surfactant and a glycol type cosurfactant will be discussed in this paper.

Experimental

Materials

Styrene and diethylene glycol monobutyl ether (butyl carbitol, BC) from Fluka were vacuum distilled under nitrogen atomsphere at 5-6 mmHg (25-26°C) and 0.1 mmHg (60°C) respectively. Cetyltrimethyl ammonium bromide (CTAB) from TCI (Japan) was recrystallized from ethanol-acetone mixture (1:3 by volume). Potassium persulphate (KPS) from Fluka was recrystallized from distilled water. All water used was distilled twice.

Polymerization

Polymerization of styrene in o/w microemulsion was carried out in a glass dilatometer. After degassing at 10 mmHg for two freeze-thaw cycles, the microemulsion was introduced directly into a dilatometer through a special joint attachment. The liquid level change in the capillary of the dilatometer was monitored as a function of time by a cathethoscope. The fractional conversion of styrene was determined from the volume change which was calculated from the height of the capillary. After polymerization, polystyrene was precipitated out from the reaction mixture into a large quantity of ethanol.

Molecular Weight Determination by Gel Permeation Chromatography

Molecular weights of polystyrene were determined by a Varian 5500 liquid chromatography system equipped with a RI-3 detector. The column used was Varian MicroPak TSK GMH6 gel and the eluent was THF. Polystyrene standards (Polyscience) in 0.2 mg/mL THF were used for calibration. The flow rate was maintained at 0.8 mL/min.

Characterization of Microlatexes

Particle size of the polymerized microemulsion latexes were examined by a Hitachi 800H electron microscope operating at 200 kv. After mixing microemulsion with glycerol (3:1 by volume) for 30 min., freeze-fracture replica was prepared with a Balzers BAS 400 freeze-etching unit. The frozen specimen was fractured at -130°C and it was shadowed by platinum (2 nm) from 45° and covered by carbon (20 nm) from 90°.

Results and Discussion

The basic compositions of the microemulsion consist of 7.5 wt% CTAB, 7.5% BC, and 85% water. Different amounts of styrene were added to the basic compositions to form the stable o/w microemulsions containing 2 to 8 wt% styrene. Initiator KPS of 0.3 to 0.6 mM in water was used to initiate the polymerization at 40, 45 50 and 60°C. The polymerized microemulsions are bluish transparent when the styrene content is less than 4 wt%. They are translucent or opaque at higher styrene content (4-8 wt%). All the polymerized microemulsions appear reddish when they are viewed against light. All of them remain stable at room temperature even after a year of preparation.

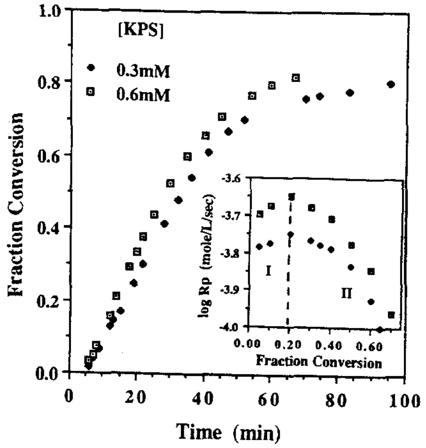

Figure 1. Polymerization curves for styrene with different KPS concentration at 50°C.

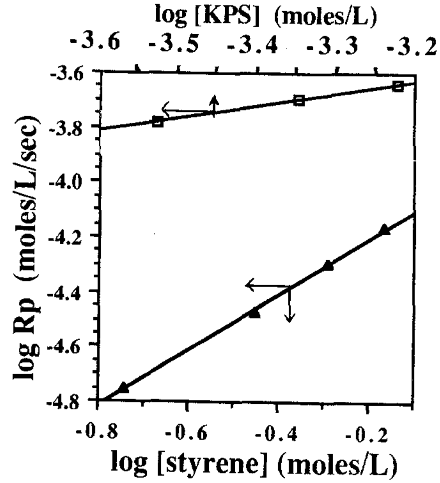

Figure 2. Dependence of Rp on KPS and styrene concentration.

Kinetics of Polymerization

Fig. 1 shows conversion-time and polymerization rate-conversion curves where the concentration of KPS was varied from 0.3 to 0.6 mM at 50°C. The overall polymerization rate was rather fast and it increased with the increasing KPS. The polymerization rate-conversion curves show two distinct reaction regions. Interval I is characterized by an increase in the rate of polymerization with conversion. It reaches to a maximum at about 20% conversion which marks the onset of Interval II. Interval I refers to the creation of new polymerizing loci in the existing microemulsion droplets. At the end of Interval I, all microemulsion droplets have disappeared either by becoming polymer particles or by being consumed through diffusion of monomer from the droplets to polymer particles. The polymerization rate begins to decrease in Interval II due to the decrease of monomer concentration in the monomer- swollen polymer particles.

The effects of the initial concentrations of styrene and KPS on the initial rate of polymerization, Rp, at 2-3% conversion is shown in Fig. 2. Rp is proportional to the 0.45 power of [KPS] and the 0.99 power of styrene concentration. The dependency of Rp on KPS concentration is quite consistent with the predication of 0.40 from the Smith-Ewart Case 2 hypothesis for emulsion polymerization [11]. The 0.99 power of styrene concentration dependency is also in very good agreement with the expected value of 1.0 for emulsion polymerization when the monomer droplets (monomer reserviors) have disappeared.

