

Synthesis and Characterization of Poly(methyl methacrylate) Nanoparticles by Emulsifier-Free Emulsion Polymerization with a Redox-Initiated System

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ABSTRACT: In this study, the emulsifier-free emulsion polymerization of methyl methacrylate (MMA) was initiated directly by a $\text{Cu}^{2+}/\text{HSO}_3^-$ redox system. Latex particles with negative charge due to the bonded anionic sulfite ion were successfully synthesized after 2 h of reaction at 40–60°C. Scanning electron microscopy pictures showed a uniform particle size distribution, and the average size decreased from 223 to 165 nm with increasing reaction temperature from 40 to 60°C. The initiation step in the polymerization mechanism was proven to be a redox reaction, in which Cu^{2+} oxidized the bisulfite ion to produce an anionic sulfite radical and proton. The produced anionic sulfite radical then initiated the polymerization of MMA. Moreover, Cu^{2+} not only served as one component in the redox initiator system but also as a chain-transfer agent

that terminated growing polymer chains to produce chains with unsaturated end groups [poly(methyl methacrylate) (PMMA)– $\text{CH}=\text{CH}_2$]. For this system, about 17% PMMA– $\text{CH}=\text{CH}_2$ was produced. The tacticities of the PMMA latex prepared at 40–60°C were almost the same, about 62–64% syndiotactic, 33–35% heterotactic, and 3% isotactic. These PMMA latexes had almost the same glass-transition temperature, 125–127°C, regardless of the reaction temperatures, and their weight-average molecular weights were in the range between 254,000 and 315,000. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3622–3630, 2008

Key words: emulsion polymerization; initiator; nanoparticles

INTRODUCTION

In recent years, emulsifier-free emulsion polymerization has been developed as a process for producing latex particles with uniform size. Extensive studies have been reported in the literature on the kinetics and mechanism of polymerization.¹ In such a polymerization, the stability of the latex depends mostly on the ionizable initiator. Many mechanisms of nucleation and particle growth have been proposed in emulsion polymerization without an emulsifier, for example, micellar-like nucleation^{2–6} and homogeneous nucleation,^{7–12} whose distinction is based on the aqueous solubility of the monomer.

Typically, the principal ingredients for an emulsifier-free system include deionized water, a water-soluble initiator such as potassium persulfate, and monomers such as vinyl and acrylates. For example, methyl methacrylate (MMA) is polymerized in the aqueous phase by potassium persulfate, where oligomeric radicals with negative charges are generated and subsequently form micelles and monomer-swollen particles.³ However, reports on complex initiator

systems containing copper compounds in emulsion polymerization are limited.^{13–15} Sahoo and Mohapatra¹³ investigated the catalytic effect of various bivalent transition metal–ethylene diamine tetraacetic acid complex systems with ammonium persulfate (APS) as the initiator to polymerize MMA by emulsion polymerization, in which the transition metal acted as a catalyst to facilitate the homolysis of the –O–O– bond in APS. They found that a Cu^{2+} –ethylene diamine tetraacetic acid/APS system showed the maximum rate of polymerization (R_p). Lu et al.¹⁴ used a complex of polyvinylamine and Cu^{2+} for MMA polymerization. They proposed a complexation–hydrogen transfer mechanism in polyvinylamine– $\text{Cu}^{2+}/\text{Na}_2\text{SO}_3/\text{MMA}$ to explain the formation of primary radicals. They believed that Cu^{2+} acted as a catalyst in their system, instead of as an oxidant. The monomer conversion they achieved was about 65%. Moustafa et al.¹⁵ investigated the aqueous polymerization of MMA with sodium bisulfite (SBS) as an initiator with soluble copper salts as a catalyst. They indicated that the catalytic effect of copper sulfate was higher than that of copper chloride. Sadek et al.¹⁶ used a catalyst of copper phthalocyanine/bentonite (CuPC/bentonite) in the presence of SBS (NaHSO_3) as a cocatalyst for the bulk polymerization of MMA. They proposed a reaction path-

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way of the living free-radical polymerization of MMA initiated by CuPC/NaHSO₃. For this CuPC/bentonite/NaHSO₃ initiating system, they believed that Cu²⁺ was first reduced by HSO₃⁻ to Cu⁺, which then acted as a catalyst in the oxidation reaction of MMA to form an active radical center. Yang et al.¹⁷ used a complex of polypropylene-*graft*-polycarboxylate with Cu²⁺/Na₂SO₃ as an initiator for the polymerization of MMA. They also explained that primary radicals were formed by a complexation-hydrogen transfer mechanism. In the aforementioned articles, all of the authors believed the Cu²⁺ acted as a catalyst.

In this research, a Cu²⁺/HSO₃⁻ redox system was chosen as the initiator for the emulsion polymerization of MMA without an emulsifier. A reaction mechanism is proposed in which the initiated mechanism of the Cu²⁺/HSO₃⁻ was proven to be a redox system by ultraviolet-visible (UV-vis) spectrophotometry. In addition to the chain structure, the monomer conversion, particle size, ξ potential, molecular weight, and thermal properties of the latex products polymerized at different temperatures were measured.

