

# A Kinetic Investigation of Thermally Initiated Emulsion Copolymerization of Styrene and Methylmethacrylate without Conventional Initiators

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**ABSTRACT:** The thermally initiated emulsion copolymerization of styrene (ST) and methyl methacrylate (MMA) was carried out in the absence of conventional initiators. The hydroperoxide (HPO) concentration in the monomers, sodium dodecyl sulfate (SDS), deionized water, and the formulation of those for emulsion copolymerization were measured. The HPO concentration in ST and MMA increased with the storage time, and were considered to be the major sources of HPO. The thermal decomposition of hydroperoxide in monomers, the thermal initiation of ST by Mayo mechanism, and the complex formation between SDS and the monomers were proposed to be three main sources of the radical generation. It was confirmed that new polymer particles were generated throughout the polymerization process, and consequently resulted in a broader distribution of polymer particle size, compared with that for conventional emulsion polymerization. Approximately 80 wt % of monomer conversion was obtained in the presence of SDS at 373 K in 24 h. The initiation rate of the 30 wt % monomer charge was faster than those of 10 wt % and 20 wt % monomer charge. The latex instability at higher solid content was improved by adding electrolyte to promote the electrostatic repulsion force between the polymer particles. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 455–467, 2002; DOI 10.1002/app.2343

**Key words:** thermal initiation; emulsion copolymerization; styrene; methylmethacrylate; kinetics

## INTRODUCTION

Thermally initiated emulsion polymerization is interesting to study in two ways. One is the mechanism of the polymerization with complexity arising from the slow nucleation and growth of polymer particles: there are various sources of initiation, from monomers, styrene in particular, emulsifier,<sup>1</sup> trace of impurities, and even dis-

solved oxygen within a certain ppm range.<sup>2</sup> The other motivation of this study is to explore the possibility of designing a high-performance reactor, which is operated continuously with a short residence time at high temperature.

We have been investigating a series of the thermal emulsion polymerizations of styrene, styrene/MMA, and MMA,<sup>3–7</sup> as well as the seeded polymerization.<sup>8</sup>

The thermally initiated emulsion polymerization of styrene (ST), which easily generates free radicals by heat, has been widely investigated by many workers. Asahara and coworkers<sup>9</sup> reported on the

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polymerization of styrene in the presence of sodium tetrapropylene benzene sulfonate (ABS) in an aqueous system without any ordinary initiators. The rate of polymerization was dependent on the concentration of the surfactant and on the initial monomer concentration. They also claimed that the ABS concentration was thought to be a factor in the production of radicals, and that the relationship between the ABS concentration and the number of polymer particles was linear. They also reported that the surface area of micelles may be one important parameter of their polymerization system: radicals are generated only on the surface of the micelles, and the number of radicals may increase with an increase of the number of micelles in their system. Said and coworker<sup>10</sup> proposed that the catalysis of thermal initiation of styrene emulsion polymerization by emulsifiers—sodium dodecyl sulfate, sodium tetrapropylene benzene sulfonate, and potassium octadecanoate—did accelerate the thermal initiation of styrene, but Triton 100 and sodium dodecyl benzene sulfonate did not, although the latter was effective in accelerating the thermal initiation of alkyl methacrylates. They also implied that the mechanism, in which emulsifiers influence the rate of thermal initiation, was not clear. Most probably, the emulsifiers favor the efficiency with which one of the radicals produced in the thermal initiation process escapes into the aqueous phase so that the emulsion polymerization may begin. If this is the case, the emulsifiers, dissolving in the continuous phase, can freely exchange with those forming micelles or those adsorbed on latex particles, and can be most effective in promoting thermal polymerization.

The thermally initiated polymerization of methyl methacrylate (MMA), which sparsely generates free radicals by heat in the bulk phase, has also been widely investigated. Asahara et al.<sup>11–17</sup> reported on the polymerization of MMA in the presence of inorganic substances with a hydroxyl group on the surface, such as clay or silica. They found that MMA polymerized readily in the presence of an anionic surface active agent in water, without the presence of a hydroxyl group on the surface, to yield poly(methyl methacrylate) having an unusually high molecular weight with good conversion. They also showed that the thermal polymerization of methyl methacrylate was greatly accelerated by emulsifiers such as sodium oleate, SDS, ABS, and especially with sodium 2-dodecylbenzene sulphonate but not with cationic cetyl pyridinium chloride and two nonionic

emulsifiers. The polymerization was inhibited by hydroquinone. The rate of polymerization was found to be proportional to the cubic root of the monomer concentration and the cubic root of the ABS concentration. Imoto and Takemoto<sup>18</sup> reported on the homopolymerization of MMA and graft copolymerization of MMA onto fibers having hydroxyl pendant groups, in particular, onto cellulose. They proposed that the initiation step of the polymerization progressed mainly by the formation of a ternary complex of the hydroxyl group, water, and MMA. Matsumoto et al.<sup>19</sup> reported on the polymerization of MMA in an aqueous medium in the presence of poly(methacrylic acid), and proposed that the initiation was due to the decomposition of peroxide induced from MMA monomers.

Copolymerization of MMA with styrene has been also investigated. Asahara et al.<sup>20</sup> observed that the final conversion was the lowest when the molar ratio of MMA/ST was 0.67 in their experiments.

In this article, we will report on the effects of monomer composition, monomer concentration, and emulsifier concentration on the thermally initiated emulsion copolymerization of ST/MMA in the presence of SDS without any conventional initiators. Investigation of the sources of hydroperoxide and a proposition for the initiation mechanism are included as well. It will be proposed that the overall propagation rate constant of the copolymerization changes with the monomer composition according to the observation by Fukuda et al.<sup>21</sup> A simple mathematical model was developed to estimate the copolymer composition by considering the partition of monomers.

## EXPERIMENTAL

### Materials

All the reagents, unless stated otherwise, were purchased from Kishida Chemical Co., Japan.

MMA and ST were commercial grade, distilled under reduced pressure, and stored in a refrigerator until use.

Sodium dodecyl sulfate (SDS, biochemistry grade, from Merck Co.), anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ , from Wako Pure Chemical Industries, Ltd., Japan), and hydroquinone (HQ, commercial grade), were all used as received.

Chloroform- $d_1$  was used as the solvent for  $^1\text{H-NMR}$  measurements.

