

Thermal Degradation Behavior of PMMA Synthesized by Emulsifier-Free Emulsion Polymerization with a $\text{Cu}^{2+}/\text{HSO}_3^-$ Redox System

Tso-Pei Chiu, Trong-Ming Don

Department of Chemical and Materials Engineering, Tamkang University, Taipei 25137, Taiwan

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ABSTRACT: In this study, poly(methyl methacrylate) (PMMA) latex was synthesized in an emulsifier-free emulsion polymerization at 60°C using a $\text{Cu}^{2+}/\text{HSO}_3^-$ redox initiator system with different concentrations of Cu^{2+} . The experimental results showed that the monomer conversion reached above 90% for all systems. Zeta potential was all negative due to the bonded bisulfite ion and the magnitude was greater than 30 mV, providing the stability of PMMA emulsion. The morphology of the latex observed by scanning electron microscope revealed a uniform particle size, and the average particle size increased from 181.9 to 234.2 nm as the Cu^{2+} ion concentration increased from 2.0 to 6.0 mM in 1M of MMA solution. Thermal degradation behavior of synthesized PMMA was studied by thermogravimetric analysis, in which a two-stage degradation behavior was observed. These two stages were found to be caused by the degradation of unsaturated end group

(PMMA-CR=CH₂) and saturated end group (PMMA-H), respectively. In addition, the higher the concentration of Cu^{2+} ion, the greater the proportion of PMMA-CR=CH₂ in the final product, and in turn rendering more weight loss in the first-stage degradation. The copper ion not only played a role in the redox initiation, but also acted as a chain transfer agent to terminate growing polymer chains, thus producing PMMA-CR=CH₂. The apparent activation energies of the first stage (E_{a1}) and second stage (E_{a2}) were calculated by Ozawa's and Boswell's method. The results showed that E_{a1} , representing the degradation of PMMA-CR=CH₂, was lower than E_{a2} for the degradation of PMMA-H. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 388–395, 2009

Key words: emulsion polymerization; redox initiator; poly(methyl methacrylate); apparent activity energy

INTRODUCTION

Poly(methyl methacrylate) (PMMA), a kind of common and important thermoplastic material, has been extensively applied in daily commodities due to its excellent properties such as brightness, transparency, rigidity, and ease in processing. Under the free radical polymerization, different termination routes result in different terminal groups in PMMA chains. For example, disproportionation would result in the formation of an equal number of two polymer molecules, one with a saturated end group (PMMA-H) and the other with an unsaturated end group (PMMA-CR=CH₂). Another termination reaction, namely, combination, would join two growing chains together to form a single polymer molecule and produces a "head-to-head" (h-h) linkage at the point of coupling (PMMA-hh). These PMMA chains with different terminal structures would degrade at different temperatures. The thermal degradation mechanism of PMMA has been investigated in

extensive studies.^{1–5} McNeil¹ investigated the thermal degradation of PMMA by thermal volatilization analysis. He pointed out that PMMA-CR=CH₂ chains would be present in the sample prepared by free-radical polymerization due to termination by disproportionation, but absent if the sample was prepared by anionic polymerization. In addition, PMMA-CR=CH₂ chains are less thermally stable than PMMA-H chains with saturated end groups. Moreover, Cacioli et al.² synthesized PMMA oligomers with different end structures. They found that PMMA-hh were the least thermally stable, degrading at a temperature around 190°C, and PMMA-CR=CH₂ chains degraded at 255°C. Those PMMA-H chains are relatively stable, degrading at temperatures in excess of 300°C. Further, Kashiwagi et al.³ deliberately prepared all PMMA-hh, PMMA-CR=CH₂, and PMMA-H chains under a free-radical polymerization using azobis(isobutyronitrile), AIBN, as initiator and various chain transfer agents used to control the amounts of various chains. They found that the degradation temperatures of PMMA-hh, PMMA-CR=CH₂, and PMMA-H are about 160, 270, and 360°C, respectively, at a heating rate of 2°C/min. The terminal structures of PMMA chains

Correspondence to: T.-M. Don (tmdon@mail.tku.edu.tw).

TABLE I
Basic Experimental Conditions for the Synthesis of PMMA Latexes Initiated by $\text{Cu}^{2+}/\text{HSO}_3^-$ Redox System

Sample	MMA (M)	NaHSO_3 (mM)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (mM)	Temperature ($^\circ\text{C}$)
S5C1	1	10	2.0	60
S5C2	1	10	4.0	60
S5C3	1	10	6.0	60

were verified by nuclear magnetic resonance technique,⁴ in which quantitative analysis of PMMA chains with different terminal structures can be carried out. Later, Manning and coworkers^{5–8} carried out numerous investigations on the thermal degradation of PMMA and proposed degradation mechanism for each type of chains with different terminal structures.