EXPERIMENTAL

Materials

The monomer, MMA, and the inhibitor, hydroquinone (99% pure), were supplied from Showa Chemical Co. (Tokyo). The MMA monomer was distilled under reduced pressure before polymerization. The redox initiator system, cupric sulfate (CuSO₄·5 H₂O) and SBS (NaHSO₃), were purchased from Shimakyu Pure Chemicals (Osaka, Japan). Tetrahydrofuran from Tedia Chemical Co. (Fairfield, OH) was used as the elution solvent for the gel permeation chromatography (GPC) experiment. 2,9-Dimethyl-1,10-phenanthroline (neocuproine; 98%, Lancaster Synthesis, Ward Hill, MA) was used to form a colored complex with Cu⁺. The commercial poly(methyl methacrylate) (PMMA; Acryrex CM-211) was purchased from Chi Mei Corp. (Taiwan) and used without further purification. All other chemicals were at least analytical grade and were used without further purification. The deionized water used for this study was distilled before use.

Polymerization procedure

The emulsion polymerization was carried out in a 1-L, round-bottom, four-necked batch reactor fitted with a mechanical stirrer, a condenser, a nitrogen inlet, and a pipette outlet. The batch reactor was immersed in a thermostated water bath to maintain a constant temperature. An appropriate amount of

TABLE I
Basic Experimental Conditions for the Synthesis of the PMMA Latices Initiated by the Cu²⁺/HSO₃⁻ Redox System

Sample	MMA (M)	NaHSO ₃ (mM)	CuSO ₄ ·5H ₂ O (mM)	Temperature (°C)
BC40	1	10	2.0	40
BC50	1	10	2.0	50
BC60	1	10	2.0	60

water and MMA monomer were first introduced into the reactor and stirred under a nitrogen atmosphere for 30 min at a stirring rate of 300 rpm. A specific amount of NaHSO₃ and CuSO₄·5H₂O were dissolved in 50 mL of water as the initiator system. The polymerization was started by the addition of the initiator solution into the reactor. The reaction was allowed to proceed at a selected temperature for 2 h. The basic experimental conditions are listed in Table I.

During the reaction, latex was formed in the reactor, and 10 mL of the latex was removed from the reactor at a fixed time interval. It was added to an ice-bathed glass vial with an equivalent amount of methanol containing 1% hydroquinone as the inhibitor to precipitate out the polymer latex. The precipitation was further facilitated by the addition of saturated NaCl_{aqueous} to coagulate the latex particles. After repeated centrifugation, filtration, and washing with a methanol/water (1/1, v/v) solution, the final product was dried in a vacuum oven at 40°C until a constant weight was reached. The monomer conversion (X ; %) at different reaction times was calculated by the following equation:

$$X = \frac{W_2}{W_1 \times M_0\%} \times 100$$

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

Characterization

Particle size and ξ potential

The particle size was measured by a light-scattering method (Malvern Zetamaster, Worcestershire, UK). During the reaction, an appropriate amount of the latex was removed to a 1% hydroquinone solution. A diluted latex sample with a desired level of turbidity was obtained by the addition of deionized water. The reported particle size diameter was an average of 10 measurements.

After 2 h of reaction, a portion of the latex sample was diluted with deionized water to obtain a desired turbidity. It was then injected into a quartz cell for

measurement of the surface charge of the particles with the Malvern Zetamaster. The ζ potentials of latex particles in various aqueous solutions with different pH values were also measured. The reported ζ potential was an average of five measurements.

Structures and thermal properties

The structure and tacticity of the PMMA latex was analyzed with an $^1\text{H-NMR}$ spectrometer (Bruker, Rheinstetten, Germany 600 MHz) with CDCl_3 as a solvent. The tacticity of the PMMA latex was determined from the integration area ratios of the triad level of $\alpha\text{-CH}_3$.^{18–20} The molecular weights and molecular weight distributions of the polymers were obtained by GPC (Waters 1515 Isocratic high performance liquid chromatography pump, Milford, MA), equipped with a refractive-index detector (Waters 2414), and a mixed bed of polystyrene gel columns (AM GPC gel). The temperature of the columns was maintained at 40°C. Tetrahydrofuran was used as the elution solvent, and the flow rate was set at 1.0 mL/min. All of the molecular weights are reported on the basis of polystyrene standards.

The apparent morphology of the latex particles was obtained by field emission scanning electron microscopy (SEM; Leo 1530, (Oberkochen, Germany)). A diluted latex sample was dropped onto a glass slide surface and dried at room temperature. It was further dried *in vacuo* at room temperature. The sample was coated with a thin layer of gold before SEM observation.

Thermograms of the samples were obtained by differential scanning calorimetry (DSC; TA 2920, TA Instruments) at a heating rate of 10°C/min from 30 to 220°C. The glass-transition temperature was determined by a half-height method from the second-run curve. Thermogravimetric analysis (TGA; Hi-Res TGA 2950 from TA Instruments, New Castle, DE) was used to measure the weight loss of the samples at a heating rate of 10°C/min from 50 to 600°C under a nitrogen atmosphere. To determine the effect of residual copper ions on the thermal degradation behavior, a commercial PMMA was blended with an equivalent amount of cupric sulfate. The mixture was then removed for TGA to measure its weight loss under heating.

Detection of Cu^+ ion by UV-vis spectrophotometry

Neocuproine, a white powder, is only slightly soluble in cold water but is soluble in hot water, ethanol, amyl alcohol, benzene, and chloroform. Neocuproine can react with Cu^+ in the pH range 3–10 to form an orange water-insoluble complex that can be completely extracted by *n*-amyl alcohol, isoamyl

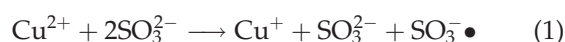
alcohol, 1-hexanol, or chloroform/ethanol under brief shaking.²¹ The colored complex is stable for several hours and exhibits an absorption maximum at 457 nm.