Tetrahydrofuran (THF, commercial grade) was used as a carrier solvent for GPC.

Distilled and deionized water was used.

### Copolymerization

The copolymerization was carried out in a four-necked, 1000-mL flask immersed in a thermostat-controlled bath. The flask was equipped with a stirrer, condenser (nitrogen outlet), nitrogen inlet tube, and rubber stopper for sampling. A slow stream of nitrogen was introduced into the reaction mixture for 2 h after the weighed portion of MMA, ST, and deionized water dissolving SDS were added into the flask. The agitation was 350 rpm. Then the mixture was heated to 373 K in 30 min with a programmed heating device (Yamato Thermo-Mate BF 600, Yamato, Japan). The time was regarded as the starting time when the temperature reached to 373 K. A blanket of nitrogen atmosphere was maintained throughout the reaction period, however, with no flow of nitrogen, so that the monomer may not be wasted.

### Analytical Method

#### Polymer Yield

Roughly 5 g of the reaction mixture was withdrawn by a syringe at definite time intervals, weighed accurately, and poured into 10 mL of methanol containing 0.1 wt % of hydroquinone, which was used to minimize further polymerization to precipitate the polymer formed. The precipitated polymer was collected by a centrifuge, thoroughly washed with methanol about three times, dried at 333 K, and weighed. The polymer yield and the conversion of monomer were determined gravimetrically.

#### Particle Size and Number of Polymer Particles

Determination of particle size was carried out by withdrawing a latex sample of roughly 1 g, and it was diluted with 10 mL of 0.1 wt % hydroquinone aqueous solution. Then, the sample was further diluted by 1000 times with water. Three droplets were placed on an aluminum sheet covering a brass sample rod, dried overnight in a desiccator, coated with gold (JEOL JFC-1200, Japan), and served for observation by a scanning electron microscope (SEM) (JEOL-5310, Japan). The average

diameter of the particles was determined by direct measurement of 200 particles in an SEM photo. The number of polymer particles was calculated from the average diameter, and polymer yield whilst the density of the polymer was assumed as  $1.0 \times 10^{-12} \text{ g}/\mu\text{m}^3$ .

### Molecular Weight

The number- and weight-average molecular weights of the copolymer,  $\bar{M}_n$  and  $\bar{M}_w$  were estimated by gel permeation chromatography (GPC, HLC-8020, Tosoh, Japan) with the column system calibrated with standard PST. Commercial grade tetrahydrofuran was used as a carrier solvent.

### Copolymer Composition

The composition of the copolymers was determined by  $^1\text{H-NMR}$ , measured at 318 K with 0.05 wt % chloroform- $d_1$  solution using a Japan Electron Datum Spectrometer (JNM-A500FT) working at 500 Mc., with tetramethylsilane as a standard. The copolymer composition was estimated using the relative area of the peak of phenyl protons of styrene unit and the peak of the  $\alpha$ -methyl protons of the methyl methacrylate unit.

### Hydroperoxide Concentration

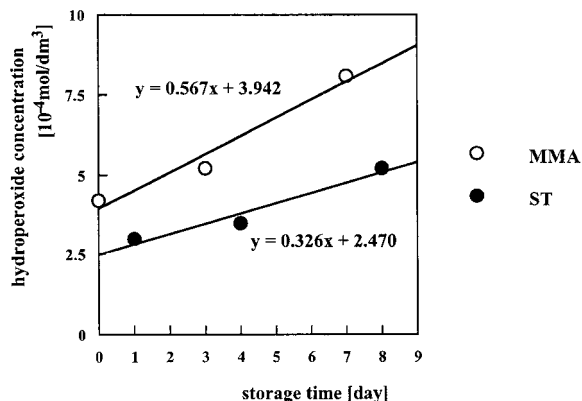
The hydroperoxide concentration in monomers, SDS solution, deionized water, and the reaction mixture at the instant of initiation of copolymerization was determined by the simplified method of Wagner.<sup>22</sup>

### Monomer Partition in the Water and Oil Phase

The solubility of ST and MMA in the water phase with different monomer composition and concentration were measured by a gas chromatograph (TCD-GC, MODEL-802T, Ohkura Electric Co., Japan) equipped with a thermal conductivity detector. The mixture of monomer and distilled water was sealed in a 30-mL screw bottle with a rubber gasket for sampling, and then immersed in a 373 K oil thermostat for 30 min. About 2  $\mu\text{L}$  of the oil phase and the water phase were separately withdrawn by a microsyringe, and then injected to a TCD-GC for measurement.

### Other Analytical Methods

The rate of copolymerization was determined from the polymer yield time curves by graphical differentiation.



**Figure 1** Accumulation of hydroperoxide concentration in monomers during the storage period.

The latex was diluted to  $1 \times 10^{-4}$  g/mL by deionized water (pH 6.7) for measurement of the zeta potential. The zeta potential was determined by direct measurement of the electrophoretic rate of particles in a 45-V direct current field, and automatically calculated by a zeta potential analyzer (ZC-050, Microtech Nichion Co., Japan).

## RESULTS AND DISCUSSION

### Measurement of Hydroperoxide (HPO) Concentration

Matsumoto et al.<sup>23</sup> extensively studied the formation of MMA peroxide, not only for a slow build-up during the storage period but also in a more positive fashion when MMA was exposed to the light or even heated up in an atmosphere of oxygen. Approximately half of the peroxides formed in the dark and at low temperature were hydroperoxides. They reported on the build-up of peroxide concentration and the increasing rate of bulk polymerization as a function of storage period.

