

# Atom Transfer Radical Polymerization of Lauryl Methacrylate

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**ABSTRACT:** The atom transfer radical polymerization (ATRP) of lauryl methacrylate (LMA) with an ethyl 2-bromobutyrate/CuCl/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine initiation system was successfully carried out in toluene, and poly(lauryl methacrylate) with a low polydispersity ( $1.2 < \text{weight-average molecular weight/number-average molecular weight} < 1.5$ ) was obtained. Plots of  $\ln([M]_0/[M])$  versus time and plots of the molecular weight versus conversion showed a linear dependence, indicating a constant number of propagating species throughout the polymerization. The rate of polymerization was 0.56-order

with respect to the concentration of the initiator and 1.30-order with respect to the concentration of the Cu(I) catalyst. In addition, the effect of the solvent on the polymerization was investigated, and the thermodynamic data and activation parameters for the solution ATRP of LMA were reported. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1117–1125, 2003

**Key words:** atom transfer radical polymerization (ATRP); living polymerization; kinetics (polym.); molecular weight distribution/molar mass distribution

## INTRODUCTION

Atom transfer radical polymerization (ATRP) is a new method for controlled/living radical polymerization that is catalyzed by transition-metal complexes. A wide range of monomers, including styrene (St) and its derivatives,<sup>1–3</sup> (meth)acrylates,<sup>4–12</sup> and acrylonitrile,<sup>13</sup> have been polymerized in a well-controlled manner.

Lauryl methacrylate (LMA) is an industrially important monomer because of its long-chain alkyl group. It can be used as a hydrophobic part in an amphiphilic block copolymer.<sup>14</sup> LMA has been polymerized through both anionic polymerization and group transfer polymerization to obtain low-polydispersity polymers,<sup>15,16</sup> and the ATRP of lauryl acrylate has been reported.<sup>17</sup> In this article, we report ATRP of LMA initiated by ethyl 2-bromobutyrate (EBrB) with CuCl/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA). Furthermore, we explore homogeneous and heterogeneous ATRP of LMA.

## EXPERIMENTAL

### Materials

LMA (98.5%; Guangzhou Shuangjian Trade Co., Ltd., Guang Zhou, China) was vacuum-distilled for purifi-

cation; PMDETA (chemically pure; Jiangsu Liyang Jiangdian Chemical Factory, Jiangsu, China) was dried with 4-Å molecular sieves and distilled *in vacuo*. EBrB was used as received from Merck. CuCl (analytical-reagent-grade; Shanghai No. 1 Chemical Reagent Factory, Shanghai, China) was dissolved in HCl (analytical grade; Jiangsu, China), precipitated into a large amount of water, and dried *in vacuo*. Tetrahydrofuran (THF; analytical-reagent-grade; Shanghai Chemical Reagent Co., Ltd., Shanghai, China) and methanol (industrial-grade, Jiangsu, China) were used as received. All the solvents were vacuum-distilled for purification.

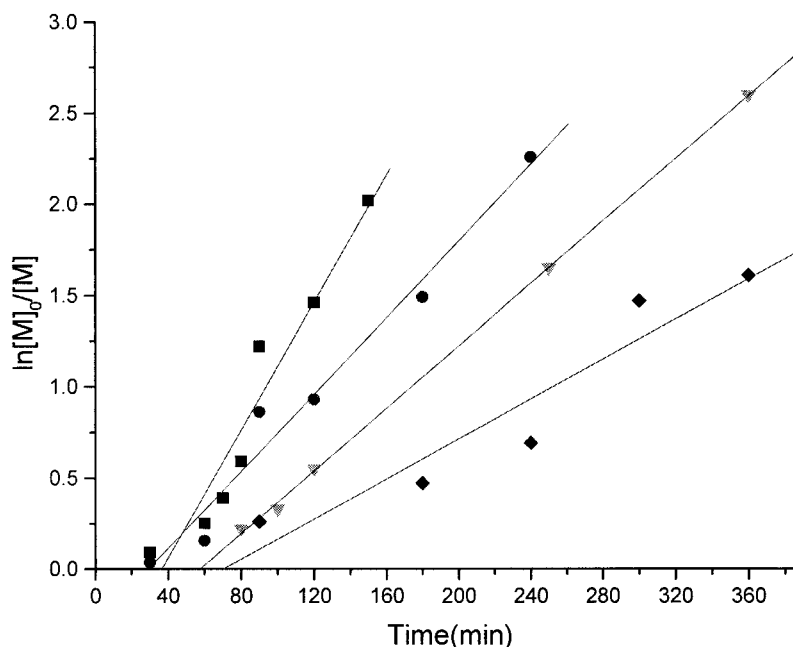
### Polymerization

The general procedure was as follows. A dry tube was filled with CuCl (0.0085 g, 0.0858 mmol), PMDETA (53  $\mu\text{L}$ , 0.258 mmol), toluene (1.5 mL), EBrB (12.5  $\mu\text{L}$ , 0.0853 mmol), and LMA (5 mL, 0.0171 mol) in that order. It was degassed *in vacuo* and charged with  $\text{N}_2$  (five times) and was sealed under  $\text{N}_2$  and placed in the oil bath at the desired polymerization temperature. The polymerizations were stopped at a desired time by the cooling of the tubes in cold water. Afterward, the tubes were opened, and the contents were transferred and dissolved in THF and were precipitated into a large amount of methanol/HCl (100/0.05 v/v). The dried polymer was then characterized with gravimetry.