The method used by Fries and Getrost²¹ was slightly modified. An aqueous solution (20 mL) containing NaHSO_3 (250 mM) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (50 mM) was heated at 60°C for 30 min, and it was then removed to a funnel for separation. Immediately, 1 mL of 10% ascorbic acid solution, 2.5 mL of 40% sodium acetate solution, and 1 mL of neocuproine solution prepared by the dissolution of 0.1 g of neocuproine in 100 mL of absolute ethanol were added to the solution sequentially. After 1 min of reaction, 5.00 mL of chloroform was added to the solution to extract the colored complex. The organic phase was separated from the funnel and measured in a 1-cm cuvette cell at 457 nm against chloroform as the blank by a UV-vis spectrophotometer (UNICAM, Waltham, MA, UV500).

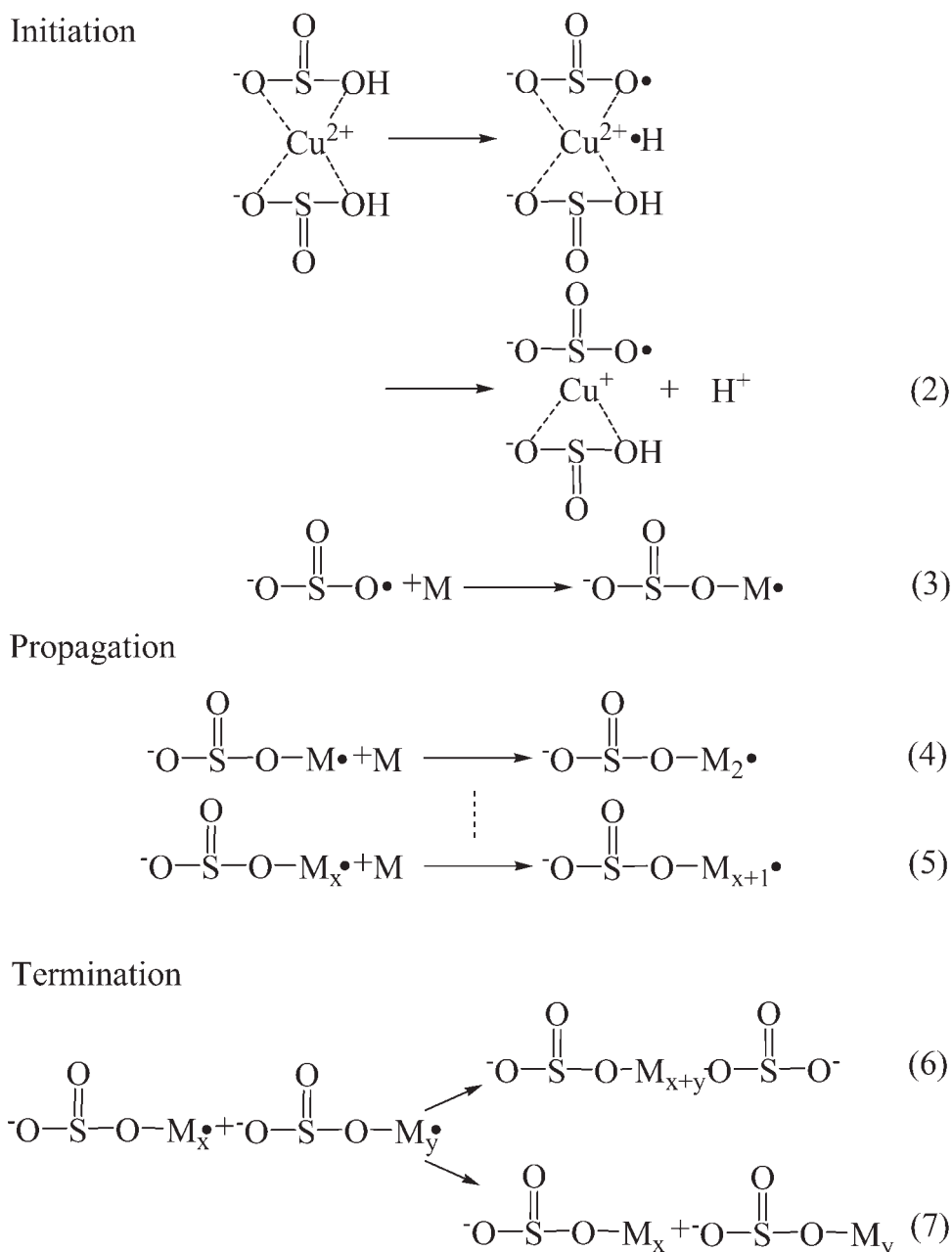
RESULTS AND DISCUSSION

Reaction mechanism and monomer conversion

The pH value of an aqueous solution of HSO_3^- was 3.75 at 60°C, and it maintained this value even after 2 h of heating at 60°C. However, with the addition of Cu^{2+} to HSO_3^- aqueous, the pH value decreased with time at 60°C. It decreased to 2.02 after 2 h. This indicated that the dissociation of HSO_3^- was facilitated by Cu^{2+} to produce a more acidic aqueous solution. For MMA polymerization, the addition of the $\text{Cu}^{2+}/\text{HSO}_3^-$ solution also resulted in a decrease in the pH value from 3.33 at the beginning to 2.86 after 2 h at 60°C. All emulsion polymerizations of the MMA monomer were carried out in a batch reactor. After 2 h of reaction, the PMMA latex particles were obtained. The reaction conditions are listed in Table I. Although Cu^{2+} has been used with sulfite ion (SO_3^{2-}) or persulfate ion ($\text{S}_2\text{O}_8^{2-}$) to initiate free-radical polymerization,^{13–17} it has generally been considered by these authors a catalyst to promote the homolysis of the initiator into two free radicals. However, in a study of the persulfate-bisulfite- Cu^{2+} initiated emulsion polymerization of vinyl chloride, Mork and Ugelstad²² believed that a redox reaction occurred between Cu^{2+} and SO_3^{2-} in which copper directly snatched an electron from the sulfite ion. The reaction is shown as follows.



