Controlled Radical Polymerization Catalyzed by CuCl/BDE Complex in Water Medium. II. Polymerization of Methyl Methacrylate and Formation of PMMA with Bimodal Molecular Weight Distribution

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ABSTRACT: The emulsion polymerization of MMA was explored for the BDE/CuCl coordinated catalyst. The M_n of PMMA linearly increased both with increasing the monomer conversion and the proceeding polymerization time, which means that the MMA polymerized in "living"/controlled characters with zero order kinetics under BDE/CuCl-catalyzed emulsion conditions. The apparent polymerization rate constants of MMA were $k_{app}^{[MMA]=3.0M} = 0.765$ mol/min, $k_{app}^{[MMA]=1.8M} = 0.760$ mol/min at 80°C, while $k_{app}^{[MMA]1.8M} = 0.228$ mol/min at 50°C, respectively. Slight differences of polymerization results were obtained when emulsifier lauryl phosphate (ADP) and Polyoxyethylene nonyl phenyl ether (OP-10) were adapted in the polymerization. Based on the "coordinated radical cage" mechanism proposed particularly to the BDE/CuCl catalyzed polymerization, reversible equilibrium between common free radical and the coordinated "living" species should exist in this system. Increasing the amount of catalyst must affect the fast equilibrium between those two species, thus, also affecting the relative content in the emulsion circumstance. Therefore, PMMA, with bimodal molecular weight distribution, was achieved through this approach. The formation of PMMA with bimodal distribution was affected by concentration of catalyst and polymerization temperature. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 3076–3081, 2002; DOI 10.1002/app.2336

Key words: emulsion polymerization; "living"/controlled radical polymerization; methyl methacrylate; bis(dimethylaminoethyl) ether; bimodal molecular weight distribution

INTRODUCTION

Emulsion polymerization has been shown to be successful in industrial application as a radical mechanism. One of the targets people have used is to produce well-defined polymers by "living"/

controlled polymerization in emulsion. As polymerization of a monomer/M_t^n/Ln/RX system has been one of the most prosperous approaches in "living" radical polymerization researches,[1,2] emulsion polymerization of this system has become noticeable. "Living"/controlled emulsion polymerization of styrene (St) and (meth)acrylates have been explored with various M_t^n/Ln/RX catalysts initiators.[3-11] Quite recently, Sawamoto et al. reported "living" radical suspension polymerization of MMA with a RuCl$_2$(PPh$_3$)$_3$ complex in water and alcohols, and polymers with high M_n

and a narrow M_w/M_n were obtained.[4] Matyjaszewski et al. reported emulsion polymerization of *n*-butyl methacrylate by reverse ATRP. "Living" polymerization nature was also approved from experiments, albeit with relatively low initiator efficiencies, ca. 0.4.[8] All these reported articles suggest that one of the necessary conditions for "living"/controlled emulsion polymerization in the M_t^n/Ln/RX system is: the polymerization rate $(-d[M]/dt)$ must be fast enough. which is in accord with the results obtained in our studies on emulsion polymerization of St with a BDE/CuCl coordinated catalyst.[9−11]

When BDE was used as a ligand, it was reported that kinetics of vinyl monomers obeyed zero order.[12] St polymerizing in a BDE/CuCl-catalyzed emulsion system showed superior "living" controllability to that in the bpy (2,2-bipyridine), etc., system, and then the poly(styrene-*b*-methyl methacrylate) block copolymer was synthesized in this system.[9,10] In this article, BDE/CuCl catalyzed "living"/controlled emulsion polymerization of MMA and its applications were explored.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA)