### Characterization

The monomer conversion was determined with gravimetry. The molecular weights and the molec-

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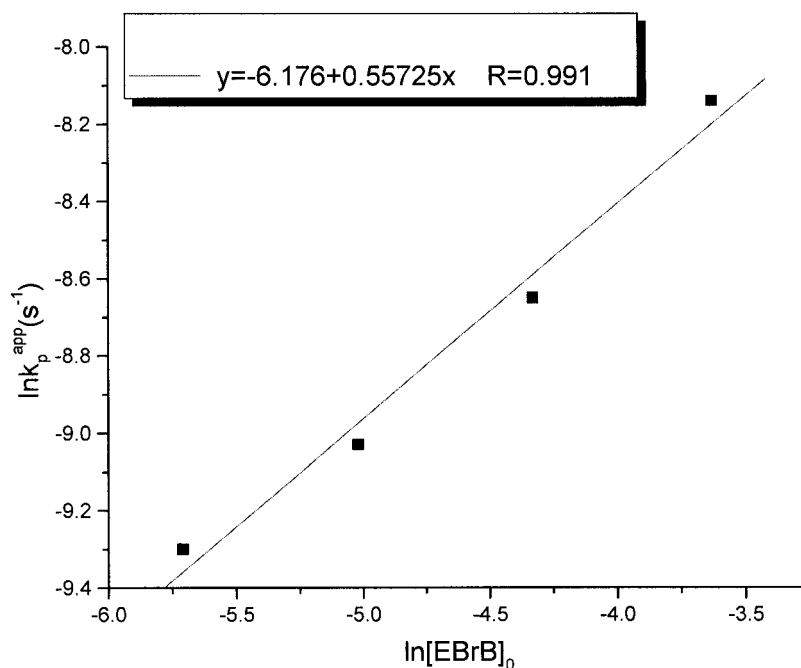
**Figure 1** Effect of the initiator concentration on the kinetic plots of ATRP of LMA in toluene at 110°C:  $[\text{EBrB}]_0 =$  (■) 0.0264M, (●) 0.0132M, (▼) 0.0066M, and (◆) 0.0033M ( $[\text{LMA}]_0 = 2.63\text{M}$ ;  $[\text{CuCl}]_0 = [\text{PMDETA}]_0/3 = 0.0132\text{M}$ ).

ular weight distributions were measured with a Waters 1515 GPC (Milford, MA) instrument with THF as a mobile phase and with a column temperature of 30°C. Polystyrene standards were used to calibrate the columns. The  $^1\text{H-NMR}$  spectrum was recorded in  $\text{CDCl}_3$  with an Inova 400-MHz (Las Vegas, NV) spectrometer at the ambient temperature.