Emulsifier-free emulsion polymerization has been developed as a process for producing latex particles with uniform size. Extensive works have been reported in the literature for kinetics and mechanism of polymerization.⁶ However, reports on complex redox systems containing copper compounds used as the initiator are limited in emulsifier-free emulsion polymerization.^{7–10} Sahoo and Mohapatra⁷ investigated the catalytic effect of the bivalent transition metal–EDTA complex with ammonium persulfate as the initiator to polymerize MMA by emulsifier-free emulsion polymerization, in which the Cu^{2+} -EDTA/ammonium persulfate system had the maximum rate of polymerization. In this research, $\text{Cu}^{2+}/\text{HSO}_3^-$ redox system was chosen as the initiator for MMA emulsion polymerization without using the emulsifier. After polymerization, thermal degradation behavior of PMMA was investigated. In addition, particle size, zeta potential, and glass transition temperature of latex products polymerized under different concentrations of Cu^{2+} ion were also measured.

EXPERIMENTAL

Materials

Monomer, methyl methacrylate (MMA, 99% pure), was purchased from Acros Organics and distilled under reduced pressure before polymerization. The redox initiator system, cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and sodium bisulfite (NaHSO_3) as well as other chemicals were at least analytical grade. For comparison, a commercial PMMA (PMMA-C, Acryrex[®] CM-211) was purchased from Chi Mei Corporation. Deionized water was distilled before use.

Synthesis of PMMA

Polymerization was carried out in a batch reactor fitted with a magnet stirrer, a condenser, and nitrogen

inlet using a Personal Organic Synthesizer (EYELA Corp., PPS-5510). A specific amount of MMA monomer was introduced into the batch reactor with water at 60°C and stirred under a nitrogen atmosphere for 30 min at a stirring rate of 300 rpm. Cupric sulfate and sodium bisulfite with fixed molar ratios were dissolved in a suitable amount of water. By adding prepared initiator solution into the reactor, the reaction was started and allowed to proceed at 60°C for 2 h. Basic experimental conditions are listed in Table I.

After reaction, 10 mL of the latex was removed from the reactor. It was poured into an ice-bathed glass vial with an equivalent amount of methanol containing 1% hydroquinone as the inhibitor, to precipitate out polymer latex. After three times of repeated centrifugation and washing with methanol:water (1 : 1), the final product was dried in a vacuum oven at 40°C until a constant weight was reached. The monomer conversion (X , %) was calculated by eq. (1)

$$X = \frac{W_2}{W_1 \times M_0\%} \times 100 \quad (1)$$

where W_1 is the weight of latex solution taken from reactor; W_2 , the weight of dry polymer; and $M_0\%$, the weight percentage of monomer initially in the reaction mixture.

Particle Size and Zeta Potential

Particle size was measured by a light scattering method (Malvern Zetamaster). At the end of the reaction, an appropriate amount of latex solution was added to a 1% hydroquinone solution, and it was then diluted by adding deionized water until the desired level of turbidity was obtained. Data reports on the particle diameter were an average of 10 measurements. Apparent morphology of latex particles was obtained by field emission scanning electron microscope (FESEM, Leo 1530). Diluted latex sample was dropped onto a glass slide surface and dried. It was further dried in vacuum at room temperature. Sample was coated with a thin gold before SEM observation. Zeta potential was also measured by Malvern Zetamaster. The diluted latex solution was injected into a quartz cell for the

TABLE II
Conversion, Average Particle Size, and Zeta Potential of PMMA Latex Polymerized With Different Cu²⁺ Concentrations After 2 h

Sample	Conversion (%)	\bar{D}_p^a (nm)	PDI ^a	\bar{D}_p^b (nm)	Zeta Potential (mV)
S5C1	90.3	200.8	0.005	181.9	-41.4
S5C2	90.6	234.7	0.034	214.6	-38.6
S5C3	92.6	271.2	0.094	234.2	-34.4

^a Measured by light scattering.

^b The average of 50 particles measured from SEM observation.

measurement of the surface charge of the particles, and data reports on zeta potential were an average of five measurements.

Molar Mass

Molecular weight and molecular weight distribution of polymers were obtained by gel permeation chromatography (GPC, Waters 1515 Isocratic HPLC Pump), equipped with a refractive index detector (Waters 2414 RI Detector), and a mixed bed of polystyrene gel column (AM GPC Gel). The temperature of the column was maintained at 40°C. THF was used as the eluent and the flow rate was set at 1.0 mL/min. GPC measurements were carried out in duplicate. All the molar masses were reported on the basis of polystyrene standards.