However, it is thought that bisulfite ion (HSO_3^-) can be produced by the acid-base equilibrium from SO_3^{2-} with H_2O and probably also takes part in the initiation reaction. In this study, the $\text{Cu}^{2+}/\text{HSO}_3^-$ ini-



Scheme 1 Proposed reaction mechanism of MMA polymerization initiated by the $\text{Cu}^{2+}/\text{HSO}_3^-$ initiator system.

tiator system was directly used. We believed it was also a redox initiation system but with a different reaction route. The reaction mechanism for this system is proposed as follows. Copper ion was first complexed with two bisulfite ions and then induced the homolysis of the O–H bond. The copper ion then oxidized the hydrogen atom to a proton, thus decreasing the pH value. The produced anionic sulfite radical then initiated the polymerization reaction. The reaction mechanism is illustrated in Scheme 1.

The evidence of the reduction of Cu^{2+} to Cu^+ was provided with the neocuproine indicator, which forms an orange water-insoluble complex with any present Cu^+ ion. After extraction with chloroform,

the organic phase was scanned by a UV–vis spectrophotometer, as shown in Figure 1. The absorption maximum occurred at 457 nm, which corresponded exactly to the absorption of the colored complex. This proved the occurrence of the reduction of Cu^{2+} to Cu^+ , as shown in eq. (2) in Scheme 1. In addition, the ξ potential values of latex particles at different reaction temperatures were all found to be negative, as shown in Table II. The negative charge on the particle surface was provided by the anionic $\bullet\text{SO}_3^-$ radical from the redox reaction of $\text{Cu}^{2+}/\text{HSO}_3^-$. After the initiation reaction, the reaction mechanism followed traditional free-radical polymerization in the emulsion system.

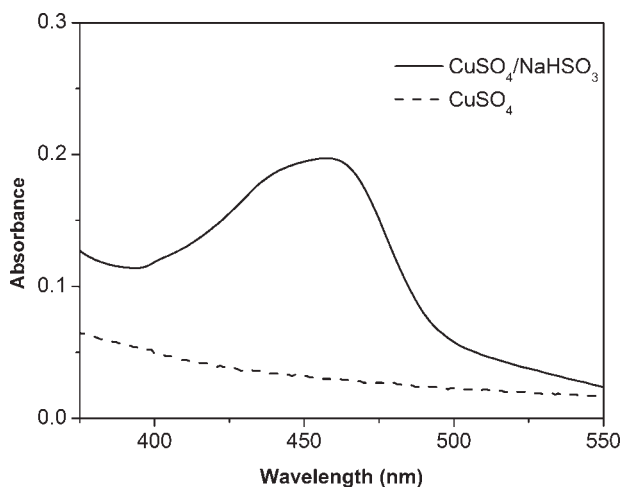


Figure 1 UV-vis spectra of a CuSO_4 aqueous solution and $\text{CuSO}_4/\text{NaHSO}_3$ aqueous solution, both heated at 60°C followed by treatment with neocuproine.

Figure 2 shows a typical monomer conversion with reaction time for the emulsifier-free emulsion polymerization of MMA initiated by the $\text{Cu}^{2+}/\text{HSO}_3^-$ redox system at 60°C . After 2 h of polymerization, the conversion reached 96.2%. The conversion-time curve followed a typical S-shaped curve. Particularly, the initial conversion of the system was almost linear with time immediately from the beginning up to a conversion of about 40%. In addition, a high slope value was observed in this linear region,

TABLE II
Monomer Conversion and ξ Potential of the PMMA Latices Polymerized for 2 h at Different Reaction Temperatures

Sample	X (%)	ξ (mV)
BC40	85.1	-28.8
BC50	94.9	-26.9
BC60	96.2	-37.2

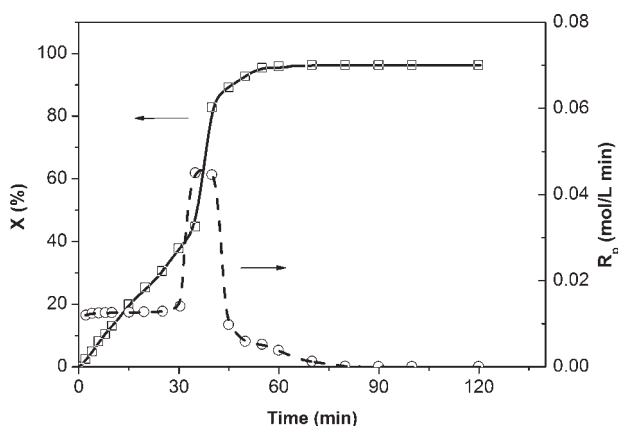


Figure 2 Monomer conversion and R_p of MMA initiated by the $\text{Cu}^{2+}/\text{HSO}_3^-$ system versus reaction time at 60°C .