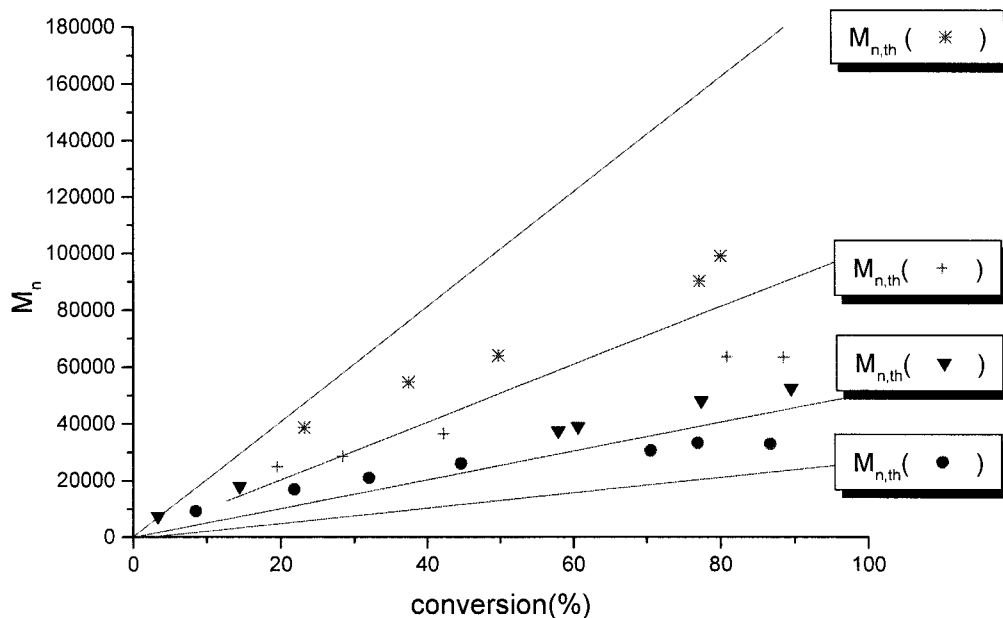
## RESULTS AND DISCUSSION

### Effect of the initiator concentration on the polymerization

Figure 1 shows kinetic plots of  $\ln[M]_0/[M]$  versus time for ATRP of LMA catalyzed by  $\text{CuCl}/\text{PMDETA}$  and initiated by  $\text{EBrB}$  at various initiator concentrations.



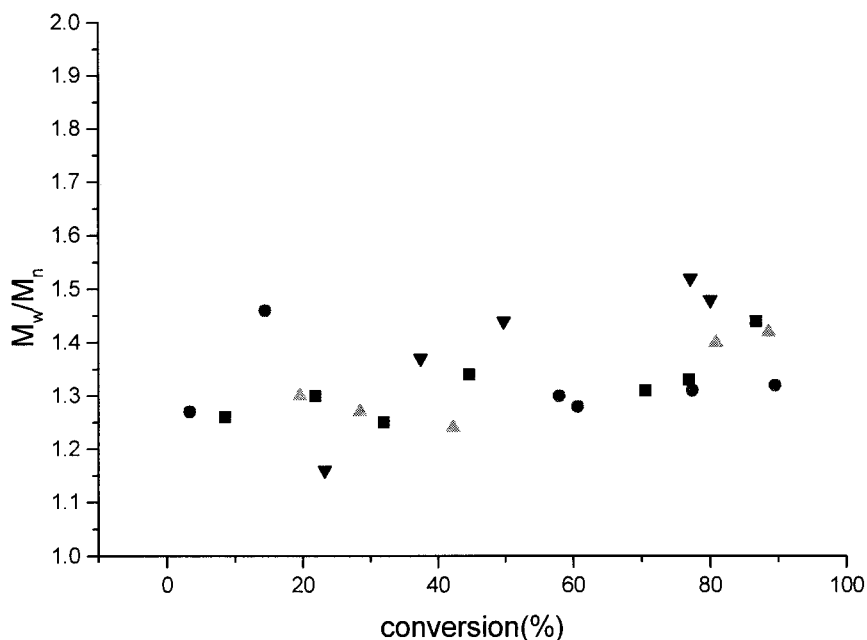
**Figure 2** Dependence of  $k_p^{\text{app}}$  on the initiator concentration for ATRP of LMA in toluene at 110°C ( $[\text{LMA}]_0 = 2.63\text{M}$ ;  $[\text{CuCl}]_0 = [\text{PMDETA}]_0/3 = 0.0132\text{M}$ ).



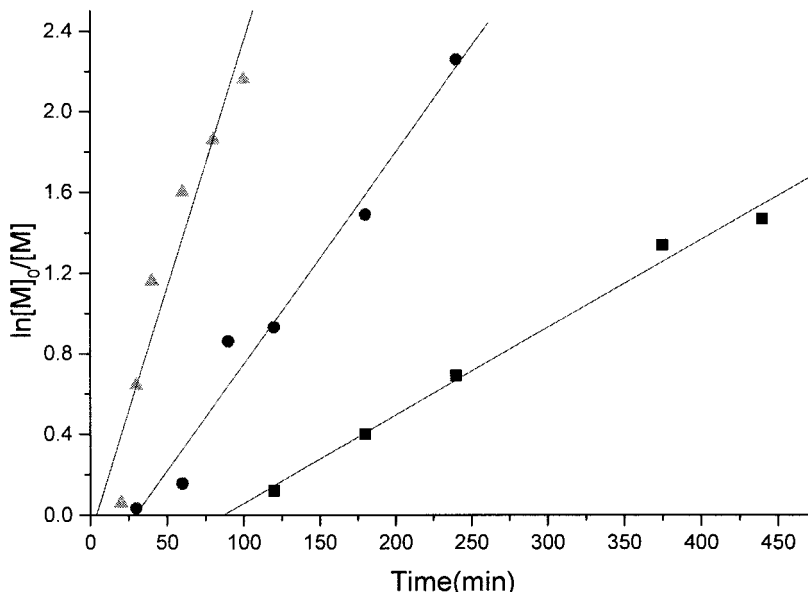
**Figure 3**  $M_n$  versus the conversion for different monomer/initiator ratios for ATRP of LMA in toluene at 110°C:  $[EBrB]_0 = (\bullet) 0.0264M$ ,  $(\blacktriangledown) 0.0132M$ ,  $(+)$   $0.0066M$ , and  $(*) 0.0033M$  ( $[LMA]_0 = 2.63M$ ;  $[CuCl]_0 = [PMDETA]_0/3 = 0.0132M$ ).

