PMMA성장핵을 사용한 스티렌유화중합의 반응속도론

조 의 환 · 이 경 우

한국과학기술원 화학과

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Polymerization Kinetics of Poly (Methyl Methacrylate) – Seeded Emulsion Polymerization of Styrene

Iwhan Cho and Kyung-Woo Lee

Department of Chemistry, Korea Advanced Institute of Science and Technology
P. O. Box 150 Chongyangni, Seoul 131, Korea

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Abstract: The polymerization kinetics of PMMA-seeded styrene emulsion polymerization was studied. Batch polymerization technique was employed and gravimetric method (Total Solid Content) was utilized to determine the monomer conversion. The monodispersed PMMA latexes were used as seed latexes. The rate of polymerization per particle was found to be increased with $K_2S_2O_8$ concentration and linearly proportional to the diameter of PMMA seed latexes. The dependence on the diameter became more pronounced at higher temperature range. However, the rate was decreased with the addition of chain transfer agent ($CHBr_3$) because of the easy desorption of the transferred radicals. The activation energy of polymerization was 53.2 KJ/mole and the propagation rate constant was 330 1/(mole-sec).

1. INTRODUCTION

Emulsion polymerization is one of important polymerization processes and widely adapted for industrial applications. The basic hypothesis for emulsion polymerization mechanism was established early by Harkins[1], and Smith and Ewart[2], and has been constantly investigated by many workers. Irrespective of the particular behaviour observed, three distinctive stages I, II, III can be discerned in all emulsion polymerizations based on the particle number and the existence of a separate monomer phase. Especially the polymerization mechanism and kinetics of styrene polymerizations are fully investigated by many workers[2,8], but certain results are still controversial.

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The seed emulsion polymerization method was utilized in order to eliminate the particle nucleation stage (Stage 1)[3,-8] and for other purposes[9,10]. When the seed latex is a mono-dispersed system, the polymerization environment of each polymerization locus is almost same and the interpretation of experimental results will become clearer. For the most of the reported kinetic studies the homogeneous seeded emulsion polymerization is adapted [3,5-8] and the heterogeneous ones have been mainly adapted for the study of latex particle morphology[10]. The only heterogeneous example for kinetics study was performed by Patsiga and his co-workers[4] on poly (vinyl acetate)-seeded styrene emulsion polymerization. In the previous work[11], we reported the particle morphology and formation mechanism of poly (methyl methacrylate) (PMMA)-polystyrene (PS) composite latex particles. In this work, we report the results of stage II emulsion polymerization kinetics of PMMA-seeded styrene emulsion polymerization.

2. EXPERIMENTAL

2-1. Materials

Reagent grade styrene and methyl methacrylate (MMA) were distilled under reduced pressure. The middle fraction was cut and stored in a refrigerator. Sodium dodecylbenzene sulfonate (SDBS, Siponate[R] DS-10 from Alcolac Chemical Co.), and Triton[R] X-100 (polyoxy ethylene isooctylphenylether from Rohm and Haas Co.) were used without further purification. Water was redistilled from basic $KMnO_4$ solution. Other chemicals were analytical grade reagents and used without purification.

2-2. Polymerization

All polymerizations were performed in an 1-liter flask under N_2 blanket. Each flask was equipped with a paddle-type stirrer, reflux condenser, sampling tube, dropping funnel and thermocouples. Polymerization temperature was controlled by an electrically regulated heating mantle and recorded with Linear[R] 141 recorder. Agitation speeds were 120 rpm for MMA polymerization and 200 rpm for PMMA-seeded styrene polymerizations. N_2-purging was started with the charge of ingredients into the flask and continued to the peak time. In a general procedure all the ingredients were first charged and then the system was heated to the required temperature before the addition of initiator solution. Because of the large heat of polymerization the temperatures of PMMA polymerization could not controlled rigorously. After the peak time the reaction systems were heat-treated at 95°C for 2 hours and then cooled with an ice-water bath to ambient temperature.