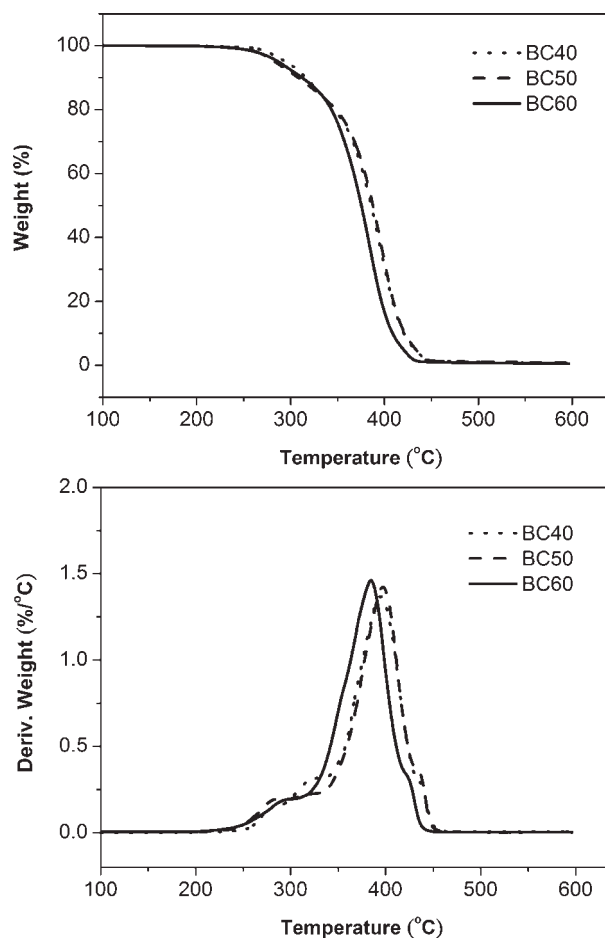


Figure 3 TGA and derivative thermogravimetric analysis curves of the PMMA latex polymer polymerized at different reaction temperatures. The heating rate was $10^\circ\text{C}/\text{min}$.

which indicated a high initial reaction rate in this redox-initiated system. The other two reactions at 40 and 50°C had the same trend as that at 60°C . Yet, as temperature decreased, the final conversion decreased, as shown in Table II. R_p was calculated from the conversion-time curve [$R_p = M_0(dx/dt)$, where M_0 is the initial monomer concentration and dx/dt is the rate of conversion]. Figure 2 also shows the results of R_p , where a bell-shaped curve was obtained. The polymerization rate was almost constant at the initial stage of reaction and then increased sharply to a maximum value because of the gel effect; after that, it decreased until the end of

TABLE III
Maximum-Rate Degradation Temperatures ($T_{\text{max}1}$ and $T_{\text{max}2}$) and RW at 600°C for the PMMA Latices Polymerized at Different Reaction Temperatures

Sample	$T_{\text{max}1}$ ($^\circ\text{C}$)	$T_{\text{max}2}$ ($^\circ\text{C}$)	RW at 600°C (%)
BC40	313.0	393.8	0.50
BC50	303.2	397.7	0.73
BC60	308.2	384.2	0.45

TABLE IV
Maximum-Rate Degradation Temperatures (T_{d1} and T_{d2}) and DEs for PMMA Polymerized at 60°C with Different Concentrations of Cu^{2+} in the Redox Initiator (MMA = 1.0M)

Sample	NaHSO ₃ (mM)	CuSO ₄ ·5H ₂ O (mM)	Maximum-rate degradation temperature (°C)			
			T_{d1} (°C) ^a	DE (%) ^a	T_{d2} (°C) ^b	DE (%) ^b
S5C1	10	2.0	305.4	12.5	408.3	87.5
S5C2	10	4.0	307.6	21.2	403.1	78.8
S5C3	10	6.0	313.9	31.8	386.1	68.2

the reaction. The high reaction rate at the initial stage indicated the rapid formation of polymer particles due to the high initiation rate in this redox-initiated system.

Chain structures

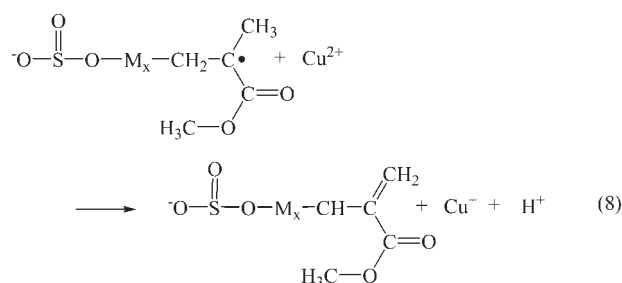
Kashiwagi et al.²³ deliberately prepared PMMA with PMMA—HH (head-to-head linkage chains by combination termination), PMMA—CH=CH₂, and PMMA—H (by disproportionation termination) under a free-radical polymerization with 2,2'-azobisisobutyronitrile as an initiator and with various chain-transfer agents used to control the amount of PMMA—HH and PMMA—CH=CH₂. They found that the degradation temperatures of PMMA—HH, PMMA—CH=CH₂, and PMMA—H were about 160, 270, and 360°C, respectively, at a heating rate of 2°C/min.²³ Therefore, we thought from the analysis of the thermal degradation behavior of the PMMA latex that the structure of chain ends and, in turn, the way of termination could be understood.