Thermal Properties

Thermograms of samples were obtained by a differential scanning calorimeter (TA 2920 from TA Instrument) with a heating rate of 10°C/min from 30 to 220°C. The glass-transition temperature (T_g) was determined by a half-height method from the second-run curve. Thermogravimetric analysis (TGA) with a Hi-Res TGA 2950 from TA Instrument was used to observe thermal degradation behavior and the weight loss of samples. Approximately 10 mg of sample was placed in a platinum pan and heated from 50 to 600°C under a nitrogen atmosphere at different heating rates of 5, 10, 15, and 20°C/min. Ozawa's method¹¹ with eq. (2) was used to calculate activation energies of thermal degradation

$$\log \beta = C_o - \frac{0.4567E}{RT} \quad (2)$$

In eq. (2), β is the heating rate, C_o is the constant for Ozawa's method, R is the gas constant, and E is the apparent activation energy. The plots of $\log \beta$ versus the reciprocal absolute temperature for a given value of fractional residual weight must give a straight line, and the slope of this gives the activation energy. For comparison, Boswell's method¹² was

also used to estimate activation energies of thermal degradation by eq. (3)

$$\ln \left(\frac{\beta}{T} \right) = C_B - \frac{E}{RT} \quad (3)$$

where C_B is the constant for Boswell's method and for values of other symbols refer to eq. (2).

RESULTS AND DISCUSSION

Structures and Glass Transition Temperatures of PMMA Lattices

In this study, Cu²⁺/HSO₃⁻ redox system was chosen as the initiator for MMA emulsion polymerization without using emulsifier, whose recipes are shown in Table I. During the reaction, the solution became milky and a stable latex solution was observed. Previously, we have studied the reaction mechanism and chemical structures of the present system.¹³ The results showed that the Cu²⁺ ion was complexed with two bisulfite ions and caused the homolysis of hydroxyl group in bisulfite to produce anionic sulfite radical and hydrogen. The hydrogen was then oxidized to proton by Cu²⁺ ion. The anionic sulfite radical thus initiated free-radical polymerization. After reaction for 2 h, all monomer conversions reached above 90% in three reaction systems, and the conversion value only increased slightly with increasing the concentration of cupric sulfate as shown in Table II.

Table II also shows zeta potential of latex particles with different Cu²⁺ ion concentrations, in which the zeta potential was negative for all three systems. The magnitude was greater than 30 mV and could reach 40 mV for the sample S5C1. It indicated that PMMA latex particles were very stable in the solution. The negative charge of PMMA latex came from SO₃⁻ radical, generated from the redox reaction of Cu²⁺/HSO₃⁻ (Cu²⁺ + HSO₃⁻ → Cu⁺ + ·SO₃⁻ + H⁺). In addition, the increase of zeta potential from -41.4 to -34.4 mV with increasing Cu²⁺ ion concentration was thought to be due to the adsorption of positive copper cation, including both Cu²⁺ and Cu⁺, on particle surface as well as the increasing particle size.

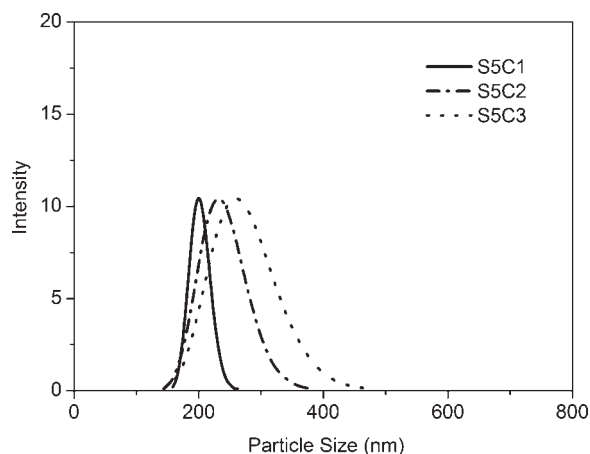


Figure 1 Particle size distributions of the PMMA lattices polymerized with different Cu^{2+} concentrations after 2 h at 60°C . S5C1 ($[\text{Cu}^{2+}] = 2 \text{ mM}$), S5C2 ($[\text{Cu}^{2+}] = 4 \text{ mM}$), S5C3 ($[\text{Cu}^{2+}] = 6 \text{ mM}$).

Final particle size after 2 h of polymerization was also determined from light scattering and the results are shown in Figure 1. Particle size was in the range between 200 and 270 nm and gradually increased as cupric sulfate concentration was increased. It has been pointed out by Tanrisever et al.⁶ that the ionic

strength of the aqueous phase has a dominant effect on particle diameter in which the particle size increases with increasing the ionic strength in solution. In this study, increasing the concentration of cupric sulfate in initiator increased the ionic strength of aqueous phase, thus causing an increase of particle size. Moreover, it has to be pointed out that S5C1 had a very narrow particle size distribution with PDI value only at 0.005. Figure 2 shows SEM pictures of latex particles from three reaction systems with different Cu^{2+} concentrations, which illustrated uniform particle size distribution and had the same trends as those measured by light scattering. Particle size values measured from SEM pictures are also listed in Table II.