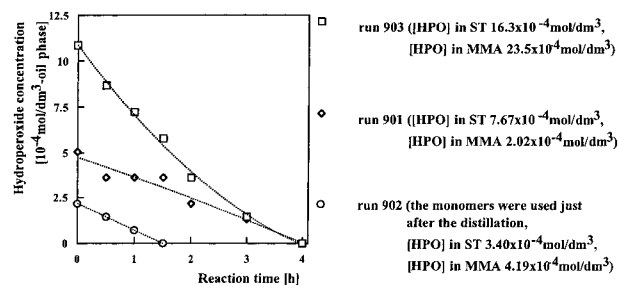
HPO concentrations in SDS aqueous solution and deionized water, and the accumulation of HPO concentration in the monomers during the storage period were measured by using the simplified method of Wagner.<sup>22</sup> HPO concentration of 0.7 wt % SDS aqueous solution was ca.  $3 \times 10^{-5}$  mol/dm<sup>3</sup>, and no HPO was detected in the distilled and deionized water. The accumulation of HPO concentration in two monomers during the storage period is shown in Figure 1. It is obvious that either with styrene or MMA monomer, the HPO concentration increased linearly with the

**Table I** Recipes of Thermally Initiated Emulsion Copolymerization

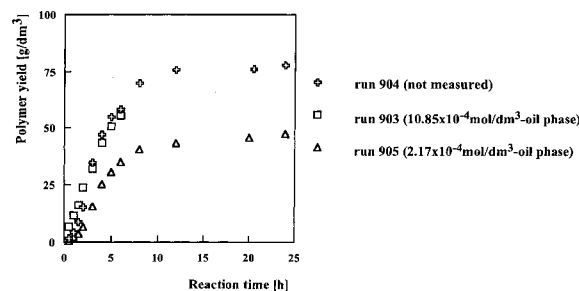
Run No.	ST (g)	MMA (g)	SDS (g)	Na <sub>2</sub> SO <sub>4</sub> (g)	Water <sup>a</sup> (g)
901	25	25	3.5	/	450
902	25	25	3.5	/	450
903	35	15	3.5	/	450
904	35	15	3.5	/	450
905	35	15	3.5	/	450
906	50	/	3.5	/	450
907	45	5	3.5	/	450
908	40	10	3.5	/	450
909	30	20	3.5	/	450
910	25	25	3.5	/	450
911	2.5	47.5	3.5	/	450
912	/	50	3.5	/	450
913	80	20	3.5	/	400
914	120	30	3.5	/	350
915	120	30	7.0	/	350
916	120	30	7.0	5	350
917	120	30	1.75	5	350
918	120	30	3.5	5	350

Reaction temperature: 373 K. Agitation rate: 350 rpm.

<sup>a</sup> Including the amount of SDS or Na<sub>2</sub>SO<sub>4</sub>.

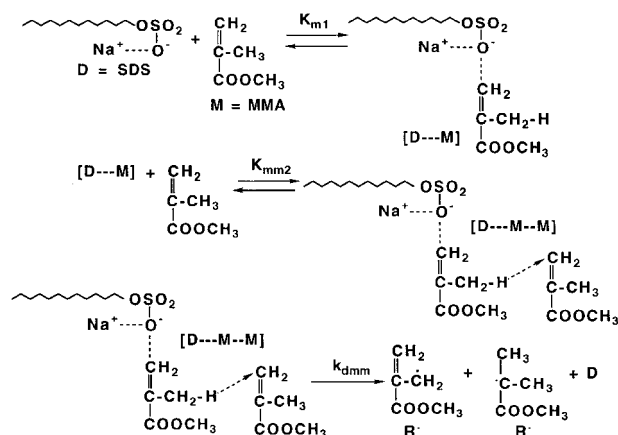


**a.** HPO decomposition during the polymerization (monomer 10 wt%, SDS 0.7 wt%, 373K)



**b.** profiles of polymer yield using the monomers with different HPO concentration.

**Figure 2** (a) The hydroperoxide (HPO) decomposition during the polymerization, and (b) effect of HPO concentration on the polymerization rate.



**Figure 3** Mechanism of radicals generation proposed by Imoto and Ouchi.<sup>26</sup>

storage time, even when the monomers were stored in a refrigerator after distillation. Notice that the HPO concentration in MMA is higher than that in styrene at the time of distillation, and increases faster during the storage period. Because the HPO concentration of styrene and MMA were 10 times higher than that of 0.7 wt % SDS aqueous solution, the monomers are to be considered as major sources of HPO.

The emulsion copolymerizations of styrene (ST) and methyl methacrylate (MMA) were carried out with different initial HPO concentrations in the oil phase. The recipes of copolymerization are shown in Table I. Figure 2(a) shows the HPO decomposition during the polymerization, and Figure 2(b) shows the profiles of polymer yield against the reaction time with different initial HPO concentrations in the oil phase. The run 903 was stopped at 8 h. The rate of HPO decomposition was very fast, as shown in Figure 2(a). If the monomers were used immediately after the distillation, HPO was consumed in 1.5 h. This implies that HPO only affected the early stage of thermally initiated emulsion polymerization. However, in emulsion polymerization, controlling the initial period is critical for practical purposes because the nucleation of polymer particles overlaps in this period, and the number of polymer particles formed will overwhelmingly affect the later progress of the reaction. Controlling the amount of hydroperoxide is, in this argument, essential to obtain reproducible results. From Figure 2(b) it can be seen that the initial rate of run 903, with higher hydroperoxide concentration, was much faster than that of the run 905

with lower hydroperoxide content. This implies that the hydroperoxides in the monomers play an important role in the initial period, a potential source of initiating radicals.