TGA and derivative thermogravimetric analysis curves for the latex polymers polymerized at different reaction temperatures in this study are shown in Figure 3. Two stages of degradations occurred: one was in the region from 260 to 340°C, and the other was in the region from 340 to 430°C. The maximum-rate degradation temperatures for the PMMA synthesized at different reaction temperatures are shown in Table III. By comparison with Kashiwagi et al.'s²³ data, the degradation at the second stage corresponded to the PMMA chains with saturated

end groups (PMMA—H), where the first-stage degradation was from the polymer chains with unsaturated end groups (PMMA—CH=CH₂). Therefore, the TGA results clearly show that with this Cu^{2+} /HSO₃⁻ redox system, PMMA chains with both saturated and unsaturated end groups were produced. By increasing only Cu^{2+} and keeping the HSO₃⁻ concentration constant, we found that the degradation extent (DE) in the first stage, corresponding to the amount of PMMA—CH=CH₂, increased, as shown in Table IV. Therefore, Cu^{2+} was thought to be responsible for the production of PMMA—CH=CH₂ during polymerization; that is, Cu^{2+} could act as a chain-transfer agent, as shown in Scheme 2.

This result agreed with the study of Rasti and Scott,²⁴ who showed that the presence of Cu^{2+} ion could scavenge free radicals such as 5-carboxypentyl radical. Therefore, Cu^{2+} served as one component in the redox initiator system to initiate polymerization and as a chain-transfer agent to terminate growing polymer chains and, in turn, produce PMMA chains with double bonds at the end. From the extent of degradation, we estimated that the compositions of PMMA—CH=CH₂ in the final PMMA polymers were approximately 17.1, 16.7, and 17.0% for the systems polymerized at 40, 50, and 60°C, respectively. The result illustrates that the composition of

Chain transfer reaction



Scheme 2 Chain-transfer reaction of the growing polymer chain by copper ions.

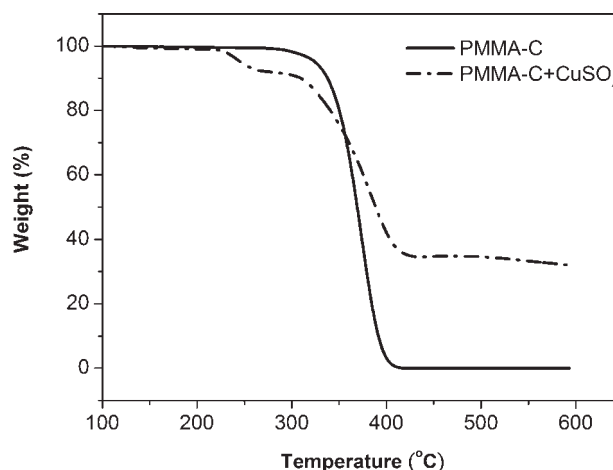


Figure 4 TGA curves of a commercial PMMA (PMMA-C) and its blend with CuSO₄ (50 wt %). The heating rate was 10°C/min.

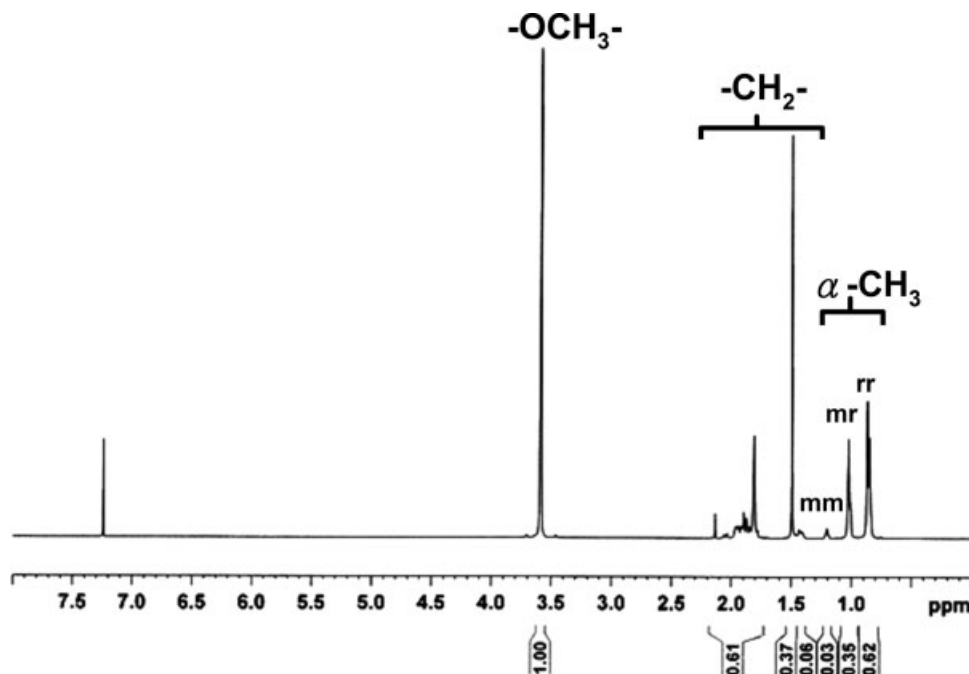


Figure 5 $^1\text{H-NMR}$ spectrum (600 MHz) of the PMMA latex polymerized at 60°C .

PMMA—CH=CH₂ was not affected by the temperature range used in this study.