Differential scanning calorimeter curves for PMMA polymerized by the $\text{Cu}^{2+}/\text{HSO}_3^-$ redox system with different initiator concentrations are shown in Figure 3. They have almost the same T_g , $124\text{--}126^\circ\text{C}$, regardless of the Cu^{2+} concentration.

Thermal Degradation Behavior

First, we needed to know the effect of Cu^{2+} ion on the thermal degradation of PMMA beforehand.

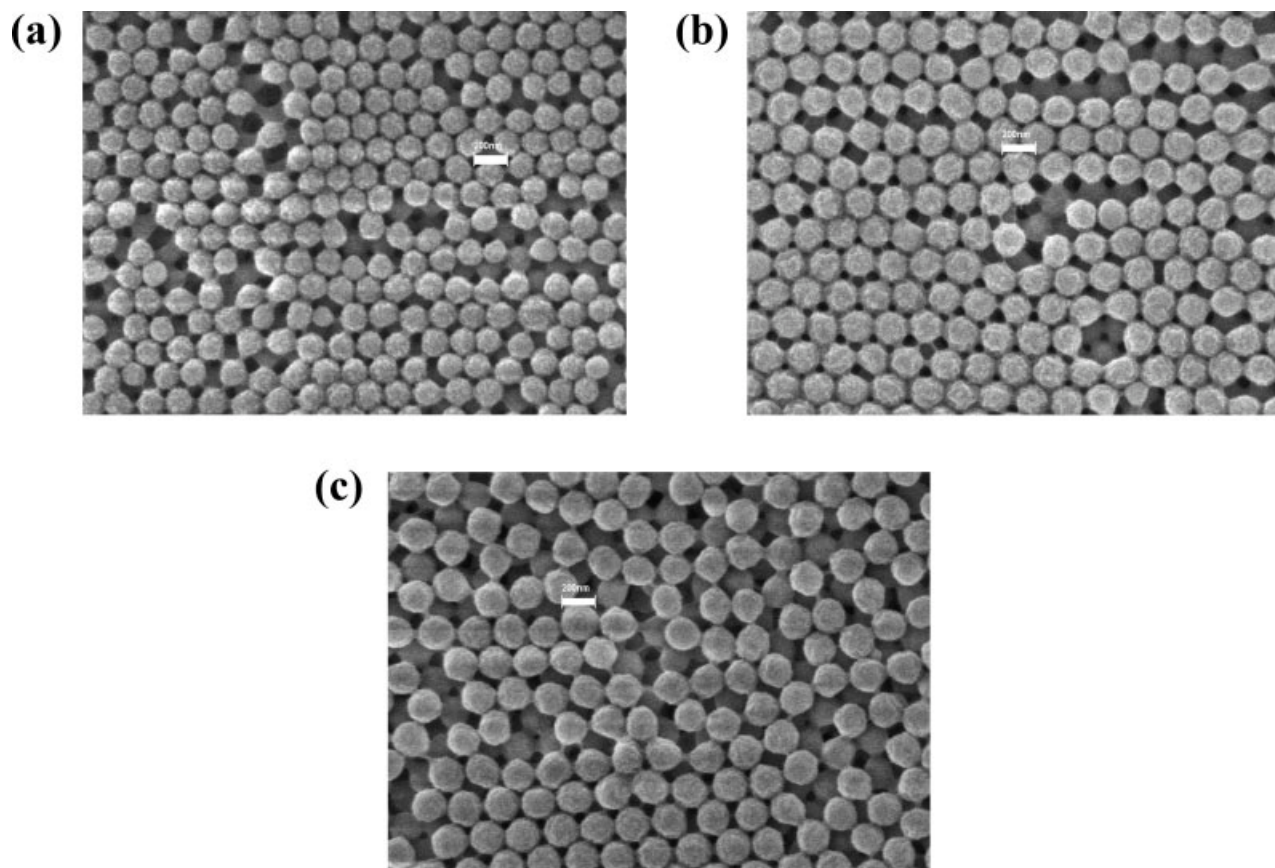


Figure 2 SEM photographs of the PMMA latex particles polymerized with different Cu^{2+} concentrations (a) S5C1 ($[\text{Cu}^{2+}] = 2 \text{ mM}$), (b) S5C2 ($[\text{Cu}^{2+}] = 4 \text{ mM}$), (c) S5C3 ($[\text{Cu}^{2+}] = 6 \text{ mM}$). The scale bar is 200 nm.