2-3. Particle Size

The particle size of PMMA latexes were measured from TEM (transmission electron micrographs). Being different from PS particle, PMMA particles were shrinked by electron beam during the process of taking TEMs. Therefore, for the determination of precise particle size, the dried PMMA latexes on the Collodion[R] grid were shadowed with silver in Vacuum Evaporater[R] (JEM-4X, manufactured by Jeol Co.). In a common procedure the sizes of 100 - 300 particles were measured and the values were averaged. The weight average D_w, the number average D_n, diameters and the dispersity U ($= \frac{D_w}{D_n}$) of PMMA latex particles were calculated as follows:

$$D_w = (\Sigma n_i D_i^6 / \Sigma n_i D_i^3)^{1/3} \qquad (1)$$

$$D_n = (\Sigma n_i D_i / \Sigma n_i) \qquad (2)$$

where n_i is the number of particles in the latex having diameter D_i.

A standard PS latex (D_n = 2538°A, standard deviation = 31°A, supplied by Dow Chemical Co.) was used as an internal standard for size calibration. TEMs were obtained with Jeol JEM-100CX electron microscope at accelerating voltage of 60KV.

2-4. Intrinsic Viscosity

Latexes were coagulated with hot methanol (1 vol. %, conc. H_2SO_4/CH_3OH). The precipitates were filtered and washed with a large volume of water. Thus obtained solid polymers were reprecipitated from THF into methanol and dried in a vacuum oven at 60°C to constant weight. Intrinsic viscosities of PMMA's were determined at 30±0.1°C with Cannon-Fenske No. 50 viscometer (concentration = 0.5 g/dl; solvent, toluene) and calculated by one-point method.

2-5. Conversion

About 1 ml of latexes were placed on a Petri dish (diameter, 5cm) and dried at 160°C for 40 min. From the weight change during this drying period TSC (total solid content) values were calculated. The conversion of monomer to polymer was calculated from the following equation:

$$\text{Conv.} = \frac{\text{TSC} \times W_{tt} - W_{tt}}{W_{tm}} \qquad (3)$$

where W_{tt} ; total weight of all ingredients
$\quad W_{ts}$; total weight of solid ingredients
$\quad W_{tm}$; total weight of monomer added
$\qquad$ to the system.

2-6. Other Measurements

Surface tension and interfacial tension were measured at room temperature by du Nouy ring methods. pH values of latexes were determined by pH meter at room temperature after the heat treatment.

3. RESULTS AND DISCUSSION

3-1. Preparation of Seed PMMA Latexes

Polymerization conditions and the properties of the resulting PMMA latexes are summarized in Table 1. Because of the difficulty in the control of the polymerization temperature, the particle size of the resulting latexes did not turn out as expected, even when the similar polymerization conditions were employed. The easy radical desorption caused by chain transfer agents decreased the particle size, exhibiting little effect on the molecular weights. The high surface tension of PMMA latexes showed that the surface of PMMA latex particles were not completely covered with emulsifiers. At any events, as shown in Table 1, the particle size distribution of each PMMA latex obtained in the present study showed good monodispersity.

3-2. Seeded Emulsion Polymerization

Emulsion polymerization takes place in complicated mechanisms, and the rate of polymerization can be affected by many parameters. In the present study, the particle nucleation stage of emulsion polymerization was by-passed by employing the seeding technique and new particle nucleation was minimized. In some cases the new particle nucleation was observed, but its amount was too small to affect the system. The basic polymerization recipe and the reaction conditions are based on that given in Table 2. Polymerization reactions were performed under various conditions and the results were appraised. The rate of polymerization was calculated from the first linear part of the conversion vs. reaction time.