Copper ion can have a catalytic effect on the degradation of PMMA, not only to increase the degradation rate but also to lower the degradation temperature.²⁵ By deliberately mixing equivalent weights of commercial PMMA and cupric sulfate, we found that an additional degradation stage occurred earlier beginning from 220°C to the end at 270°C with a maximum-rate degradation temperature at 250°C , as shown in Figure 4. This result agreed with the report of Chandrasiri et al.²⁵ However, the TGA curves shown in Figure 3 do not have this stage of degradation, which proves that the residual copper ion in these systems did not affect the degradation of PMMA. This was because the residual copper ion was too scarce because the weight ratio of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to MMA monomer in the feed was only 0.5%, which agreed with the residual weight (RW) at 60°C , as shown in Table III.

The tacticity of the PMMA latex was analyzed from the triad level on the basis of the absorption peaks of the $\alpha\text{-CH}_3$ group in the $^1\text{H-NMR}$ spectrum. Figure 5 shows a typical $^1\text{H-NMR}$ spectrum of the

PMMA latex polymerized at 60°C . The syndiotactic (rr), heterotactic (mr), and isotactic (mm) triad signals of $\alpha\text{-CH}_3$ were at 0.857, 1.014, and 1.204 ppm,^{18–20} respectively, and their percentages obtained by the integration areas of triad signals are shown in Table V. The tacticities of the PMMA latex were almost the same, about 62–64% rr, 33–35% mr, and 3% mm. The PMMA latex prepared by the $\text{Cu}^{2+}/\text{HSO}_3^-$ redox system was thus abundant in syndiotactic sequence in comparison with a commercial PMMA (47% rr, Acryrex CM-211, Chi Mei).

The molecular weight of PMMA was determined by GPC on the basis of polystyrene standards, and the results are listed in Table VI. The average molecular weight of the latex polymer synthesized at 60°C was greater than those at 40 and 50°C . This was probably because of the nature of the redox initiator system, which had a lower activation energy in the initiation step than a thermal decomposition initiator system. Thus, the dependence of molecular weight on temperature became positive. Furthermore, the polydispersity index did not have significant differences for these three systems.

TABLE V
Tacticities for the PMMA Latices Polymerized at Different Reaction Temperatures

Sample	rr	mr	mm
BC40	0.64	0.33	0.03
BC50	0.63	0.34	0.03
BC60	0.62	0.35	0.03

TABLE VI
Weight-Average Molecular Weight (M_w) and Number-Average Molecular Weight (M_n) Values of the PMMA Latices Polymerized at Different Reaction Temperatures

Sample	M_w (g/mol)	M_n (g/mol)	Polydispersity index
BC40	254,000	90,000	2.82
BC50	258,000	87,000	2.97
BC60	315,000	114,000	2.76

TABLE VII
 \bar{D}_p and N_p of the PMMA Latices Polymerized for 2 h at Different Reaction Temperatures

Sample	$\bar{D}_{p,LS}$ (nm) ^a	Polydispersity index ^a	$\bar{D}_{p,SEM}$ (nm) ^b	Standard deviation ^b	$N_p \times 10^{-16}$ (number/L of H ₂ O)
BC40	230	0.021	223	3.9	1.05
BC50	215	0.015	191	3.3	2.12
BC60	192	0.017	165	4.4	3.39

^a Particle size as measured from light scattering.

^b Average of 50 particle sizes as measured from SEM.

Morphology and thermal properties

The particle size after 2 h of reaction was determined by the light-scattering method. The sizes of the latex particles were in the range 192–230 nm, which decreased as reaction temperature was raised, as shown in Table VII. Figure 6 shows SEM pictures with different magnifications of the latex particles polymerized at 60°C, which illustrate the uniform particle size distribution. The average particle size based on 50 particles was 165 nm for the system polymerized at 60°C and increased to 223 nm as the

temperature was decreased to 40°C (Table VII). Compared to the data obtained from the light-scattering method, slightly smaller particle sizes were observed by SEM because of the different sample preparations and techniques. Still, the trends agreed with each other. The reason that the particle size decreased with increasing reaction temperature could be explained by the calculation of the total number of latex particles (N_p) in the water phase (number/L of H₂O) as follows:²⁶

$$N_p = \frac{6XW_M}{V_W \rho_c \pi (\bar{D}_p \times 10^{-8})^3}$$

where W_M is the weight of the feeding monomer, V_W is the volume of the water phase (cm³), ρ_c is the density of the polymer (g/cm³), and \bar{D}_p is the average particle size. The results in Table VII show that the particle number increased as the reaction temperature was increased, which in turn, decreased the particle size.

The DSC curves for the PMMA polymerized by the Cu²⁺/HSO₃⁻ redox system at different reaction temperatures are shown in Figure 7. They had almost the same glass-transition temperature, 125–127°C, regardless of the reaction temperatures.