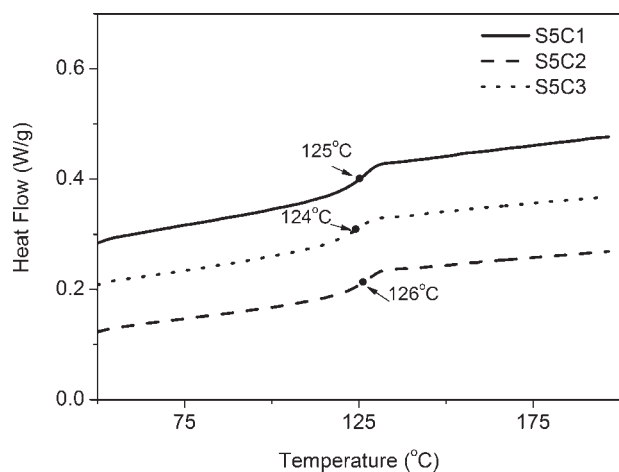


Figure 3 DSC curves for PMMA latex particles polymerized with different Cu^{2+} concentrations. S5C1 ($[\text{Cu}^{2+}] = 2$ mM), S5C2 ($[\text{Cu}^{2+}] = 4$ mM), S5C3 ($[\text{Cu}^{2+}] = 6$ mM).

Chandrasiri et al.¹⁴ investigated the effect of transition metal chlorides on the thermal degradation of PMMA and found an additional degradation stage beginning from 220 to 290°C for a physical blend of PMMA with CuCl_2 . They explained that the effect on the degradation of PMMA blends is due to coordination occurring between the transition metal ion and the carbonyl oxygens of PMMA. For comparison, Figure 4 shows thermal degradation behavior for a commercial PMMA (PMMA-C), a PMMA polymerized using potassium persulfate (termed as PMMA-KPS) as initiator and S5C3 sample. In the case of the commercial PMMA, only one stage of thermal degradation starting from 300 to 410°C was observed with a maximum-rate degradation temperature at 373°C. Kashiwagi et al.³ pointed out that degradation of PMMA chains with saturated end groups (PMMA-H) occurred at this stage and was caused by random scission within the polymer chain. Thus, this commercial PMMA has chains mostly with saturated ends. For the PMMA-KPS polymer, two stages of thermal degradation were observed: one was in the temperature range from 270 to 320°C, and the other in the range 320 to 430°C. The degradation at the first stage was caused by the end-initiated depolymerization from the unsaturated vinyl ends (PMMA-CR=CH₂) formed by disproportionation. The second stage was caused by the degradation of PMMA-H. For the S5C3 sample, a two-stage thermal degradation behavior was also observed, which would be further discussed in the following paragraph. Yet, the catalyzed effect by Cu^{2+} ion on the thermal degradation of S5C3 sample was not observed, which would occur between 220 and 270°C.¹⁴ This is explained by the scarcity of the Cu^{2+} ion added into the system. The weight ratio of

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to MMA monomer in the feed for S5C3 was only 1.5%, and at the end of the reaction, most of residual Cu^{2+} ion in latex solution was further removed by the washing procedure with a large amount of methanol:water (1 : 1) solution. It is known that the processing temperature of PMMA is commonly controlled between 200 and 250°C, and the prepared S5C3 sample thus could be processed without the occurrence of thermal degradation.

Figure 5 shows thermal gravimetric curves of PMMA latex with different Cu^{2+} ion concentrations at a heating rate of 10°C/min. It can be seen that all synthesized PMMA lattices have two stages of thermal degradation, namely, the first stage is in the temperature range from 260 to 320°C due to the degradation of PMMA-CR=CH₂, and the second stage in the range 320 to 450°C attributed to the PMMA-H chains. Obviously, as explained previously, the catalytic degradation of PMMA by Cu^{2+} ion was not observed for all systems. However, increasing the concentration of Cu^{2+} ion in initiator system, the weight loss was increased in the first stage, i.e.,

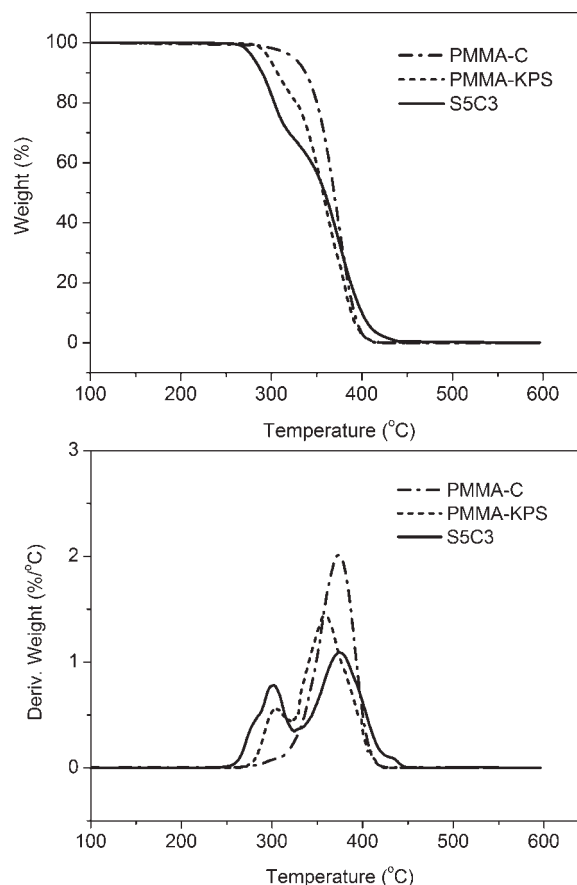


Figure 4 TGA and DTGA curves of a commercial PMMA (PMMA-C), PMMA-KPS, and S5C3 sample. The heating rate was 10°C/min.