3-2-1. Initiator Concentration

As previously reported[11], the swelling time and pH of the reaction medium (3≤pH≤12) did not affect the polymerization kinetics. The

Table 1. Polymerization Conditions and Properties of PMMA Seed Latexes

Sample Name	PMMA-1	-2	-3	-4	-5	-6
Ingredients[a]						
H_2O	180	180	180	180	180	180
MMA	100	100	100	100	100	100
Triton X-100	3.01	3.0	3.0	3.0	3.0	3.0
SDBS	0.30	0.30	0.30	0.15	0.30	0.30
$K_2S_2O_8$	0.5	0.5	0.49	0.5	0.5	0.5
$CHBr_3$	–	–	–	–	0.5	2.3
Properties						
D_n(nm)	156	161	170	318	133	117
U	1.003	1.003	1.002	1.001	1.002	1.004
pH	2.2	2.2	2.9	2.4	2.4	2.5
Surface Tension (dyne/cm)	44.5	46.4	45.3	42.3	48.9	50.6
Intrinsic Viscosity	1.78	1.75	1.74	1.82	1.74	1.60

a ; Quantities are in weight parts.

Table 2. Basic Polymerization Recipe and Conditions

Ingredients	
H_2O	475g
Styrene	75
Seed Latex (dry base)	25
$K_2S_2O_8$ (KPS)	0.5
KOH (0.1 Normal)	25
Conditions	
Polymerization Temperature	60±1℃
Agitation Speed	200 rpm
Atmosphere	N_2
Swelling Time	ca. 1 hour
Post Heat-treating Time	ca. 2 hours

Table 3. Effect of Initiator Concentration on PMMA - Seeded Styrene Emulsion Polymerization

	PMS-6	PMS-7	PMS-17	PMS-12	PMS-18
Seed Latex	PMMA-1		PMMA-2		
KPS (g/500g H_2O)	0.5	2.0	0.052	0.5	2.0
KOH (g/500g H_2O)	–	–	25	25	25
pH[a]	3.0	2.6	10.9	10.6	4.3
R_{pp}[b]	1.90	2.22	1.43	1.90	2.28

a ; pH as mesured after post heat-treatment.
b ; Rate of polymerization per particle
   (unit, $\times 10^{17}$g/(min·particle))

concentration. Smith[3] reported that the rate of polymerization was independent of $K_2S_2O_8$ concentration over a sixteenfold range. However, Gerrens[12, 13] reported an increase of 1.3 – 2.14 times of the original by post addition of $K_2S_2O_8$ in the range of 5 – 34 times of the initial concentration during the polymerization. Chatterjee and his coworkers[14] also reported that it was affected by post addition of $K_2S_2O_8$. The latter two cases might be caused by the low monomer concentration in the system (ca. 6%) or the new particle nucleation.

Recently Hasan has found that trace of O_2 remained in PS-styrene retarded the polymerization[15] and the rate of polymerization[8] increased sharply from virtually zero with the increase of initiator concentration at low level, but remained constant in $K_2S_2O_8$ concentration range between 1.0 and 6.13 g/l aqueous phase. Hawkett and his coworkers[7] also observed that the rate of Polymerization was almost unchanged, when the initiator concentration was greater than 1.7 g/l. In these two cases the effect of radical desorption from the latex particles could affect the quasi-steady state value of n by reducing from its equilibrium value at a low initiator concentration. And the rapid depletion of initiator synergistically caused the retardation in the system which contained low concentration

effect of initiator concentration on the rate of polymerization is shown in Table 3. The rate of polymerization of styrene was increased with the initiator concentration regardless of pH of the polymerization systems.

According to the Smith-Ewart's Case 2 theory[2], the rate of polymerization of PS-styrene (PS-seeded styrene emulsion polymerization) was not affected by the change in initiator

of initiator. In the conclusion the rate of poly-merization in PS-styrene system was independent of $K_2S_2O_8$ concentration above a critical level was apparently consistent with the Smith-Ewart's Case 2 theory with $\bar{n}$ = ½. However, when the particles have more than one radical in a finite time, the rate of polymerization could increase.

