

RADIATION-INDUCED EMULSION POLYMERIZATION OF STYRENE IN SOAP-FREE SYSTEM*

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ABSTRACT

Radiation-induced emulsion polymerization of styrene in soap-free system has been studied and the monodisperse polystyrene lattices were obtained. Both its purity and emulsion conversion are better than that of chemically initiated polymers.

Chemically initiated emulsion polymerization of styrene in soap-free system have been reported by Matsumoto and Ochi^[1], but radiation-induced emulsion polymerization of styrene in soap-free system have not been reported yet. Radiation-induced emulsion polymerization of styrene in soap-free system has been studied and the monodisperse polystyrene lattices were obtained. Both its purity and emulsion conversion are better than that of chemically initiated polymers.

EXPERIMENTAL

Polymerization Procedure

Pyrex glass ampoules of 20 mm o. d. and 160 mm length were used as the reaction vessels. The ampoules were filled with the required volume of purified styrene and once-distilled water and then very carefully degassed by the freeze-thaw technique to a residual air pressure of approximately 10^{-3} Torr. After a final pumping cycle, the ampoules were sealed and removed from the vacuum line, then were irradiated in a 60,000-curie Co^{60} -source.

At the end of a run the ampoules were taken from the source, opened, and the polymer isolated by drying in vacuum to constant weight. Conversion was calculated from the initial amount of styrene used. The number average molecular weights of polymer were determined from intrinsic viscosity measurements in benzene at 30°C.

Determination of Polymer Particle Diameter

One drop of latex was diluted to 20–30 ppm polymer with distilled water. The specimen for the electron microscope was made by drying one drop of 20–30 ppm polymer concentration latex on a copper grid which was previously coated with a thin film.

The mean volume diameter is determined as follows:

Mean volume diameter = $(\sum n_i D_i^3 / \sum n_i)^{1/3}$ where n_i is the number of particles of diameter D_i .

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RESULTS AND DISCUSSION

The ratio of water to monomer is an important factor influencing the properties of latex, as shown in Figs. 1, 2 and 3. Both the conversion of emulsion and the stability and the size homogeneity of the latex particles increase with increasing water-monomer ratio of the system. It was found that charged particles existed in the system after irradiation due to the presence of large amount of water. The rate of polymerization is found to be proportional to the 0.5th power of irradiation intensity, i. e., $V_p \propto I^{0.5}$ (Fig. 4). The apparent activation energy of polymerization obtained from Fig. 5 is 7.5 Kcal/mole which approaches to 7.9 Kcal/mole obtained by Stannett^[2] in γ -induced emulsion polymerization of styrene in the presence of emulsifier. The molecular weight distribution of polymer produced in soap-free system is narrower than that obtained from chemically initiated as shown in Fig. 6. The polymer latex with higher purity has been obtained by radiation-induced polymerization and its electric conductivity is obviously lower than that obtained chemically, as shown in Table 1.

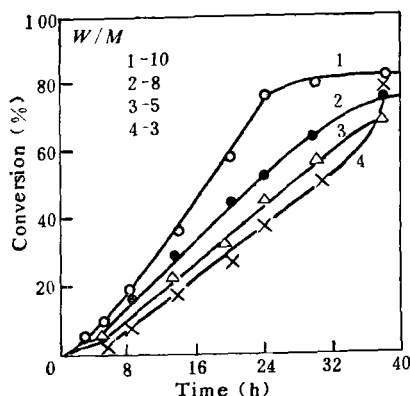


Fig. 1 Effect of W/M on polymerization reaction
 1 $W/M = 10$; 2 $W/M = 8$;
 3 $W/M = 5$; 4 $W/M = 3$;
 $I = 5.5 \times 10^5$ rad/h; 30°C

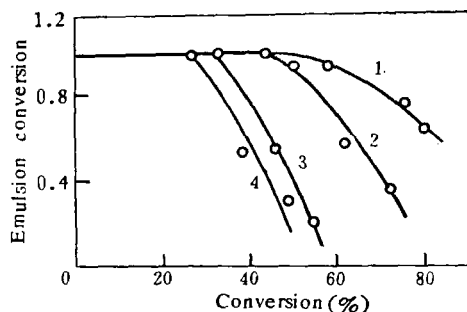
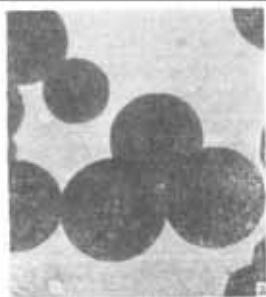
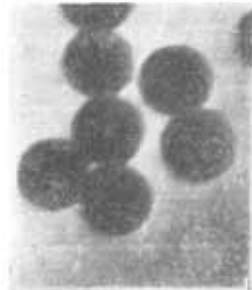