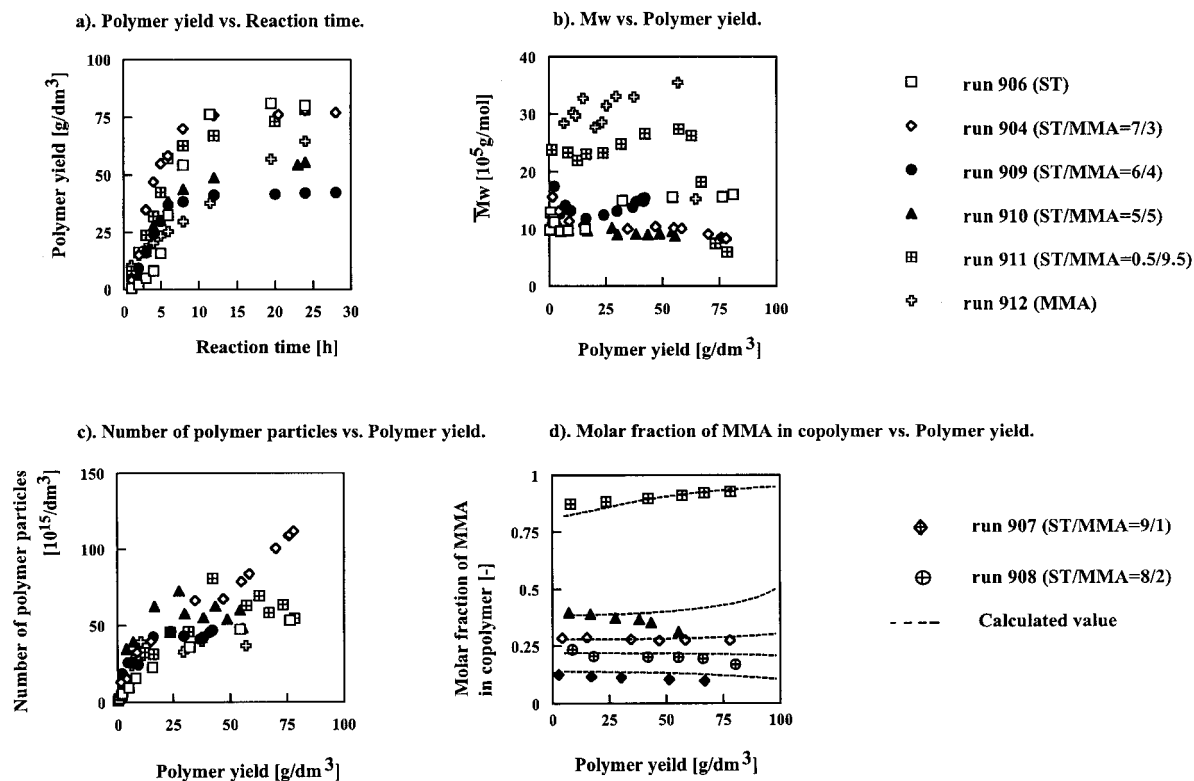
### Proposed Mechanism of Initiation

From these results, we propose that there are three kinds of initiation routes that contribute to the thermally initiated emulsion copolymerization of ST/MMA. The first is the so-called thermal initiation involving a Diels-Alder dimer and a monomer (tri-molecular initiation process) as proposed by Mayo.<sup>24,25</sup> The second is the initiation from the complex formed with hydrophilic additives and monomers as shown in Figure 3. Imoto and Ouchi<sup>26</sup> proposed this mechanism with P(styrene-*co*-NaSS) dissolved in water. In Figure 3, where MMA is chosen as a counterpart of the complex formation, the sulfate group in SDS is supposed to play a role of complex formation instead of the sulfonic group of NaSS. Any combination of monomer pair in the present system can undergo the three processes, the third being the radical formation from impurities present in the reaction system such as oxygen, hydroperoxides, and others. All of these mechanisms are regarded as the background initiation by Gilbert and his coworkers in their kinetic investigations of conventional emulsion polymerization.<sup>27-29</sup>

Considering that the oil phase in the present system is approximately 10%, the initiation by HPO in the oil phase cannot be neglected at the initial stage. The initiation by the Mayo mechanism will continue as long as styrene monomers are present in an appreciable amount.<sup>7</sup> The Imoto-Ouchi model will be mainly applied to the surface of soap micelles and polymer particles where a majority of soap molecules are present. We expect to draw some quantitative information from the thermally initiated seed emulsion copolymerization now under investigation, in which a further complication caused by the particle nucleation is eliminated.

### Effect of the Composition of Charged Monomers

The copolymerization was carried out to investigate the effect of the composition with 10 wt % monomer to the total reaction mixture (run 904, and runs 906-912 in Table I). As shown in Figure 4(a), without using any ordinary initiator, the polymer yields reached as high as 80 wt % in 24 h

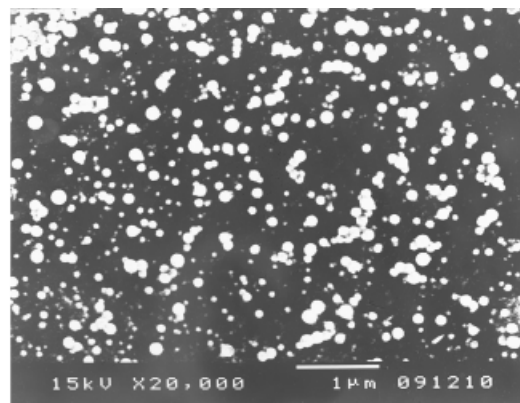


**Figure 4** Effect of monomer composition on the thermally initiated emulsion copolymerization.

in the presence of SDS, except for those runs employing 6/4 and 5/5 ST/MMA weight ratios. Asahara et al.,<sup>20</sup> who investigated the same copolymerization system by using sodium tetrapropylene benzene sulfonate (ABS) as the emulsifier, also reported that the polymer yield was the lowest when the molar ratio was about 6/4, a trend also found in this work. A plausible solution may be obtained from the report by Fukuda et al.<sup>21</sup> In their extensive kinetic investigation of solution copolymerization of styrene and MMA, they claimed that the experimental data can be correlated only by introducing a penultimate model rather than the conventional terminal model, and proposed a set of reactivity ratios that allowed calculation of the overall rate constant of propagation as shown in Appendix 1. According to the calculation,  $\bar{k}_{p0}$ , the overall propagation rate constant is correlated to the initial mol fraction of MMA as shown in Figure A1, which has a minimum value around  $z_m = 0.7$ . If small changes of those parameters are allowed to shift the minimum at  $z_m = 0.6$ , and the low capacity of MMA to generate thermal radicals is considered as a com-

bined effect, then the observed stalling of polymerization as shown in Figure 4(a) can be understood qualitatively.

The variations of the number of polymer particles are shown in Figure 4(c). It was observed that



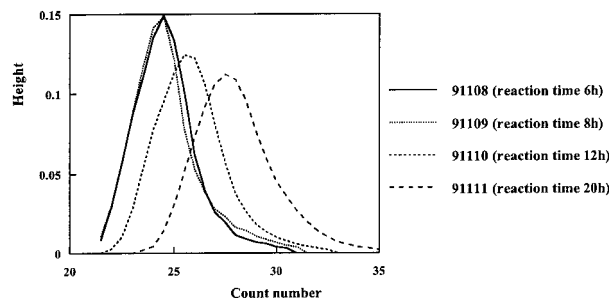
ST/MMA = 8/2, the total monomer content 10wt%, SDS 0.7wt%, 373K, polymer yield 75 g/dm<sup>3</sup>.