In the presently investigated PMMA-styrene system the particle size of PMMA latex and the range of $K_2S_2O_8$ concentration (0.104 - 4.9g/1) were almost similar to those of the system investigated by Hasan[8], but the rate of poly-merization was increased along with $K_2S_2O_8$ concentration. In the previous work[11] we reported that styrene was a common solvent to PS and PMMA but at high polymer concentration (the maximum possible weight fraction was 0.75) the PS- and PMMA-styrene phases started to separate[16,17] as soon as styrene polymerization took place. Therefore, in a polymerizing particle a propagating radical in PMMA-rich phase could not terminate by another radical in PS-rich phase during relatively short period of time, namely before the molecular weight of the propagating oligomeric radical was smaller than the critical molecular weight for phase separation. And the morphology of PMMA-PS particle could change from the "inverted core-shell" to the "core-shell" along with the increase in the $K_2S_2O_8$ con-centration. Thus, being different from the homogeneous PS-styrene system, the diffusion of propagating radicals was restricted by the PMMA-rich phase. Accordingly the increase of entry rate of radicals in the PMMA-PS-styrene particle makes the propagation proceed in more than one loci. From these observation it can be stated that the rate of polymerication of PMMA-styrene system is increased along with $K_2S_2O_8$ concentration due to the increase of $\bar{n}$.

3-2-2. Particle Size of Seed Latex

The effect of PMMA-latex particle size on the rate of polymerization per particle is

Table 4. Effect of Particle Size of PMMA Seed Latex on the R_{pp} at 60°C

Experimental Number	Seed Latex	D_n(nm)	R_{pp}
PMS – 46	PMMA – 6	117	0.91
PMS – 38	PMMA – 5	133	1.16
PMS – 11	PMMA – 1	156	2.05
PMS – 12	PMMA – 2	161	1.89
PMS – 19	PMMA – 3	170	1.84
PMS – 31	PMMA – 4	318	4.22

Table 5. Effect of Particle Size of PMMA Seed Latex on the R_{pp} at 80°C

Experimental Number	Seed Latex	R_{pp}
PMS – 34	PMMA – 5	3.23
PMS – 24	PMMA – 2	5.53
PMS – 30	PMMA – 4	23.95

shown in Table 4, 5 and Fig. 1. As shown in Fig. 1, the rate of polymerization per particle was directly proportional to the size of PMMA seed latexes.

Smith and Ewart[2] assumed that the rate of polymerization per particle is independent of the particle size and in Case 2 two radicals can not coexist in a polymerizing particle simultane-ously. It was based on the fact that the particle size is too small, relative to the bimolecular termination rate constant, to accomodate more than one radical. However Poehlein and Vander-hoff[5] have shown that the rate of polymerization of styrene was proportional to 1.5 the power of the particle size of PS seed latex. Hasan[8] re-ported that the rate of polymerization per particle of styrene in stage II was proportional to the square of the particle size of PS seed latex. In another styrene polymerization $\bar{n}$ was in-creased with conversion during stage II[18]. There-fore, in PS-styrene system the rate of polymeri-zation per particle should increase, but the dependence of the growth rate of $\bar{n}$ still remains controversial.
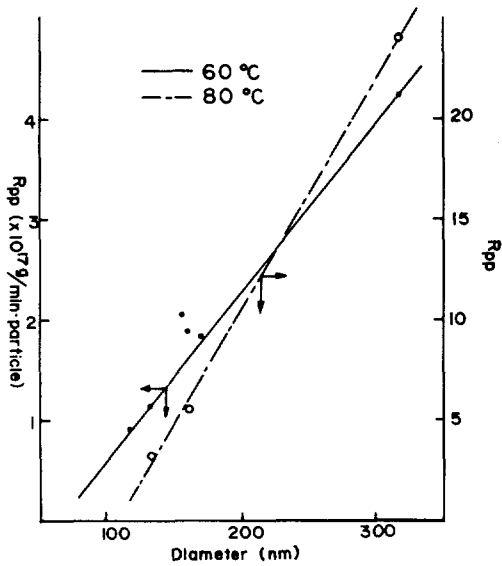
Fig. 1. Relationship between the rate of polymerization per particle and the particle size of PMMA seed latex.