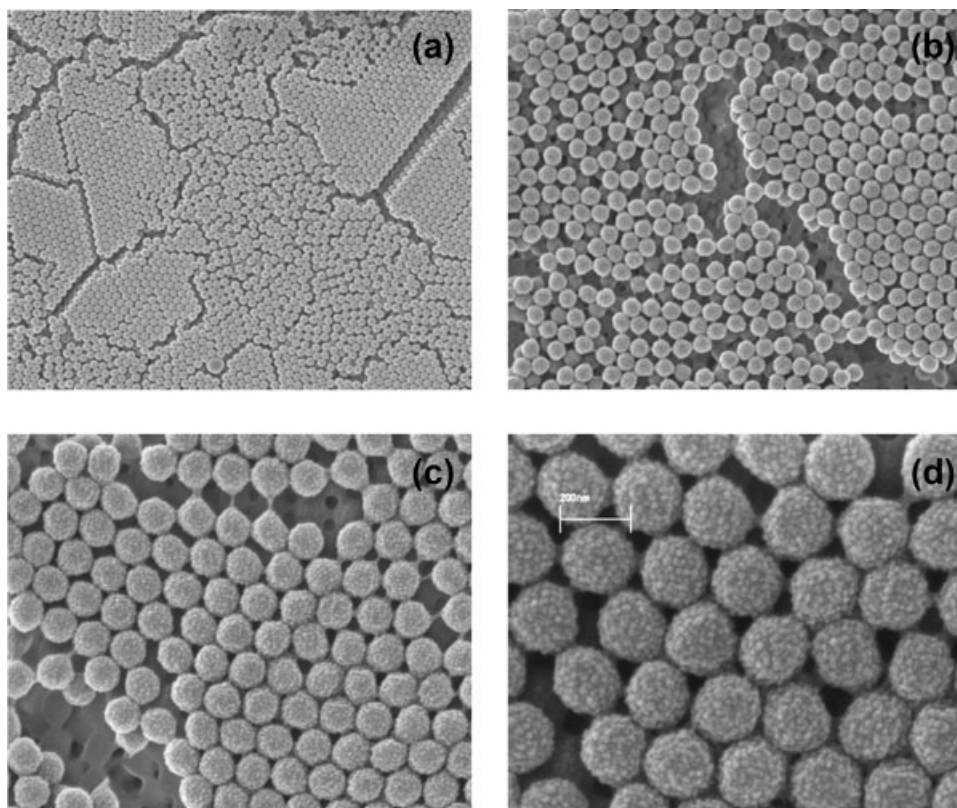


Figure 6 SEM photographs with different magnifications of the PMMA latex polymerized at 60°C (a) 20,000, (b) 50,000, (c) 100,000, and (d) 200,000 \times . The scale bar is 200 nm.

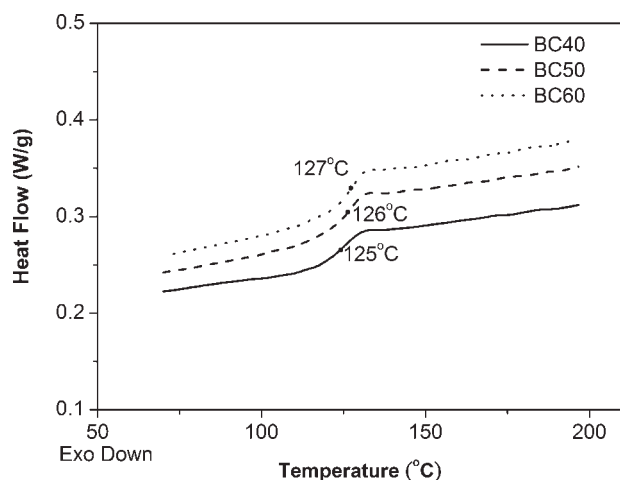


Figure 7 DSC curves of PMMA latices polymerized at different reaction temperatures. The heating rate was 10°C/min.

CONCLUSIONS

PMMA latex was synthesized in an emulsifier-free emulsion polymerization with a $\text{Cu}^{2+}/\text{HSO}_3^-$ initiator system at 40, 50, and 60°C. The initiation mechanism of $\text{Cu}^{2+}/\text{HSO}_3^-$ was proven to be a redox system by the evidence of cuprous ion with a neocuproine indicator. A reaction mechanism was proposed in this article. First, the copper ion was complexed with two bisulfite ions and caused the homolysis of hydroxyl group in bisulfite to produce an anionic sulfite radical and hydrogen. The hydrogen was then oxidized to a proton by copper ion. The anionic sulfite radical thus initiated free-radical polymerization. A high reaction rate at the beginning of the reaction was observed, and the ξ potential of the latex was negative for all systems because of the bonded anionic sulfite ion; both results further support the redox nature of the initiation system. The synthesized PMMA had two stages of thermal degradation in the TGA curves, which were found to be the degradation of $\text{PMMA}-\text{CH}=\text{CH}_2$ with unsaturated end groups and $\text{PMMA}-\text{H}$ with saturated end groups. Under these reaction conditions with a constant molar ratio of $\text{Cu}^{2+}/\text{MMA}$ of 2.0×10^{-3} , the produced PMMA had about 17% $\text{PMMA}-\text{CH}=\text{CH}_2$. However, increasing Cu^{2+} ion concentration in the feed increased the proportion of $\text{PMMA}-\text{CH}=\text{CH}_2$ in the produced latex. Therefore, Cu^{2+} ion not only served as one component in the redox initiator system but also as a chain-transfer

agent to terminate growing polymer chains and, in turn, produce PMMA chains with a double bond at the end. Furthermore, the tacticities of the PMMA latex prepared by this $\text{Cu}^{2+}/\text{HSO}_3^-$ redox system had a predominant composition in syndiotactic content, with about 63% rr sequences as calculated from NMR spectra. The morphology of the latex observed by scanning electron microscope exhibited a uniform particle size distribution, and the size decreased from 223 to 165 nm as temperature was raised from 40 to 60°C.

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