Fig. 2 Effect of W/M on emulsion stability
 1 $W/M = 10$; 2 $W/M = 8$;
 3 $W/M = 5$; 4 $W/M = 3$;
 $I = 5.5 \times 10^5$ rad/h; 30°C



(a) Magnification 19,400 $\times$
 $[M] = 0.87$ mol/l



(b) Magnification 19,400 $\times$
 $[M] = 0.22$ mol/l

Fig. 3 Effect of W/M on monodispersity of latex

$I = 1.44 \times 10^5$ rad/h; 30°C

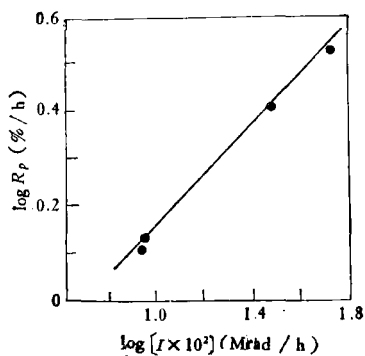


Fig. 4 Effect of dose rate on polymerization rate

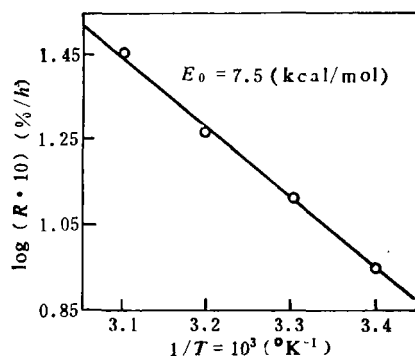


Fig. 5 Effect of temperature on polymerization rate

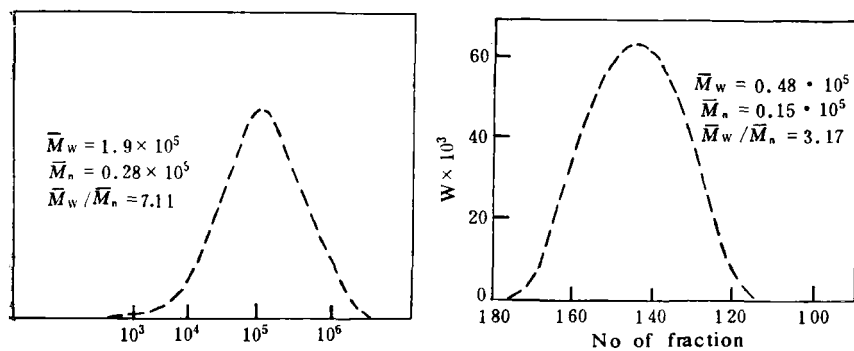


Fig. 6 Molecular weight distribution of polystyrene

(a) Chemical

 $[M] = 0.87 \text{ mol/l;}$

Time = 1440 (min)

 $[Cat] = 37 \times 10^{-4} \text{ mol/l;}$ 70°C

(b) Radiation

 $[M] = 0.87 \text{ mol/l; } 30^\circ\text{C}$ $I = 1.44 \times 10^6 \text{ rad/h; Time = 1440 (min)}$

Table 1 Electric conductivity of latex

Radiation			Chemical		
W/M	I (rad/h)	$1/R(\Omega^{-1})$	W/M	$C_{KPS}(g/ml)$	$1/R(\Omega^{-1})$
20	1.44×10^5	8.9×10^{-6}	10	2×10^{-4}	6.2×10^{-4}
20	1.44×10^5	9.1×10^{-6}	10	8×10^{-4}	3.0×10^{-3}
40	1.44×10^5	1.0×10^{-5}	20	2×10^{-4}	5.9×10^{-4}
40	1.44×10^5	1.1×10^{-5}	40	2×10^{-4}	8.2×10^{-4}