Table 6. Monomer Concentration of PMMA Seed Latexes at 60 and 80℃ (unit, mole/1)

Seed Latex	60℃	80℃
PMMA – 1	5.55	5.28
PMMA – 4	6.35	5.75

Table 7. Effect of Temperature on the Rate of Polymerization in PMMA – Styrene Emulsion Polymerizations

Experimental Number	Polymerization Temperature (℃)	$R_{\bar{p}}$(g/min.)	R_{PP}
PMS – 20	50	1.61	1.02
PMS – 19	60	2.89	1.84
PMS – 21	70	5.02	3.19
PMS – 24	80	8.70	5.53

* PMMA – 2 was used as seed latex.

Like those observed in PS-styrene system the rate of polymerization per particle of PMMA-styrene system changed with the seed particle diameter. As shown in Fig. 1, it was linearly dependent upon the diameter and the magnitude increased with the polymerization temperature. According to Smith-Ewart theory the R_{pp} is

$$R_{pp} = k_p \cdot [M] \cdot n \qquad (4)$$

As shown in above equation, the concentration of monomer in a particle, calculated from the swelling ratio, and $\bar{n}$ were important for R_{pp}. But the increase of monomer concentration (Table 6) is small compared to the increase of R_{pp}. The increase ratios of R_{pp} are 2.64 at 60°C and 4.49 at 80°C as calculated from Fig. 4. Therefore, the increase of R_{pp} is mainly based on the increase in $\bar{n}$, and it is affected by the phase separation of PMMA- and PS-rich phases. Besides of the restricted diffusion of radicals, the average number of PS-rish regions in a particle can also contribute to the increase of R_{pp}. The segregation of PS-rich domains occur

increasingly in the large particles, and each of them operated as an independent polymerization locus.

As discussed in the previous section, the increase of the rate of radical generation makes $\bar{n}$ larger in PMMA-styrene system and also induces the increase of R_{pp}. Consequently, the increase of temperature made greater the dependence of R_{pp} on the seed latex particles.

3-3. Polymerization Temperature

The effect of polymerization temperature is shown in Table 7. As expected, the rate of polymerization increased with polymerization temperature. In Fig. 2 an Arrhenius plot of ln R_p against $1/T$ (°K) is shown. The activation energy of polymerization, E_p, during the initial constant rate period was calculated to be 53.2 KJ/mol (12.7 Kcal/mol). The literature values are 49.1[2,3] and 43.0[8] KJ/mol on the PS-styrene or styrene polymerization system. The presently obtained value of E_p for PMMA-styrene emulsion polymerization is in good agreement with that for the styrene emulsion polymerization, indicating that the propagation of styrene polymerization
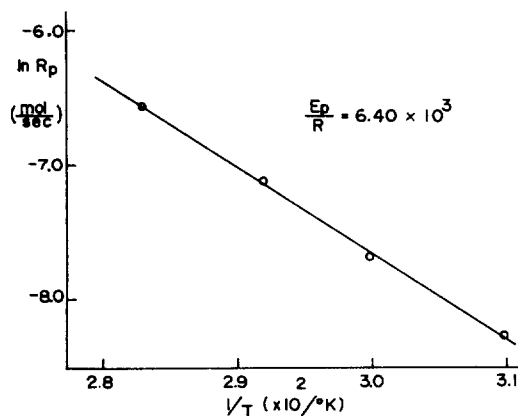
Fig. 2. Arrhenius plot of ln R_{PP} against 1/T for PMMA-styrene emulsion polymerization reaction.

takes place mainly in PS-rich phase in a particle.