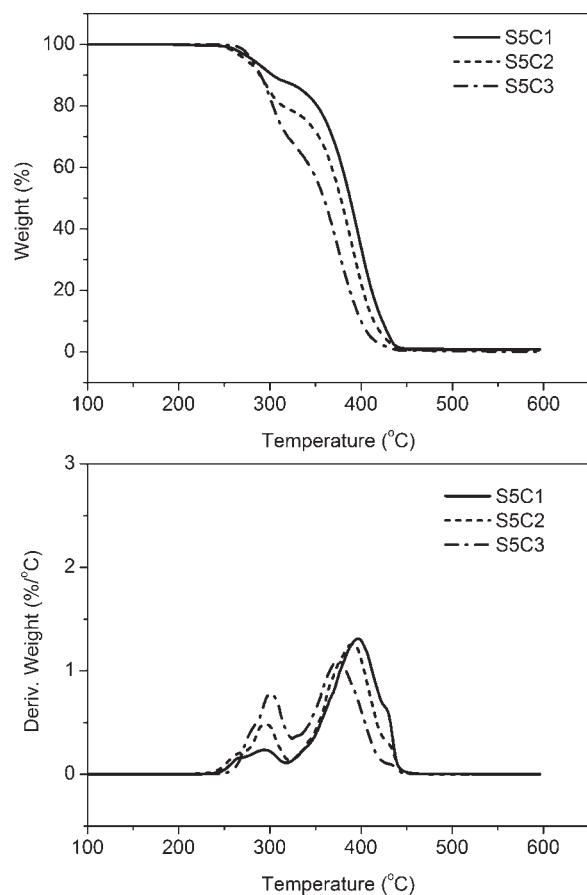


Figure 5 TGA and DTGA curves for PMMA latex particles polymerized with different Cu^{2+} concentrations at a heating rate of $10^\circ\text{C}/\text{min}$. S5C1 ($[\text{Cu}^{2+}] = 2 \text{ mM}$), S5C2 ($[\text{Cu}^{2+}] = 4 \text{ mM}$), S5C3 ($[\text{Cu}^{2+}] = 6 \text{ mM}$).

increasing the Cu^{2+} ion concentration increased the proportion of PMMA- $\text{CR}=\text{CH}_2$ during polymerization. The same behavior was observed for other heating rates as shown in Table III, which lists all the calculated data from TGA curves including first maximum-rate degradation temperature (T_{d1}), second maximum-rate degradation temperature (T_{d2}),

and first stage weight loss. Therefore, Cu^{2+} is responsible for the increase of PMMA- $\text{CR}=\text{CH}_2$ proportion during polymerization. Rasti and Scott¹⁵ indicated that the presence of Cu^{2+} ion could scavenge free radical such as 5-carboxypentyl radical. On the basis of their results, a reaction scheme is proposed to describe the formation of double bond at the end of the polymer chains as shown in Figure 6.

In other words, it seems that Cu^{2+} ion not only played a role in initiator system for polymerization, but also acted as a chain transfer agent to terminate growing polymer chains. As S5C3 had the highest concentration of Cu^{2+} ion, it produced the most amount of unsaturated vinyl ends (PMMA- $\text{CR}=\text{CH}_2$) indicated by the degradation extent (cf. Table III). Moreover, the first maximum-rate degradation temperature (T_{d1}) shifted toward higher temperature and the second maximum-rate degradation temperature (T_{d2}) decreased toward lower temperature with increasing Cu^{2+} concentration, as shown in Table III. This inversion effect has been observed by McNeill's.¹ He synthesized PMMA with different molecular weights using AIBN as the initiator and found that the sample having higher molecular weight would have higher degradation temperature in the first stage yet lower degradation temperature in the second-stage degradation. This phenomenon was also observed and discussed by Grant and Bywater¹⁶ and MacCallum¹⁷ in connection with the results of a number of isothermal degradations. Therefore, the molecular weight of PMMA was measured and the results are shown in Table IV. Indeed, the inversion effect caused by the molecular weight was clearly observed where the highest-molecular-weight S5C3 had the highest T_{d1} and the lowest T_{d2} .