The variation of the average diameter of the polymer latex r with polymerization time are shown in Fig. 7, which may be expressed by an empirical equation as:

$$r^2 = ct \quad (1)$$

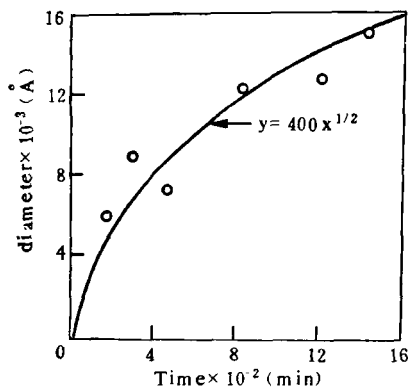


Fig. 7 Relation between diameter of particles and polymerization time
 $I = 5.5 \times 10^5$; $W/M = 10$; 30°C

where c is a constant and equals to 400 for the cited experiment. This result agrees with Core-Shell theory, but not agree with Smith-Ewart's theory. If the growth process of the polymer latex is described by an equation in analogy to Fick's law:

$$dr^2 / dt = K_1 \quad (2)$$

where K_1 is a constant proportional to the diffusion coefficient, and the rate of polymerization in a particle R_p is proportional to the growing rate of volume of particles

$$\begin{aligned} R_p &\propto dr^3 / dt \\ dr^3 / dt &= 3/2 K_1 r \end{aligned} \quad (3)$$

From the point of view of kinetics, the rate of polymerization in latex particle is $R_p = K\bar{n} [M_p]$, where $\bar{n}$ and $[M_p]$ are the average number of growing free radicals and the concentration of monomer within the particles respectively. If $[M_p]$ remains constant, then:

$$K\bar{n} [M_p] = 3/2 K_1 r \quad (4)$$

$$\bar{n} = K_2 r \quad (5)$$

The above equations indicate that the average number of growing free radicals within the particles is not constant but increases with increasing particle size. The experimental results indicate that the conversion versus time plot is nonlinear before 30% conversion as shown in Fig. 1, at that time the diameter of particles increased gradually, so the rate of polymerization is also changed, and linear within its range of conversion 30–60%, the polymer particles seem to be precipitated and diameter reached maximum, thus the rate of polymerization becomes constant.

From equation (3), the following equation may be obtained

$$\frac{1}{r} \frac{dr}{dt} = \frac{2K_1}{\pi} \frac{1}{r^2} \quad (6)$$

where $\frac{1}{r} \frac{dr}{dt}$ is the relative rate of growth of particle diameter and shows that there is a preferential growth of small particles, therefore, the particle size distribution of the latex become narrow gradually before precipitation occurs, as shown in Fig. 8. The relationship between the number of particles and the polymerization time in the polymerization process was determined, and the results are shown in Fig. 9. It seems that during the primary stage of polymerization the precipitation of particles occurred and the number of particles were decreased, degrees of monodisperse became better and better.

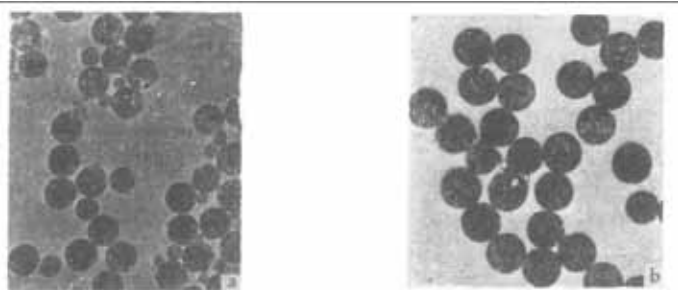


Fig. 8 Effect of conversion on monodispersity of latex

(a) Conversion 4.6%

(b) Conversion 19%

Magnification 8800×

Magnification 8800×

$I = 5.5 \times 10^5$ rad/h; 30°C

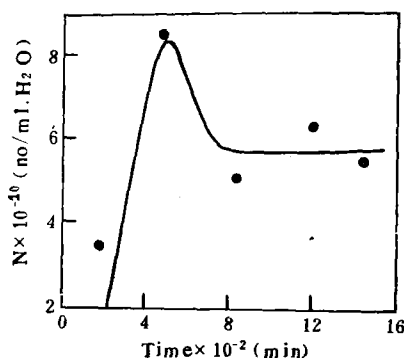


Fig. 9 Relation between number of particles and polymerization time

The mechanism of radiation-induced emulsion polymerization of styrene in a soap-free system may be deduced as follows: The free radicals are just produced in aqueous phase and then initiate the monomer dissolved in water to form a surface active (charged) oligomeric radicals. The growing oligomeric radicals eventually seems to reach a chain length in solution, at which they would be precipitated, subsequent particle growth occurring in these precipitated nuclei, but the primary small particles would aggregate into group till a colloiddally stable particle is formed. This can be observed in the experiment.

REFERENCES

- [1] Matsumoto, J. and Ochi, A., *Kobunshi Kagaku*, **1965**, 22, 481.
- [2] Stannett, V. T., Shiota, H., Garreau, H. and Williams, J. L., *J. Colloid and Interface Sci.*, **1979**, 71, 1.