CP: MMA was distilled under vacuum just before use. Ethyl-2-bromopropionate (EPN-Br): 98%, Acros product, used directly. Bis(2-dimethyl-amino-
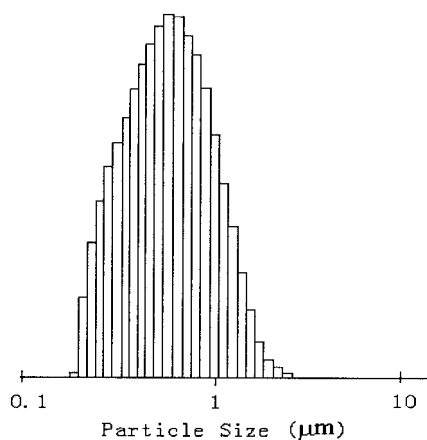

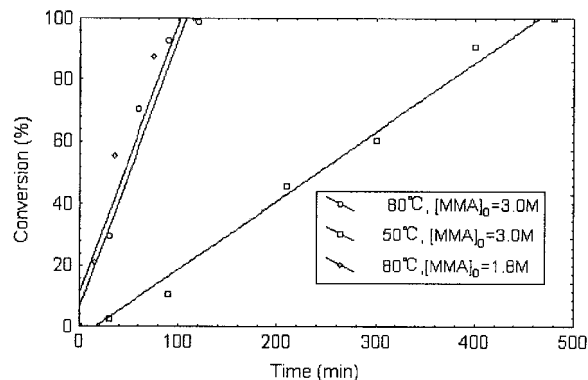**Figure 2** "Living"/controlled radical emulsion polymerization of MMA with [CuCl] : [BDE] : [EPN-Br] : [MMA] 1 : 3 : 1 : 300.

ethyl) ether (BDE): commercial product from Nangjing Jinling Petrochemical Co., distilled in vacuum. Cuprous chloride (CuCl): CP, purified according to the literature.[13] Polyoxyethylene nonyl phenyl ether (OP-10): synthesized by Shanghai Gaoqiao Petrochemical Co., and purified in 50% toluene solution by acid clay for 2 h at 90°C, then filtered and dried in vacuum before used. Lauryl phosphate (ADP): Fluka AG. product, used directly. Deionized water was used.

Polymerization

The reaction vessel was a 50-mL three-necked flask. In the flask, there was a magnetic stirrer bar. One neck was for sample taking and the others were installed with thermometer, vacuum tube, and inert gas tube, respectively. The general procedure of emulsion polymerization was as follows: before adding materials, the flask was de-

Figure 1 Particle size distribution of the latex prepared by emulsion polymerization of MMA at 80°C with [CuCl] = [EPN-Br] = 0.01 mol/mL, [BDE] = 0.03 mol/mL, [MMA] = 3.0 mol/mL, [OP-10] = 1.0 g/100 mL, solution.
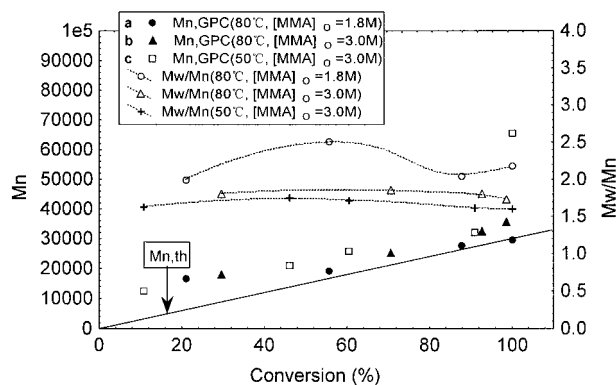

Figure 3 "Living"/controlled radical emulsion polymerization of MMA with the same conditions as in Figure 2.

Table I   Surfactant Influence on Emulsion Polymerization of MMA at 50°C[a]

Surfactants	Time min	Conv wt %	$M_{n,\text{SEC}}$	$M_{n,\text{th}}$	M_w/M_n
[OP-10] = 1.0 g/100 mL	90	10.6	12600	3180	1.63
	210	45.9	21000	13770	1.75
	410	90.9	32300	27270	1.61
	480	100	65500	30000	1.60
[ADP] = 1.0 g/100 mL	60	15.1	19400	4530	1.36
	240	66.2	25600	19860	1.78
	360	100	32800	30000	2.51

[a] [CuCl] = [EPN-Br] = 0.01 mol/mL, [BDE] = 0.03 mol/mL, [MMA] = 3.0 mol/mL.

gassed under vacuum and replaced with argon two times. After the surfactant and catalyst (CuCl, BDE) were added in the vessel, the system was degassed and replaced with argon again, then water. MMA and initiator were added in sequence with stirring under argon atmosphere, and finally immersed in an oil bath at 80°C.