The polymerizations are approximately first-order with respect to the monomer concentration. The slopes of the kinetic plots indicate that in the polymerization processes, the number of active species is constant, and the termination reactions can be neglected. With an increasing concentration of the initiator, the apparent rate constant of polymerization ( $k_p^{app}$ ) also increases. Plotting  $\ln k_p^{app}$  against  $\ln[EBrB]_0$  elucidates the dependence of the apparent rate of polymerization

on the concentration of initiator. In Figure 2, the slope of the line indicates an apparent 0.56 order with respect to the initiator in this system. The results are different from the first-order dependence of the rate on the initiator concentration observed for ATRP of St and methyl methacrylate (MMA) reported by Matyjaszewski and coworkers.<sup>3,18</sup> The deviation from the first order can be attributed to the lower initiator efficiency. It has been found for ATRP of MMA that, of



**Figure 4**  $M_w/M_n$  versus the monomer conversion for different monomer/initiator ratios for ATRP of LMA in toluene at 110°C:  $[EBrB]_0 = (\blacksquare) 0.0264M$ ,  $(\bullet) 0.0132M$ ,  $(\blacktriangle) 0.0066M$ , and  $(\blacktriangledown) 0.0033M$  ( $[LMA]_0 = 2.63M$ ;  $[CuCl]_0 = 0.0132M$ ;  $[PMDETA]_0 = 0.0396M$ ).



**Figure 5** Effect of the polymerization temperature on the kinetic plots of ATRP of LMA in toluene: (■) 90, (●) 110, and (▲) 130°C ( $[LMA]_0 = 2.63M$ ;  $[EBrB]_0 = 0.0132M$ ;  $[CuCl]_0 = 0.0132M$ ;  $[PMDETA]_0 = 0.0396M$ ).

alkyl halide initiators, tertiary structures provide faster initiators than secondary structures, which, in turn, are faster than primary alkyl halides.<sup>19,20</sup> In Figures 3 and 4, the number-average molecular weights ( $M_n$ 's) increase linearly with the monomer conversion with low polydispersities throughout the polymerization. When the ratio of initial monomer concentration and initial ethyl 2-bromobutyrate concentration ( $[M]_0/[EBrB]_0$ ) ratio is less than 400:1, the experimental molecular weight is close to the theoretical value, and when the  $[M]_0/[EBrB]_0$  ratio is 800:1, the two values are very different.

#### Effect of the polymerization temperature on the polymerization

The effect of the polymerization temperature on the rate of polymerization for the solution ATRP of LMA was investigated. Figure 5 shows a good linear relationship between  $\ln[M]_0/[M]$  and the polymerization time. The rate of polymerization increases with increasing temperature, and the induction period becomes shorter when the polymerization temperature increases. The stationary concentration of the propa-

gation radicals during the solution ATRP of LMA can be estimated by the combination of the values of  $k_p^{app}$  in eq. (1) ( $k_p^{app} = d\ln[M]/dt$ ) and the rate constant of radical propagation for LMA calculated according to the eq. (2).<sup>21,22</sup> The data are shown in Table I:

$$R_p = k_p^{app}[M] = k_p[M][P\cdot] \quad (1)$$

$$\ln k_p = \ln A_p - E_p/RT = 14.67 - 2503/T \quad (2)$$

As shown in Table I, the rate of polymerization apparently increases with an increasing polymerization temperature because of the increases in both the rate constant for radical propagation and the atom transfer equilibrium constant.<sup>23</sup>

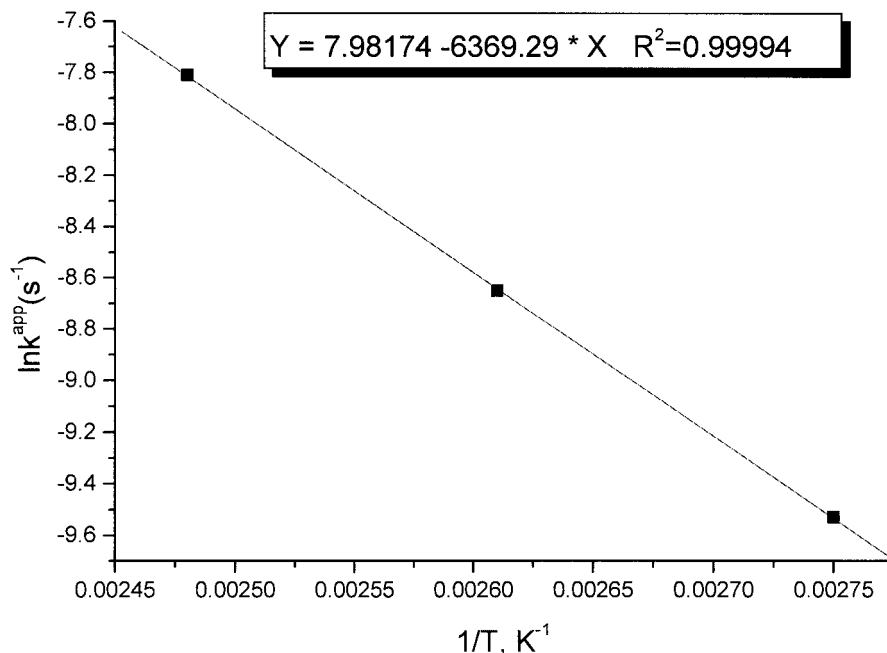
$$\Delta H_{eq}^0 = \Delta H_{app}^\ddagger - \Delta H_{prop}^\ddagger \quad (3)$$