**Figure 5** A typical SEM photograph of polydisperse polymer particles.

the number of polymer particles increased as the copolymerization progresses. It implies that the new polymer particles were generated throughout the polymerization, which can also be confirmed by the SEM photograph, as shown in Figure 5. Polydispersity, a characteristic of typical thermally initiated emulsion polymerization, was observed. Two factors were suggested to be the reasons for the generation of new particles. One is that the generation rate of radicals of thermally initiated emulsion polymerization was very slow. The other is that the radical was apt to escape from the polymer particles, and consequently, the nucleation in the aqueous phase was highly probable because of the slow entry of radicals and low radical capture efficiency of the polymer particle. It can be concluded that the thermally initiated emulsion polymerization is a system in which the nucleation period exists in parallel to the growth process of polymer particles throughout the polymerization process.

Figure 4(b) shows the changes of weight-average molecular weight of polymer as the copolymerization progresses. Generally, the weight-average molecular weight tends to decrease at the initial stage of polymerization. The initial high molecular weight is rather inevitable because of the experimental necessity to raise the temperature from ambient temperature to 373 K. We paid utmost attention to achieve consistent heating of the reaction mixture for each run, and employed a programmed control system to raise the temperature. During this period, while raising the temperature from ambient to 373 K, gradually polymerization was initiated, and small amounts of higher molecular weight polymers were formed. The weight-average molecular weight with higher MMA composition (especially run 911) and that of PMMA (run 912) was higher than those obtained from the runs of a lower MMA charge. Because the molecular weight of MMA is approximately equal to that of ST, this implies that the degree of polymerization increased as the MMA composition increased. In bulk polymerization, PMMA normally exhibits a higher viscosity than polystyrene. The viscosity in the polymer particles tends to be higher with an increasing amount of MMA in the monomer composition, the mobility of polymeric radicals being hindered, and leading to the slower termination rate.

Although the homopolymerization of styrene (run 906), and the run with higher composition of styrene (run 907, not shown), showed no such

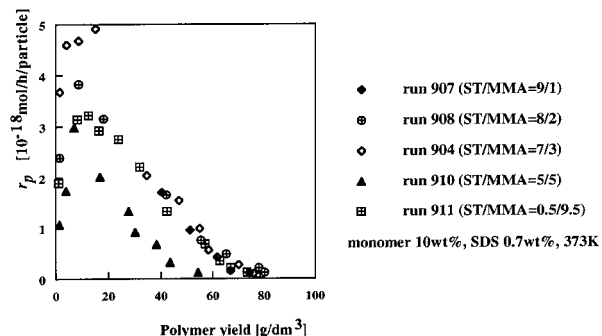


**Figure 6** Normalized GPC chart based on GPC measurement for run 911.

tendencies, the weight-average molecular weight of the two runs, the highest MMA content (ST/MMA = 0.5/9.5, run 911) and pure MMA (run 912), decreased remarkably towards the end of copolymerization. Gilbert<sup>27</sup> described the formation of low molecular weight polymers due to the dwindling mobility of polymeric radicals, leading to the increased possibility of the termination reaction between the polymeric chain and the entering radical. In soapless emulsion polymerization of MMA, Chiu et al.<sup>30</sup> reported that as the conversion became higher, the viscosity in polymer particles increased rapidly and limited the mobility of longer polymer chains, so the chance for the growth of short chains increased. It was probably related to the termination dominated by the disproportionation of MMA end radicals. The normalized curves of MWD of run 911 are shown in Figure 6. The same tendency was observed from the measurement of run 912. Apparently, the fraction of lower molecular weight increased in the later stage. In the end, the ST monomer was almost consumed, and only the MMA monomer remained in the copolymerization system. Viscosity average molecular weight measurements were tried to confirm these unexpected results. However, concentrations of the polymer dissolved in acetone, benzene, and 2-butanone were too low to obtain any reliable results.

The composition of copolymers at definite time intervals were measured by the <sup>1</sup>H-NMR technique. The results are shown in Figure 4(d). The trend of the plots is consistent with that predicted from the mathematical model as shown in Appendix 2, where the partition of MMA is taken into consideration. The azeotropic composition of MMA in homogeneous system is calculated as,

$$y_{\text{azeo.}} = \frac{1 - 0.523}{2 - 0.46 - 0.523} = 0.47 \quad (1)$$



**Figure 7** Rate of copolymerization per particle vs. polymer yield.

The reactivity ratios are set as 0.523 for styrene and 0.46 for MMA<sup>21</sup> in our heterogeneous system. One noticeable discrepancy from the mathematical model arose at the later stage of run 910 with the monomer weight ratio, 5/5. As the copolymerization progressed, the molar fraction of MMA in the copolymer was lower than that calculated. In connection with the polymer yield profile [Fig. 4(a)], the polymer yield remained low when the monomer weight ratio was 5/5. This implies that the MMA monomer located in the polymer particles was less than that expected from the partition data. The stalling of polymerization in the later stage may be related, although the exact reason is still unknown.

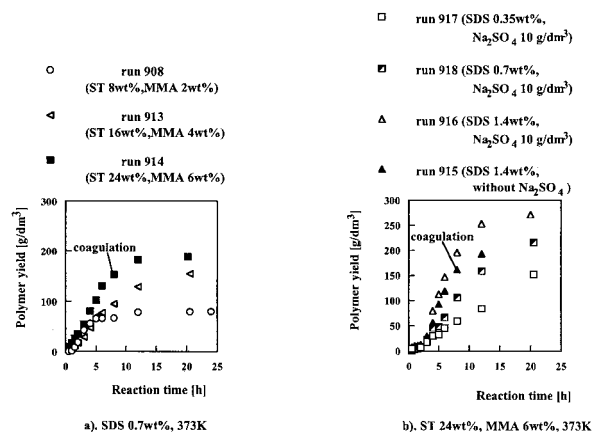
The rate of copolymerization was determined from the polymer yield-time curves by using a graphical differentiation method. An ordinary plot between the rate of copolymerization per polymer particle and polymer yield is shown in Figure 7, although the number of polymer particles never attained a constant value. In thermally initiated emulsion polymerization, the rate of polymerization per polymer particle in the initial stage increases rapidly until approximately 20% monomer conversion. After HPO was rapidly consumed, as shown in Figure 2(a), the rate of polymerization per polymer particle began to decrease rapidly. The reason for the rapid decrease is the prolonged increase of the number of polymer particles as well as the slow entry of radicals and the low radical capture efficiency of the polymer particle.