To estimate the apparent activation energy of thermal degradation, Ozawa's method¹¹ was used, which required thermal degradation curves of PMMA at different heating rates. Figure 7 shows

TABLE III
Thermal Degradation Properties of PMMA Latex Polymerized With Different Cu^{2+} Concentrations

Sample	Heating Rate ($^\circ\text{C}/\text{min}$)	T_{d1} ($^\circ\text{C}$)	T_{d2} ($^\circ\text{C}$)	First stage weight loss (%)
S5C1	5	274.8	380.0	18.0
S5C2	5	284.4	371.8	22.5
S5C3	5	290.7	355.6	36.1
S5C1	10	296.3	396.3	13.8
S5C2	10	301.2	391.1	22.1
S5C3	10	307.0	375.1	33.7
S5C1	15	297.0	399.1	20.3
S5C2	15	305.4	392.3	21.7
S5C3	15	309.2	381.0	29.1
S5C1	20	304.8	406.5	17.7
S5C2	20	314.5	404.6	23.3
S5C3	20	313.9	388.2	28.5

T_{d1} and T_{d2} are maximum-rate degradation temperatures at first and second stage, respectively.

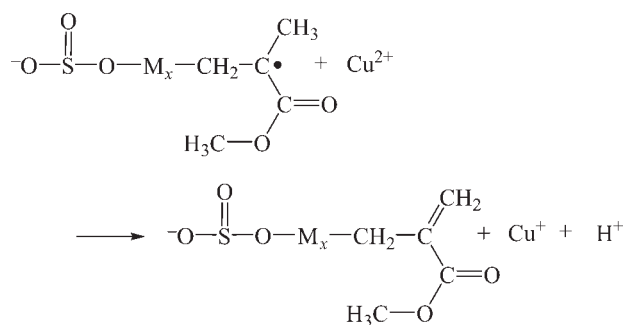


Figure 6 Chain transfer reaction of growing polymer chain by copper ion.

thermal degradation curves of S5C3 sample at different heating rates (β), and the Ozawa's plots, i.e., logarithm of heating rates ($\log \beta$) versus reciprocal of temperature ($10^3/T$) are shown in Figure 8. A good linearity of these lines is observed. Hence, the apparent activation energies can be determined from the slopes of these lines. However, two stages of thermal degradations were observed, and thus two apparent activation energies were determined as E_{a1} and E_{a2} , respectively. The calculated activation energies for thermal degradation of PMMA latex with different Cu^{2+} ion concentrations in initiator system are shown in Table V. The apparent activation energies of the first-stage degradation, E_{a1} , corresponding to the degradation of PMMA-CR=CH₂, were in the range of 124 to 135 kJ/mol and slightly decreased with increasing the Cu^{2+} ion concentration. Furthermore, the apparent activation energy of the second-stage degradation, E_{a2} , corresponding to the degradation of PMMA-H, decreased from 213 to 156 kJ/mol with increasing the Cu^{2+} concentration from 2.0 to 6.0 mM. E_{a1} values are much smaller than E_{a2} values because the unsaturated bond at the chain end is relatively a scission of weak linkage than that of saturated end group. Accordingly, PMMA-CR=CH₂ needs less energy to be attacked at the end group and once it starts, polymer chains are degraded by unzipping. Moreover, the pre-exponential factors for both stages of degradation were also calculated as shown in Table V. In the case of S5C1, the pre-exponential factors are 1.98×10^{11} and 4.26×10^{16} (1/min) for the first-stage and second-stage degradation, respectively. In addition, it was found that a

TABLE IV
Weight-Average (M_w) and Number-Average (M_n)
Molecular Weight of PMMA Latex Polymerized With
Different Cu^{2+} Initiator Concentrations After 2 h

Sample	M_n	M_w	PDI
S5C1	49,000	105,000	2.14
S5C2	69,000	170,000	2.46
S5C3	85,000	222,000	2.61

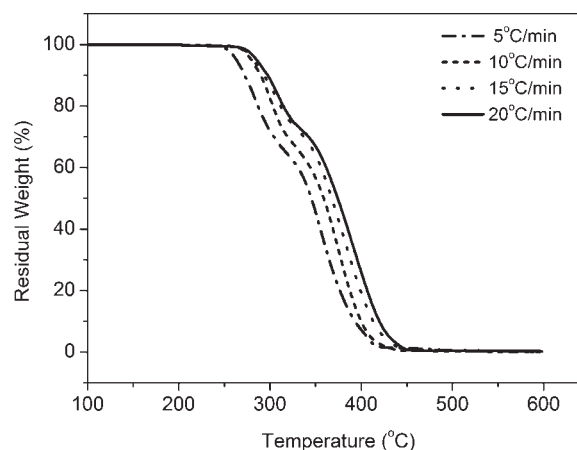


Figure 7 TGA curves for S5C3 sample at different heating rates.

first-order reaction is most suitable for the fitting of experimental data. For comparison, the apparent activation energy was also estimated by Boswell's method.¹² The linear plots are shown in Figure 9. The estimated results are similar to those obtained from Ozawa's method as shown in Table V. According to the literature,¹⁸ the mean activation energies of PMMA polymerized by using AIBN initiator in the first stage and second stage are 148 and 220 kJ/mol, respectively, estimated also by Ozawa's method. It can be seen that both activation energies for the present samples using $\text{Cu}^{2+}/\text{HSO}_3^-$ as initiator are lower than the reported values using other initiator systems.