The Arrhenius plot for the CuCl/PMDETA-catalyzed polymerization of LMA is plotted in Figure 6. Based on the slope, an apparent enthalpy of activation,  $\Delta H_{app}^\ddagger = 12.6 \text{ kcal mol}^{-1}$ , is calculated. According to eq. (3), with  $\Delta H_{prop}^\ddagger = 4.95 \text{ kcal mol}^{-1}$  for LMA,  $\Delta H_{eq}^0$

**TABLE I**  
Kinetic Data for ATRP of LMA at Different Polymerization Temperatures

Temperature (°C)	$k_p^{app}$ ( $\times 10^{-5} \text{ s}^{-1}$ )	$k_p$ ( $\times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ )	[P] ( $\times 10^{-8} \text{ mol L}^{-1}$ )
90	7.28	2.38	3.06
110	17.1	3.41	5.01
130	40.8	4.72	8.64

$[LMA]_0 = 2.63M$ ;  $[EBrB]_0 = 0.0132M$ ;  $[CuCl]_0 = 0.0132M$ ;  $[PMDETA]_0 = 0.0396M$ ;  
 $V_{LMA}/V_{\text{toluene}} = 5/1.5$ .



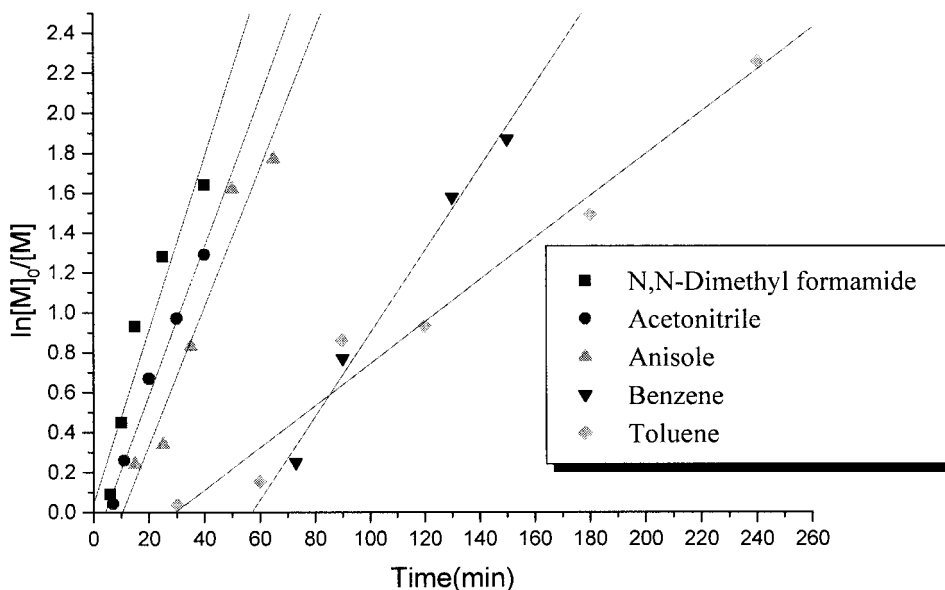
**Figure 6**  $\ln k_p^{app}$  versus the reciprocal of the temperature ( $1/T$ ) for ATRP of LMA in toluene ( $[LMA]_0 = 2.63M$ ;  $[CuCl]_0 = 0.0132M$ ;  $[PMDETA]_0 = 0.0396M$ ;  $[EBrB]_0 = 0.0132M$ ).

$= 7.65 \text{ kcal mol}^{-1}$  can be calculated for the Cl-mediated ATRP of LMA.<sup>20,24,25</sup> This value is much lower than the corresponding values for MA<sup>9</sup> ( $\Delta H_{eq}^0 = 23 \text{ kcal mol}^{-1}$  for ATRP initiated by methyl 2-bromopropionate) and MMA<sup>18</sup> ( $\Delta H_{eq}^0 = 9.7 \text{ kcal mol}^{-1}$  for ATRP initiated by *p*-toluene sulfonyl chloride).