### Effect of Total Monomer and Emulsifier Concentration

Experiments were carried out changing the total monomer content (10, 20, and 30 wt %). The pro-

files of polymer yield against the reaction time are shown in Figure 8(a). From Figure 8(a) it can be seen that the initial rate of the 30 wt % monomer charge (run 914) was faster than the other runs of 10 and 20 wt %. Two reasons can be considered to explain this. The first is that the increasing number of polymer particles was observed with run 914. The second is that the initiation rate became higher, in particular, the initiation due to the decomposition of HPO. The maximum monomer conversion as high as about 80 wt % was obtained in the case of 10 and 20 wt % of the monomer charge. However, in the case of 30 wt % monomer charge, it was barely over 60 wt %, and coagulum was formed in the latex. The formation of coagulum was considered to be induced by an inadequate amount of emulsifier based on the 30 wt % monomer charge.

To overcome the instability of latex observed at the higher solid content, the concentration of SDS was increased, and the result is shown in Figure 8(b). In run 915, which is equivalent to the run 914 in terms of monomer charge, coagulation still occurred after 8 h, and reaction was stopped after 12 h. The reason for coagulation was speculated to be due to the deficient surface charge of polymer particles. Zeta potential measurements revealed  $-30$  to  $-50$  mV for these latices, while the conventional persulfate-initiated latices covered a  $-80$  to  $-100$ -mV range. An additional polymerization was carried out by adding  $\text{Na}_2\text{SO}_4$  as an electrolyte. The result is shown in Figure 8(b) as run 916. As expected, the polymerization steadily progressed, and no coagulation was observed until the end. Notice the polymer yield increased up



**Figure 8** Effect of monomer and emulsifier concentration on the profiles of polymer yield.



to 254 g/dm<sup>3</sup> at 12 h, an increase of 60 g/dm<sup>3</sup> compared to run 916. The zeta potential of the resultant latex was about -80 mV. It was confirmed that the number of polymer particles did not increase, only the surface charge of polymer particles increased by adding Na<sub>2</sub>SO<sub>4</sub>.

Figure 8(b) also shows the effect of SDS concentration by employing 0.35, 0.7, and 1.4 wt % of SDS content. A small amount of coagulum was formed in the lower SDS runs, 917 and 918.

From Figure 8(b) it was observed that the rate of copolymerization increased with the SDS concentration. As the SDS content increased, the number of soap micelles in emulsion increased; consequently, the number of generated polymer particles increased. The measured number of polymer particles of runs 917, 918, and 916 were 31(10<sup>15</sup>/dm<sup>3</sup>-lx), 74(10<sup>15</sup>/dm<sup>3</sup>-lx), 160(10<sup>15</sup>/dm<sup>3</sup>-lx), respectively, at 100 g/dm<sup>3</sup> polymer yield, at which point the coagulum was not formed. Because the polymer particles are the locus of polymerization, the rate of copolymerization increased by the increase of SDS content.

## CONCLUSION

Thermally initiated emulsion copolymerization of ST/MMA was carried out in the absence of conventional initiators. The thermal decomposition of hydroperoxide in monomers, the thermal initiation of ST and the complex formation between SDS and the monomers were proposed to be three main sources of radical generation. New polymer particles were generated throughout the polymerization process, and consequently, resulted in a broader size distribution of polymer particle size. Because the radical generation was very slow, the slow entry of radicals as well as the low radical capture efficiency caused the high probability of nucleation in the aqueous phase. Nearly 80 wt % of monomer conversion was obtained in the presence of SDS at 373 K for 24 h. The initial polymerization rate of the run with 30 wt % monomer charge was faster than those of 10 and 20 wt % due to the higher HPO concentration in the total mixture. The latex instability at higher solid content was improved by adding an electrolyte to develop electrostatic repulsion force between the polymer particles.

## APPENDIX 1: OVERALL PROPAGATION RATE CONSTANT FOR STYRENE-MMA COPOLYMERIZATION

For two component emulsion copolymerization system, the overall reaction rate for total monomers can be written as follows,

$$r_p = \bar{k}_{p0} [M_t] \frac{\bar{n}N}{N_A} \quad (\text{A1})$$

where,  $r_p$  = overall reaction rate of total monomers,  $\bar{k}_{p0}$  = overall propagation rate constant,  $[M_t]$  = total monomer concentration in polymer particles,  $\bar{n}$  = average number of radicals per particle,  $N$  = number of polymer particles, and  $N_A$  = the Avogadro number.

Fukuda et al.<sup>21</sup> derived the expression of  $\bar{k}_{p0}$  by adopting the penultimate model.

$$\bar{k}_{p0} = \frac{\bar{\gamma}_m z_m^2 + 2z_s z_m + \bar{\gamma}_s z_s^2}{\frac{\bar{\gamma}'_m z_m}{k_{pmmm}} + \frac{\bar{\gamma}'_s z_s}{k_{psss}}}$$

$$\bar{\gamma}_m = \gamma'_m \left( \frac{\gamma_m z_m + z_s}{\gamma'_m z_m + z_s} \right), \quad \bar{\gamma}_s = \gamma'_s \left( \frac{z_m + \gamma_s z_s}{z_m + \gamma'_s z_s} \right)$$

$$\bar{\gamma}'_m = \gamma'_m \left( \frac{\gamma_m z_m + z_s/q_m}{\gamma'_m z_m + z_s} \right), \quad \bar{\gamma}'_s = \gamma'_s \left( \frac{z_m/q_s + \gamma_s z_s}{z_m + \gamma'_s z_s} \right)$$

$$\gamma_m = \frac{k_{pmmm}}{k_{pmsm}}, \quad \gamma'_m = \frac{k_{psmm}}{k_{psms}}, \quad \gamma_s = \frac{k_{psss}}{k_{psms}}, \quad \gamma'_s = \frac{k_{pmsm}}{k_{pmsm}}$$

$$q_m = \frac{k_{psmm}}{k_{pmmm}}, \quad q_s = \frac{k_{pmsm}}{k_{psss}} \quad (\text{A2})$$

where,  $z_m, z_s$  = molar fraction of MMA and styrene in polymer particles, respectively, and  $k_{pijk}$  ( $i, j, k = m$  or  $s$ ) = propagation rate constant of the radical with  $\sim ij$  ends to react with monomer  $k$ .

They proposed the parameters as  $\gamma_m = \gamma'_m = 0.460$ ,  $\gamma_s = \gamma'_s = 0.523$ ,  $q_m = 0.53$ ,  $q_s = 0.30$ .