The dilution effect by toluene on the kinetics of styrene microemulsion polymerization was studied by varying the weight ratio of styrene/toluene from 8/0, 6/2, 4/4 to 2/6 at a given amount of oil phase. By keeping the oil content constant it is expected that microemulsion droplets with similar size will lead to similar competition for radicals. It was found that Rp, for the system using 0.6 mM KPS and at 45°C, decreased from 6.17, 3.97, 2.19 to 0.79x10^{-5}

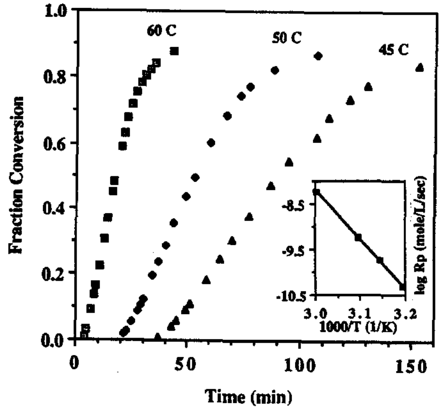

Figure 3. Polymerization curves for styrene at different temperatures and Rp vs 1/T.

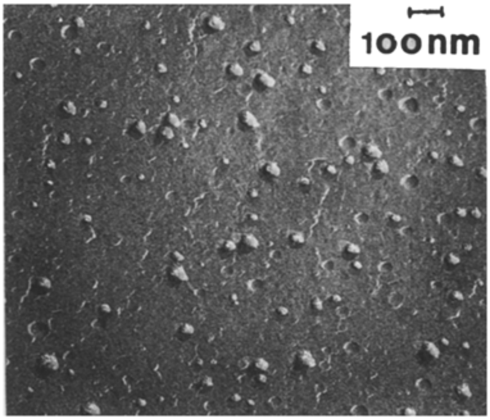

Figure 4. EM micrograph of the polystyrene latex replica.

mol $L^{-1}sec^{-1}$ respectively. The dependency of Rp on styrene concentration in the presence of toluene is 1.47 power as compared to that of 0.99 power of bulk styrene. However, the dependency of 2.33 power for Rp versus styrene concentration was obtained by Guo et al [8] for their microemulsion system using SDS and pentanol. They account for the much depression in Rp not only due to dilution of the monomer, but also due to the chain transfer with diluent as it accumulates in the particles. Chain transfer leads to formation of small radicals which may diffuse out from the particles.

The effect of temperature on polymerization of the microemulsion containing 6 wt% styrene and 0.6 mM KPS was studied at 40, 45, 50 and 60°C. The conversion-time curves and the Arrhenius plot of log Rp versus 1/T are shown in Fig. 3. The overall activation energy for the microemulsion polymerization of styrene is 89.5 kJ/mol which is comparable to 94 kJ/mole obtained from the microemulsion using SDS and pentanol [8].

Latex Particle and Molecular Weight

The replica of the microemulsion latex particles examined by EM show broad particle size distributions (Fig.4). The particles appeared to be quite spherical with diameters ranging from about 10 to 40 nm. These latex particle sizes are much larger than the microemulsion droplets of about 5 nm [12]. This indicates that not all microemulsion droplets become polymer particles. Some of the droplets only act as monomer reservoirs to supply monomer for nucleation in Interval I of polymerization. The broad particle size distribution is due to the long nucleation period, i.e. up to about 20% conversion of styrene.

The weight average molecular weight ($\overline{M}w$) of polystyrene produced from microemulsion polymerization at 40°C is very high ($5\text{-}10\times10^6$) as shown in Table 1. $\overline{M}w$ increased from about 5 to 10×10^6 as the content of styrene in the microemulsion was increased from 2 to 6 wt%. There is

Table 1. **Molecular weight distribution of polystyrene microemulsion polymerization at 40°C.**

Microemulsion basic compositions	variable component composition	$\bar{M}_n$ (10^6)	$\bar{M}_w$ (10^6)	PDI
7.5% CTAB	styrene (wt%)			
7.5% BC	2	1.40	5.08	3.63
85.0% H_2O	4	2.52	8.10	3.21
0.6 mM KPS	6	4.09	10.10	2.48
7.0% CTAB	KPS (mM)			
7.0% BC	0.3	1.89	7.81	4.13
80.0% H_2O	0.45	1.55	6.99	4.51
6.0% styrene	0.60	1.37	6.77	4.94

also a slight dependence of $\bar{M}_w$ on KPS concentration (about -0.17 power). The polydispersity index ($\bar{M}_w/\bar{M}_n$) for these polystyrene varied slightly from about 3.6 to 2.5. The small microemulsion droplets are the direct consequence of producing high molecular weight polystyrene and low dependence on KPS concentration in the range of 0.3-0.6 mM. This is because small microemulsion droplets cause low rate of free radical absorption. Thus, the probability of a bimolecular termination reaction in a monomer-polymer particle is much reduced. The calculations show that only 2-4 polymer chains of $\bar{M}_n = 2\times10^6$ exist in a single latex particle with a diameter ranging from 20 to 30 nm. Similarly, Guo et al [8] also reported that only 2-3 polystyrene chains exist in each microemulsion latex particle.

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