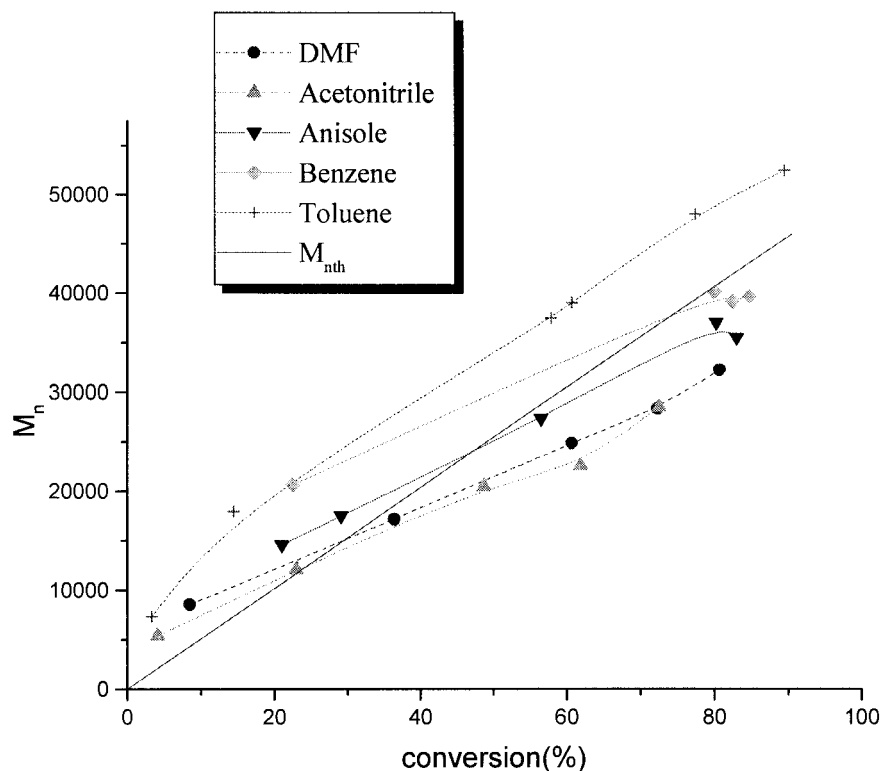
**Effect of the solvent on the polymerization**

ATRP of LMA was conducted in five different solvents. The dielectric constants of the five solvents are

in the following order:  $\epsilon_{\text{dimethylformamide}}$  (37.6, 20°C),  $\epsilon_{\text{acetonitrile}}$  (37.5, 20°C),  $\epsilon_{\text{anisole}}$  (4.33, 25°C),  $\epsilon_{\text{toluene}}$  (2.39, 20°C), and  $\epsilon_{\text{benzene}}$  (2.28, 20°C). In toluene and benzene, the systems are still heterogeneous, but in dimethylformamide (DMF), anisole, and acetonitrile, the systems are homogeneous. The plots of  $\ln[M]_0/[M]$  versus time are shown in Figure 7. The rate of polymerization is first-order with respect to the monomer concentration, and this indicates that in these solvents the concentration of the active species is constant. The rate of polymerization in DMF is faster than that in



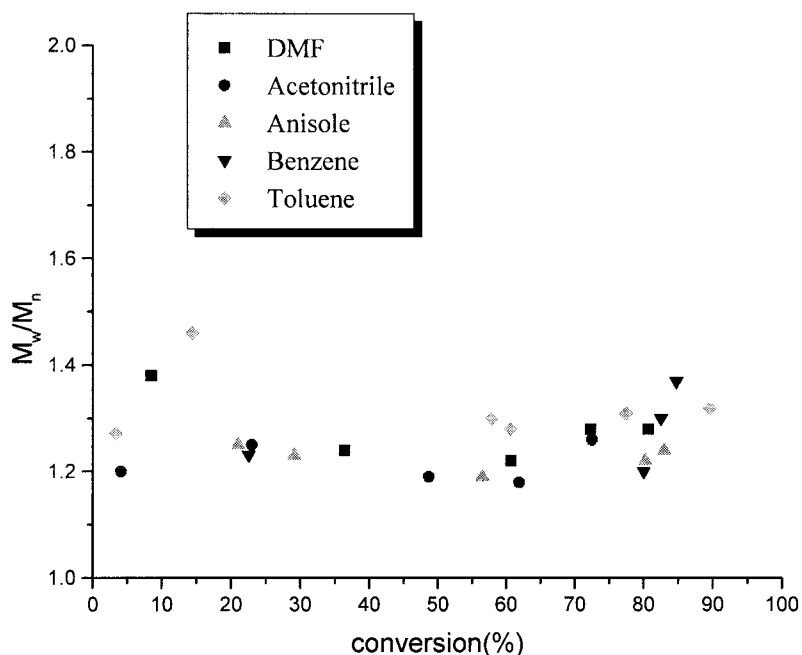
**Figure 7** First-order kinetic plots for ATRP of LMA initiated by EBrB with CuCl/PMDETA in various solvents at 110°C ( $[LMA]_0 = 2.63M$ ;  $[EBrB]_0 = 0.0132M$ ;  $[CuCl]_0 = 0.0132M$ ;  $[PMDETA]_0 = 0.0396M$ ;  $V_{LMA}/V_{\text{solvent}} = 5/1.5$ ).