$k_{pmmm}$  and  $k_{psss}$  will be given at 373 K as  $4.90 \times 10^6$  dm<sup>3</sup>/mol/h and  $2.73 \times 10^6$  dm<sup>3</sup>/mol/h, respectively.

The calculated  $\bar{k}_{p0}$  was plotted against  $z_m$ , and is shown in Figure A1. Notice that the conventional terminal model yielded quite an opposite profile.

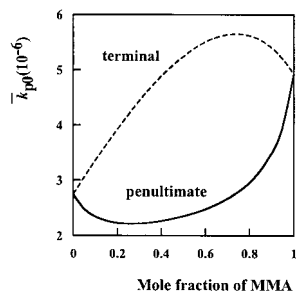


Figure A1.  $\bar{k}_{p0}$  values in two different models.

## APPENDIX 2: AVERAGE COMPOSITION OF COPOLYMER FORMED BY EMULSION POLYMERIZATION

The kinetic model, consistent with the experimental observations of thermally initiated emulsion copolymerization, has not been established by us because of the lack of sufficient and quantitative information about the initiation rate, and therefore, the particle nucleation step. However, corresponding to the Lewis-Mayo-Alfrey-Sakurada equation for homogeneous copolymerization system, the average composition of copolymers produced by the heterogeneous system can be estimated if only an accurate estimation of monomer concentrations in polymer particles is provided. This means that the partition of monomers between the polymer particles, monomer droplets (if they still exist), and the aqueous phase are available either from the thermodynamical equilibrium theory or from empirical correlations.<sup>31</sup> In this appendix, a simple mathematical model is proposed to estimate the average composition of copolymer (instantaneous and cumulative) formed by emulsion copolymerization by using empirical correlations for monomer partitions.

### Mathematical Expressions

The Lewis-Mayo-Alfrey-Sakurada equation can be extended to a heterogeneous system by introducing the monomer concentrations at the site of polymerization (polymer particles) as follows,

$$\frac{dM_m}{dM_s} = \frac{(M_{ps} + \gamma_m M_{pm})M_{pm}}{(\gamma_s M_{ps} + \gamma_m M_{pm})M_{ps}} \quad (\text{A3})$$

where,  $M_m$  and  $M_s$  = concentrations of MMA and styrene monomer based on the total latex volume ( $\text{mol}/\text{dm}^3\text{-lx}$ ),  $M_{pm}$  and  $M_{ps}$  = those in polymer

particles ( $\text{mol}/\text{dm}^3\text{-pp}$ ), respectively. lx = latex, and pp = polymer particle. Notice that  $\bar{\gamma}_m$  and  $\bar{\gamma}_s$  in eq.(A2) are reduced to  $\gamma_m$  and  $\gamma_s$ , because  $\gamma_m = \gamma_m'$  and  $\gamma_s = \gamma_s'$ .

Equation (A3) can be written in terms of polymer yields,

$$\frac{dw_m}{dw} = \frac{(M_{ps} + \gamma_m M_{pm})M_{pm}M_{wm}}{(M_{ps} + \gamma_m M_{pm})M_{pm}M_{wm} + (\gamma_s M_{ps} + \gamma_m M_{pm})M_{ps}M_{ws}} \quad (\text{A4})$$

where,  $w_m$  and  $w$  = weight of MMA copolymerized and total polymer yield ( $\text{g}/\text{dm}^3\text{-lx}$ ),  $M_{wm}$  and  $M_{ws}$  = molecular weights of MMA and styrene ( $\text{g}/\text{mol}$ ), respectively.  $w = w_m + w_s$ .  $w_s$  = weight of styrene copolymerized ( $\text{g}/\text{dm}^3\text{-lx}$ ). Total mass balance of each monomer can be written as,

$$w_{m0} - w_m = \phi_p a_{pm} + (1 - \phi_p)(a_{mm} + a_{wm}) \quad (\text{A5})$$

$$w_{s0} - w_s = \phi_p a_{ps} + (1 - \phi_p)a_{ms} \quad (\text{A6})$$

$$\begin{aligned} a_{pm} &= M_{pm}M_{wm}, \quad a_{mm} = M_{mm}M_{wm}, \quad a_{wm} = M_{Hm}M_{wm}, \\ a_{ps} &= M_{ps}M_{ws}, \quad a_{ms} = M_{ms}M_{ws} \end{aligned} \quad (\text{A7})$$

where,  $w_{m0}$  and  $w_{s0}$  = initial feed weight of MMA and styrene ( $\text{g}/\text{dm}^3\text{-lx}$ ), respectively, and  $\phi_p$  = volume fraction of polymer particles ( $\text{dm}^3\text{-pp}/\text{dm}^3\text{-lx}$ ).  $M_{mm}$  and  $M_{ms}$  = concentrations of MMA and styrene in monomer droplets defined as ( $\text{mol}/\text{dm}^3\text{-lx}$ ), respectively,  $M_{Hm}$  = concentration of MMA in the aqueous phase defined as ( $\text{mol}/\text{dm}^3\text{-lx}$ ).

The amount of styrene dissolved in the aqueous phase was neglected here. A more strict treatment was given elsewhere.<sup>32,33</sup>  $\phi_p$  can be calculated from the following relationship.

$$\phi_p = \frac{w/\rho_p}{1 - V_m(M_p + S_p)} \quad (\text{A8})$$

where,  $V_m$  = molar volume of two monomers (approximately equal) ( $\text{dm}^3/\text{mol}$ ),  $\rho_p$  = density of copolymer ( $\text{g}/\text{dm}^3$ ).

Weight-average instantaneous composition of MMA in copolymer,  $y_{wMMA}$ , is directly calculated from the righthand equation of eq. (A4), and the cumulative one is given as follows,

$$Y_{wMMA} = \frac{w_m}{w} = \frac{w_m}{w_m + w_s} \quad (\text{A9})$$

Transformation to the molar average compositions is a mere routine.