Characterizations

M_n and M_w/M_n of polymers were determined by a Waters 150 GPC/ALC. The GPC is equipped with Waters HT2 and HT4 polystyrene gel columns at 25°C. Calibration was based on monodispersity molecular weight polystyrene standards. Particle distribution of MMA emulsion polymerization system was measured by a MALNERN Master Size MS 20 instrument.
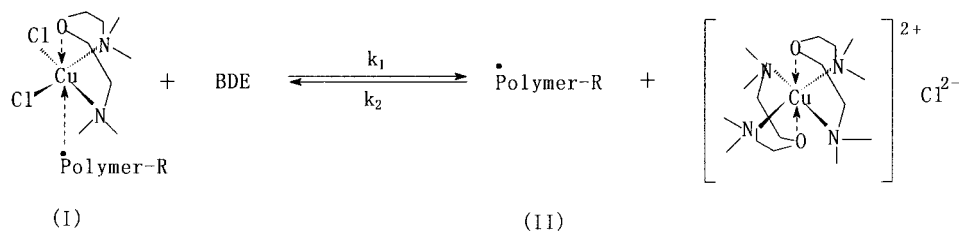
RESULTS AND DISCUSSION

Emulsion Polymerization

The particle size of the latex was measured by laser diffraction. Shown in Figure 1, the sample has a number-average diameter $d_n = 0.67$ μm,

suggesting a true emulsion nature of polymerization of MMA.

As shown in Figure 2, the conversion of MMA was approximately linearly increased to the polymerization time under each BDE-catalyzed emulsion system, which means the kinetics of MMA polymerizing in the emulsion system also showed zero order as well as the kinetics we explored in BDE-catalyzed bulk polymerization systems. Compared to kinetics of St under the same emulsion polymerization conditions (first order),[11] both monomer conversion and polymerization rate of the MMA were higher than those of St, which were similar to the results obtained in Matyjaszewski's bpy system.[8] It is supposed these differences may be due to the higher solubility of catalysts in the MMA phase than those in the St phase,[8] i.e., the partition ratio K_1 ([catalyst]$_{\text{water}}$/[catalyst]$_{\text{MMA}}$) is lower than K_2 ([catalyst]$_{\text{water}}$/[catalyst]$_{\text{st}}$).[14]

Also, as shown in Figure 2, polymerization at the same temperature (80°C), the obtained apparent polymerization rate constants (k_{app}) were comparable with different monomer concentrations ($k_{app}^{[MMA]=3.0M} = 0.765$ mol/min; $k_{app}^{[MMA]=1.8M} = 0.760$ mol/min), which seems that the concen-

Scheme 1   Equilibrium between common free radical (II) and coordinated radical species (I).

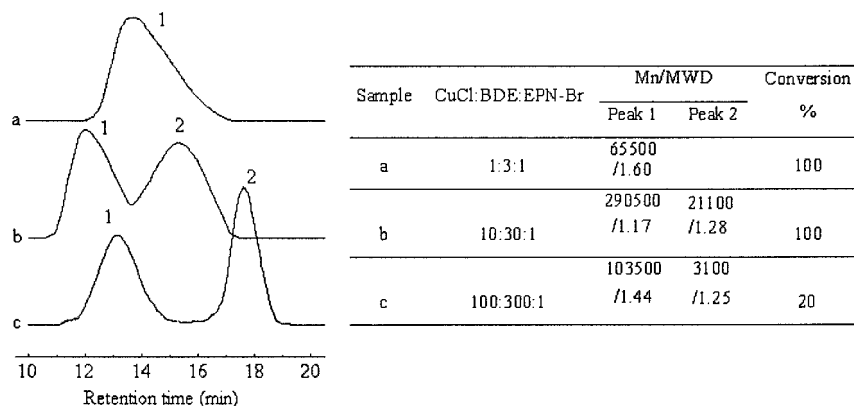| Sample	CuCl:BDE:EPN-Br	Mn/MWD		Conversion %
		Peak 1	Peak 2	
a	1:3:1	65500 /1.60		100
b	10:30:1	290500 /1.17	21100 /1.28	100
c	100:300:1	103500 /1.44	3100 /1.25	20