**Figure 8** Dependence of  $M_n$  on the monomer conversion for ATRP of LMA initiated by EBrB in various solvents at 110°C ( $[LMA]_0 = 2.63M$ ;  $[EBrB]_0 = 0.0132M$ ;  $[CuCl]_0 = 0.0132M$ ;  $[PMDETA]_0 = 0.0396M$ ;  $V_{LMA}/V_{solvent} = 5/1.5$ ).

others; it can be explained that CuCl/PMDETA has good solubility in DMF and that the concentration of the catalyst is larger than that in others. As shown in

Figure 7, the induction period is longer in benzene and toluene than in the others. The induction period is perhaps caused for two reasons: the presence of oxy-



**Figure 9** Dependence of  $M_w/M_n$  on the monomer conversion for ATRP of LMA initiated by EBrB with CuCl/PMDETA in various solvents at 110°C ( $[LMA]_0 = 2.63M$ ;  $[EBrB]_0 = 0.0132M$ ;  $[CuCl]_0 = 0.0132M$ ;  $[PMDETA]_0 = 0.0396M$ ;  $V_{LMA}/V_{solvent} = 5/1.5$ ).

TABLE II  
Effect of the  $V_{\text{LMA}}/V_{\text{solvent}}$  Ratio on the Polymerization of LMA in Toluene

$V_{\text{LMA}}/V_{\text{solvent}}$	Conversion (%)	$M_{n,\text{th}}$	$M_{n,\text{GPC}}$	$M_w/M_n$	$f$
5/0	46.6	23,700	41,100	1.30	0.58
5/1	32.6	16,600	27,000	1.22	0.61
5/1.5	14.4	7,300	17,900	1.46	0.41
5/3	7.3	3,700	20,800	1.25	0.18

[LMA]<sub>0</sub> = 2.63M; [EBrB]<sub>0</sub> = 0.0132M; [CuCl]<sub>0</sub> = 0.0132M; [PMDETA]<sub>0</sub> = 0.0396M; polymerization temperature = 110 °C; polymerization time = 60 min.

gen and impurities and the effect of the solvent. The polarity of the solvents may affect the induction period. In this study, the induction period in a homogeneous system is shorter than that in a heterogeneous system under the same conditions. The active catalyst is easier to form in a homogeneous system. In addition, the polarity of the solvent can also affect the metal complex structure. In a polar solvent,  $\text{Cu}^+(\text{PMDETA})_2\text{Cl}^-$  may exist, but in a less polar solvent,  $(\text{PMDETA})\text{CuCl}_2\text{Cu}(\text{PMDETA})$  could exist.<sup>18</sup> The molecular weights and molecular weight distributions are shown in Figures 8 and 9, respectively. The weight-average molecular weight/number-average molecular weight ratio ( $M_w/M_n$ ) ranges from 1.2 to 1.4 in all solvents, and the molecular weights increase with the monomer conversion. Under the same monomer conversion, the greater the polarity is, the lower the experimental molecular weight is. It may be explained that in polar solvents, the processes have

higher initiator efficiencies than those in nonpolar solvents.

As shown in Table II, in the same polymerization time, the conversion decreases with a decreasing  $V_{\text{LMA}}/V_{\text{solvent}}$  ratio. When  $V_{\text{LMA}}/V_{\text{solvent}}$  is 5/1, the initiator has higher initiator efficiencies than in other systems.

#### Effect of the concentration of the catalyst on the polymerization

In Figure 10, a plot of  $\ln k_p^{\text{app}}$  versus  $\ln[\text{CuCl}]_0$  shows that the rate of polymerization in toluene follows a 1.30 order with respect to the concentration of the Cu(I) catalyst. This is different from previous reports in which the rates of ATRP for St and MMA are first-order in  $[\text{CuX}]_0$ .<sup>3,18</sup> This may be due to the poor solubility of the catalyst complex formed with PMDETA and Cu(I)Cl in both LMA and the nonpolar solvent (toluene).