If we assume $\bar{n}$ = ½ at PMMA-6 (the smallest seed latex) and the linear change of monomer concentertion against particle size, then [M] is 5.33 mol/l (in small PS particle (below 100nm) and 5.42 mol/l at $60^{\circ}C^{19}$). From these values the k_p can be calculated with equation (4) in case of PMS-46.

$$R_{pp} = 9.1 \times 10^{-18} /60g/(sec.volume\ of\ particle)$$

$$k_p = \frac{1.52 \times 10^{-19} \times 6.023 \times 10^{23}}{104.15 \times 0.5 \times 5.33}$$

$$= 330\ 1/(mol.sec)$$

where 6.023×10^{23} ; Avogadro's number

104.15 ; molecular weight of styrene

This is in reasonable agreement with the literature value[20] of K_p = 376 1/(mol.sec) at $60^{\circ}C$ for styrene emulsion polymerization. But Patsiga and his coworkers[4] obtained k_p = 153 1/mol.sec) at $60^{\circ}C$ in poly (vinyl acetate)-styrene emulsion polymerization system and others in PS-styrene system k_p s are 615[8] and 736 1/mol/sec[3]. The reliability of k_p value may be questioned because of its dependence on [M] and $\bar{n}$, since the meaningful evaluation of these values have remained debatable.

3-4. Chain Transfer Agent

The effect of chain transfer agent is shown in Table 8. In principle, chain transfer agent should not affect the kinetics of the free radical polymerization in bulk and solution systems, although it reduce the molecular weight of the polymer formed. However, in emulsion polymerization chain transfer agent may significantly reduce not only the molecular weight of the polymer but also the rate of polymerization[21,22]. This reduction in rate was shown[21] to arise, at least in part, from the breakdown in the extent of compartmentalization of the free radicals in latex particles. The presence of chain transfer agent can promote the escape of free radicals from the latex particles, and the reduction effect on the rate of polymerization would be enhanced by taking a chain transfer agent of higher transfer constant and solubility in water[22].

As shown in Table 8, the rate of polymerization of PMMA-styrene system also decreased with the addition of chain transfer agent ($CHBr_3$). And the particle size of PMMA seed latexes (Table 1) decreased with the addition of it. It is apparent that a compound which can behave as a chain transfer agent in homogeneous polymerization may function effectively as a retarder in emulsion polymerization system regardless of the seeded or non-seeded emulsion polymerization by radical desorption from the latex particles, even though its principal role remains to be that of the control of polymer molecular weight.

4. CONCLUSION

The rate of polymerization per particle was increased with the increase in $K_2S_2O_8$ concentration and the increase was linearly proportional to the diameter of PMMA seed latex particles. It was caused by the facts that the increase of the entry rate of radicals into the separated

Table 8. Effect of Chain Transfor Agent on the Rate of Polymerization of PMMA-Styrene at 60°C

Experimental Number	Seed Latex	CHBr$_3$ (pphm)^a	Peak Time (hours)	R$_{PP}$
PMS-31	PMMA-4	–	9.8	4.22
PMS-32	″	0.667	12.3	–
PMS-38	PMMA-5	–	3.8	1.16
PMS-35	″	0.667	4.8	~1.09

PMMA-rich and PS-rich phases in a particle made the propagation takes place in more than one locus in a latex particle. Additionally the increase of the average number of PS-rich domains in a particle contributed to the dependence of seed particle diameter. It was based on the fact that the propagating radicals could not terminate with each other, when they existed in segregated PS-rich domains in a particle. Dependence of the rate of polymerization upon the temperature became more pronounced with the increase in the polymerization temperature. But the rate of polymerization per particle decreased with the addition of chain transfer agent (CHBr$_3$) because of the easy desorption of the transferred radicals from the polymerizing particles. The activation energy of polymerization calculated from Arrhenius plot was 53.2 KJ/mol and the propagation rate constant, k_p, was 330 1/(mol. sec). The latter was calculated from Smith-Ewart Case 2 theory of PMS-46 (D$_n$ of PMMA seed latex, 117 nm) polymerized at 60°C.

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