CONCLUSIONS

In this study, PMMA was polymerized in an emulsifier-free emulsion polymerization at 60°C by using $\text{Cu}^{2+}/\text{HSO}_3^-$ redox initiator system under different

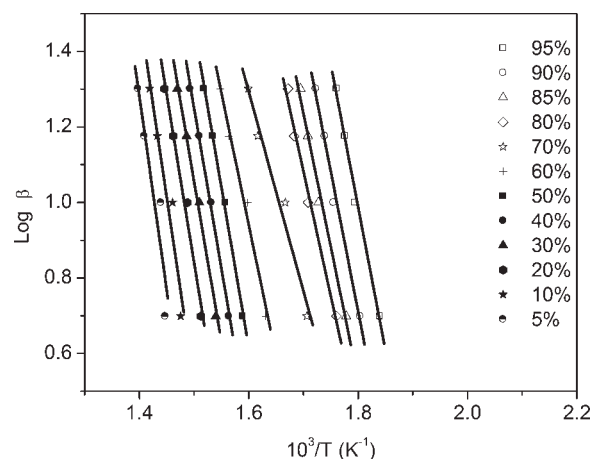


Figure 8 Ozawa's plot for the degradation of S5C3 from TGA curves with different heating rates: 5, 10, 15, and 20°C/min.

TABLE V
Activation Energies for the Thermal Degradation of PMMA Latex Polymerized With Different Cu^{2+} Concentrations

Sample	Ozawa's Method				Boswell's Method	
	E_{a1} (kJ/mol)	A_1 (min^{-1})	E_{a2} (kJ/mol)	A_2 (min^{-1})	E_{a1} (kJ/mol)	E_{a2} (kJ/mol)
S5C1	135 ± 11	1.98×10^{11}	213 ± 8	4.26×10^{16}	136 ± 12	219 ± 9
S5C2	129 ± 23	7.28×10^{12}	174 ± 12	1.12×10^{14}	130 ± 25	177 ± 12
S5C3	124 ± 17	1.45×10^{11}	156 ± 4	2.53×10^{12}	125 ± 18	159 ± 4

concentrations of Cu^{2+} , and the effect of Cu^{2+} ion on thermal degradation of PMMA was investigated. Very stable PMMA emulsions were obtained because of the large negative surface charge of latex particles due to the bonded anionic bisulfite (SO_3^-). A very uniform particle size distribution could be obtained for sample S5C1 with PDI value only 0.005. The average particle size was in the range of 200–271 nm and it increased with increasing Cu^{2+} concentration. The TGA curves of PMMA latex revealed two stages of degradation, which were caused by the degradation of PMMA chains with unsaturated end group (PMMA-CR=CH₂) and with saturated end group (PMMA-H), respectively. Increasing the concentration of Cu^{2+} ion in the initiator system increased the weight loss on the first-stage degradation. That is, the higher the concentration of Cu^{2+} ,

the more the PMMA-CR=CH₂ chains were produced. Therefore, Cu^{2+} not only played a role in the initiation reaction, but also acted as a chain transfer agent to terminate growing polymer chains thus producing PMMA-CR=CH₂. The apparent activation energies of two degradation stages were estimated by the Ozawa and Boswell methods. Both activation energies of two degradation stages were lower than the reported values using other initiator systems, in which S5C3 having the highest concentration of Cu^{2+} had the lowest activation energies.

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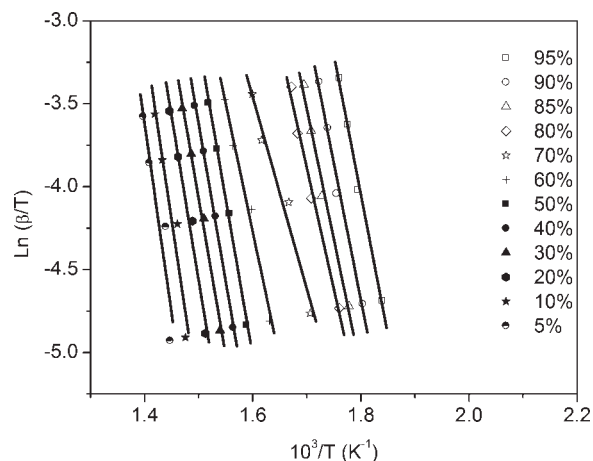


Figure 9 Boswell's plot for the degradation of S5C3 sample from TGA curves with different heating rates: 5, 10, 15, and 20°C/min.