Figure 4 Bi-MWD PMMA formed with different catalyst concentrations adapted in emulsion polymerization of MMA. [EPN-Br] : [MMA] = 1: 300, [OP] = 1.0 g/100 mL, [MMA] : [H$_2$O] = 1 : 4 (volume ratio), polymerizing at 50°C for 7 h.

tration of the monomer did not affect the polymerization rate, whereas at the same concentration of monomer ([MMA] = 3.0 M), a polymerization rate at 80°C was three times faster than that at 50°C ($k_{app}^{80°C}$ = 0.765 mol/min, $k_{app}^{50°C}$ = 0.228 mol/min).

Figure 3 shows $M_{n,\text{SEC}}$ of polymer vs. the concentration plot, $M_{n,\text{SEC}}$ nearly agree with $M_{n,th}$ although they disagree with each other at low conversion, which was in accord with the emulsion polymerization results obtained from Matyjaszewski's dNbpy–dAbpy system.[8] Besides that $M_{n,\text{SEC}}$ seems closer to $M_{n,th}$ at lower concentration of monomer yet M_w/M_n was broader. Effect of temperature on M_w/M_n was not serious.

The effects of two commercial emulsifiers were compared in Table I. It was shown that when ADP was used as an emulsifier, $M_{n,\text{SEC}}$ almost agree with $M_{n,th}$ with conv. % up to 100%, and the polymerization rate is faster than that in the OP-10 system; but M_w/M_n obtained in the later system was narrower than that in the previous.

Formation of PMMA with Bimodal Molecular Weight Distribution (Bi-MWD)

Multi-MWD of polymers induced by multiactive species in systems were observed to be rather common in anionic polymerizations.[15–17] In the BDE/CuCl system, based on the corresponding "coordinated radical cage" mechanism,[12] the reversible equilibrium of coordinated radical cage species {R$^\bullet$ + CuCl$_2$/BDE} (I) and the common free radical (II) could coexist (Scheme 1). Based on Scheme 1, increasing the catalyst concentration of BDE/CuCl will shift the equilibrium to the right side, i.e., benefit to the formation of species (II), which implicates the relative content of species in emulsion circumstance should be affected. In addition, if the propagation rate of two species I and II are faster than the reversible equilibrium rate (k_1 and k_2 in Scheme 1), Bi-MWD polymer will be formed.

As shown in Figure 4, the remaining CuCl :

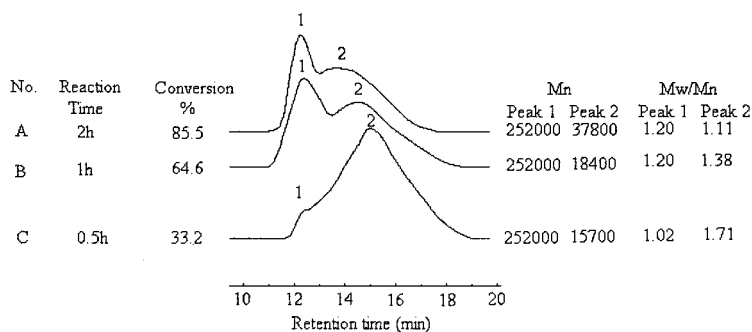| No.	Reaction Time	Conversion %	Mn		Mw/Mn	
			Peak 1	Peak 2	Peak 1	Peak 2
A	2h	85.5	252000	37800	1.20	1.11
B	1h	64.6	252000	18400	1.20	1.38
C	0.5h	33.2	252000	15700	1.02	1.71