The purpose of the program is to calculate the average composition of MMA in copolymer based on the monomer partition correlations and numerical integration of eq. (A4). Equations (A5)–(A8) are necessary to determine the monomer partition together with the following empirical relationships. Solubility of MMA in water at 373 K was best fitted as,

$$\text{Log} \frac{1}{x_{wm}} = \alpha + \frac{\beta}{x_{mm}} \quad (\text{A10})$$

$$x_{wm} = \frac{(1 - \phi_p)a_{wm}}{(1 - \phi_p)a_{wm} + W_H}, \quad x_{mm} = \frac{a_{mm}}{a_{mm} + a_{ms}} \quad (\text{A11})$$

$$\alpha = 1.091, \quad \beta = 0.246$$

where,  $x_{wm}$  and  $x_{mm}$  = weight fractions of MMA in the aqueous phase and monomer droplets, respectively,  $W_H$  = weight of water in the latex (g/dm<sup>3</sup>-lx).

The empirical relationships proposed by Nomura et al.<sup>34</sup> for the monomer partitions between two oil phases (polymer particles and monomer droplets) are slightly modified as follows,

$$\frac{1}{a_{pm}} = \delta_m + \frac{\lambda_m}{x_{mm}} \quad (\text{A12})$$

$$\frac{1}{a_{ps}} = \delta_s + \frac{\lambda_s}{x_{ms}} \quad (\text{A13})$$

From the correlations by Nomura et al. at 323 K,  $\delta_m = -3.62(10^{-4})$ ,  $\lambda_m = 1.81(10^{-3})$ ,  $\delta_s = 4.48(10^{-4})$ ,  $\lambda_s = 1.29(10^{-3})$ .  $x_{ms}$  = weight fraction of styrene in monomer droplets defined as similar to  $x_{mm}$  in eq. (A11). It was assumed that the partition of MMA between the polymer particles and the aqueous phase was expressed by the following relationship after the monomer droplets disappeared.

$$\frac{M_{Hm}}{M_{pm}} = \left( \frac{M_{Hm}}{M_{pm}} \right)_c = \omega \quad (\text{A14})$$

where, suffix  $c$  corresponds to the time when monomer droplets are consumed.

### Initial Conditions

$$w = \varepsilon \quad w_m = \varepsilon z_{wm0} \quad (\text{A15})$$

For numerical calculations, a very small value,  $\varepsilon$ , was assigned to  $w$ .  $z_{wm0}$  = the weight fraction of MMA in the feed comonomer.  $\varepsilon$  was set as  $10^{-5}$  (g/dm<sup>3</sup>-lx) for all iterations.

### Calculation of Monomer Partition

#### Monomer Droplets Are Present

Introduce the following variables.

$$A_x = \phi_p a_{pm}, \quad A_y = (1 - \phi_p) a_{mm}, \quad A_z = (1 - \phi_p) a_{wm}$$

$$m = \frac{a_{ms}}{a_{mm}}, \quad p = \frac{a_{ps}}{a_{pm}} = \frac{\delta_m + (m + 1)\lambda_m}{\delta_s + \frac{(m + 1)\lambda_s}{m}} \quad (\text{A16})$$

Equations (A5)–(A6) can be written by these new variables as follows,

$$A_x + A_y + A_z = w_{m0} - w_m = a_m \quad (\text{A17})$$

$$pA_x + mA_y = w_{s0} - w_s = a_s \quad (\text{A18})$$

$a_m$  and  $a_s$  are equal to the weights of MMA and styrene monomer remaining unreacted (g/dm<sup>3</sup>-lx). Assuming that  $W_H \gg (1 - \phi_p)a_{wm}$ , we obtain,

$$A_z = \frac{x_{wm}}{1 - x_{wm}} W_H \quad x_{wm} = 10^{-[\alpha + \beta(m+1)]} \quad (\text{A19})$$

$A_x$  and  $A_y$  are given as the functions of  $p$  and  $m$ .

$$A_x = \frac{a_s - ma_m + mA_z}{p - m} \quad (\text{A20})$$

$$A_y = \frac{a_s - pa_m + pA_z}{m - p} \quad (\text{A21})$$

$\phi_p$  is given from eq. (A8) as follows,

$$\phi_p = \frac{w}{\rho_p} + V_m(M_{pm} + M_{ps})\phi_p = \frac{w}{\rho_p} + \frac{(1+p)}{\rho_m} \left( \frac{a_s - ma_m + mA_z}{p-m} \right) \quad (\text{A22})$$

and also obtained independently from the following relationship.

$$\phi_p = \frac{A_x}{a_{pm}} = [\delta_m + \lambda_m(m+1)] \left( \frac{a_s - ma_m + mA_z}{p-m} \right) \quad (\text{A23})$$

where,  $\rho_m$  = density of two monomers (approximately equal) ( $\text{g/dm}^3$ ). Combining two solutions for  $\phi_p$ , we obtain,

$$f(m) = \frac{w}{\rho_p} (p-m) + (a_s - ma_m + mA_z) \times \left[ \frac{(1+p)}{\rho_m} - \delta_m - \lambda_m(m+1) \right] = 0 \quad (\text{A24})$$

Notice that  $A_z$  and  $p$  are functions of  $m$ , and eq. (A24) can be solved for  $m$ .

Once  $m$  is solved for given value of  $w$ , all the concentrations of monomers (in polymer particles, in monomer droplets, and in aqueous phase) can be determined, and the average compositions of MMA (instantaneous and cumulative) are given. The Newton-Raphson method was successfully employed for numerical iterations.

### Monomer Droplets Are Consumed

$a_{mm}$  and  $a_{ms}$  disappear from eqs. (A5)–(A6). Derivation procedure is simplified, and eventually, the following quadratic equation is derived for  $p$ .

$$C_2 p^2 + C_1 p + C_0 = 0$$

$$C_2 = \left( \frac{w}{\rho_p} + \frac{a_s}{\rho_m} \right) a_m$$

$$C_1 = \left[ \frac{w}{\rho_p} (1-\omega) + \omega + \frac{a_m}{\rho_m} - \frac{(1-\omega)a_s}{\rho_m} \right] a_s$$

$$C_0 = (1-\omega) \frac{a_s^2}{\rho_m} \quad (\text{A25})$$

To get a better fitness with the observed data, the partition coefficients in eq. (A10) and eqs. (A12)–(A13) were shifted slightly as follows.

$$\alpha = 1.037, \quad \beta = 0.234$$

$$\delta_m = -3.44(10^{-4}), \quad \lambda_m = 1.90(10^{-3}), \\ \delta_s = 4.26(10^{-4}), \quad \lambda_s = 1.23(10^{-3})$$

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