Figure 5 SEC trace of Bi-MWD PMMA in emulsion polymerization of MMA at 50°C; [CuCl] : [BDE] : [EPN-Br] : MMA = 10 : 30 : 1 : 300, [OP] = 1.0 g/100 mL, [MMA] : [H$_2$O] = 1 : 4 (volume ratio).
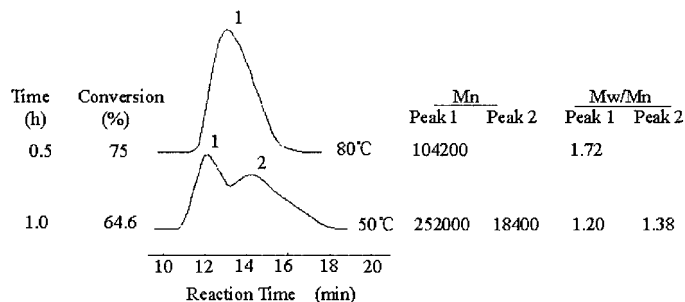
Figure 6   Temperature influence on formation of Bi-MWD PMMA in emulsion polymerization of MMA, [CuCl] : [BDE] : [EPN-Br] : [MMA] = 10 : 30 : 1 : 300, [OP] = 2.0 g/100 mL, [MMA] : [H$_2$O] = 1 : 4 (volume ratio).

BDE = 1 : 3 (mol ratio) Bi-MWD PMMA could not be obtained when the mol ratio of the coordinated catalyst to initiator was 1 : 1. However, when the later was increased to 10 : 1 and 100 : 1, Bi-MWD PMMA were produced. Calculated by the integral peak area, the relative content of peak 1 to peak 2 is 0.9 : 1 in curve b and 1 : 1.1 in curve c. Moreover, in curve b, the monomer conv. % could reach to 100% in 7.0 h. The higher $M_{n,\text{SEC}}$ was 290,500, the M_w/M_n was 1.17, the lower $M_{n,\text{SEC}}$ was 21,100, and the M_w/M_n was 1.28. Nevertheless, monomer conv. % is limited to 20% with much a higher catalyst amount (curve c), yet two more separated peaks (PMMA with Bi-MWD) can be obtained.

Taking the system b in Figure 4 ([coordinated catalyst] : [initiator] = 10 : 1) as an example, the characterization of SEC in the course of polymerization is showed in Figure 5. The M_n of peak 1 (up to 250,000) remained unchanged as the polymerization proceeded, which implicates peak 1 represents a common radical propagation initiated by species (II). The M_n of peak 2 increased gradually as the polymerization time remained. Undoubtedly, it is a "living"/controlled process contributed by "living" species (I). The relative intensity of peak 1 was increased during polymerization, while that of peak 2 was decreased, which should be induced through this process: the common radical was terminated at a high M_n (peak 1, $M_{n,\text{SEC}}$ = 252,000) gradually in the course of polymerization, then reason out the transformation of living species I into common radical II simultaneously, that is, the equilibrium existing in Scheme 1 tends to move to the right side in polymerization, so that it induces changing the relative content of these two peaks.

The affect of temperature on the formation of Bi-MWD PMMA was then explored. At room temperature polymerization of MMA could not occur in the present system, along with the Bi-MWD PMMA, which implicated decomposition of the initiator (RX) to form "living" species should be confined, or the propagation rate of MMA was too slow to be observed at room temperature. At higher temperature (Fig 6, 80°C) Bi-MWD PMMA could not be obtained, yet it could be easily obtained at a medium temperature (Fig 6, 50°C), which implicated the higher temperature benefits of setting up a quick equilibrium between "living" species and common radical, so polymerization only shows "living" nature (single peak in Fig. 6, 80°C). Therefore, the proper range of polymerization temperature for a formation of Bi-MWD PMMA should be around 50°C.

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