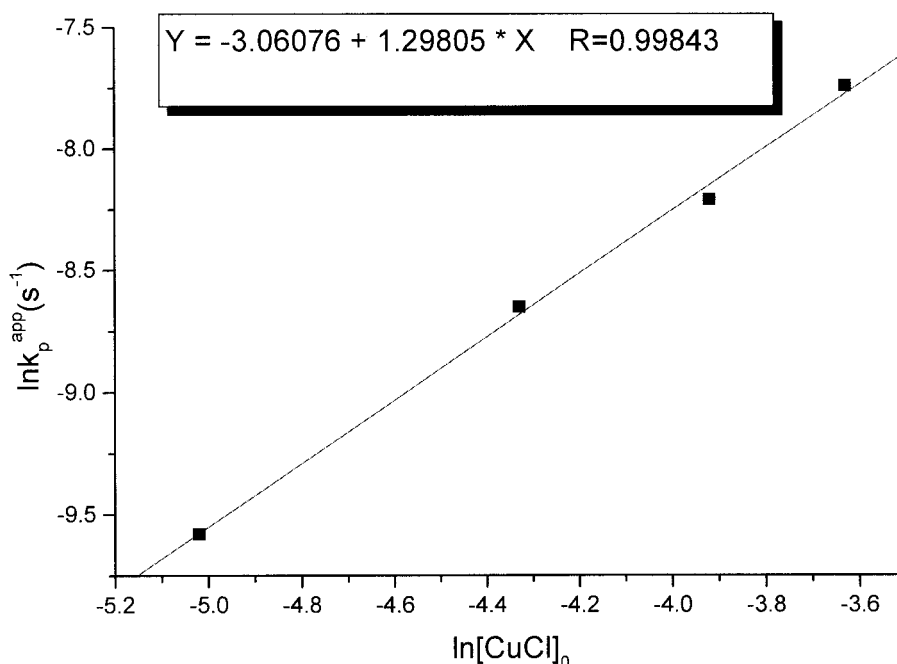
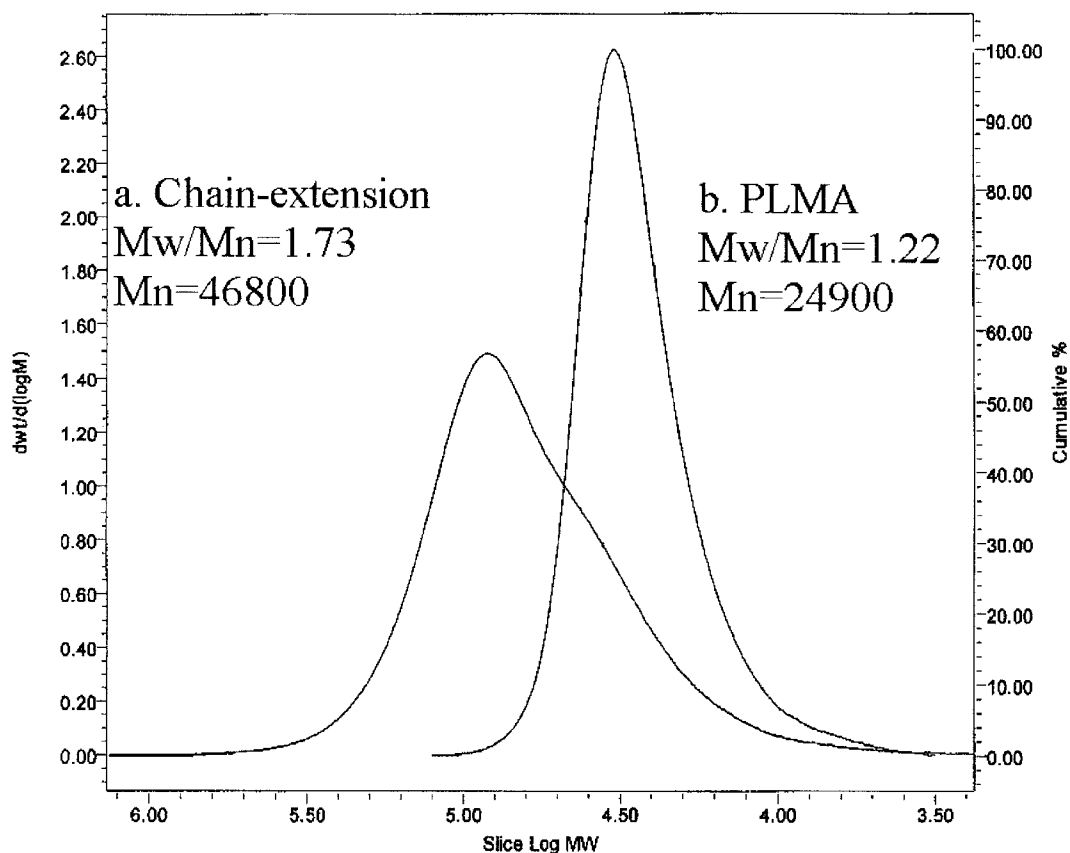
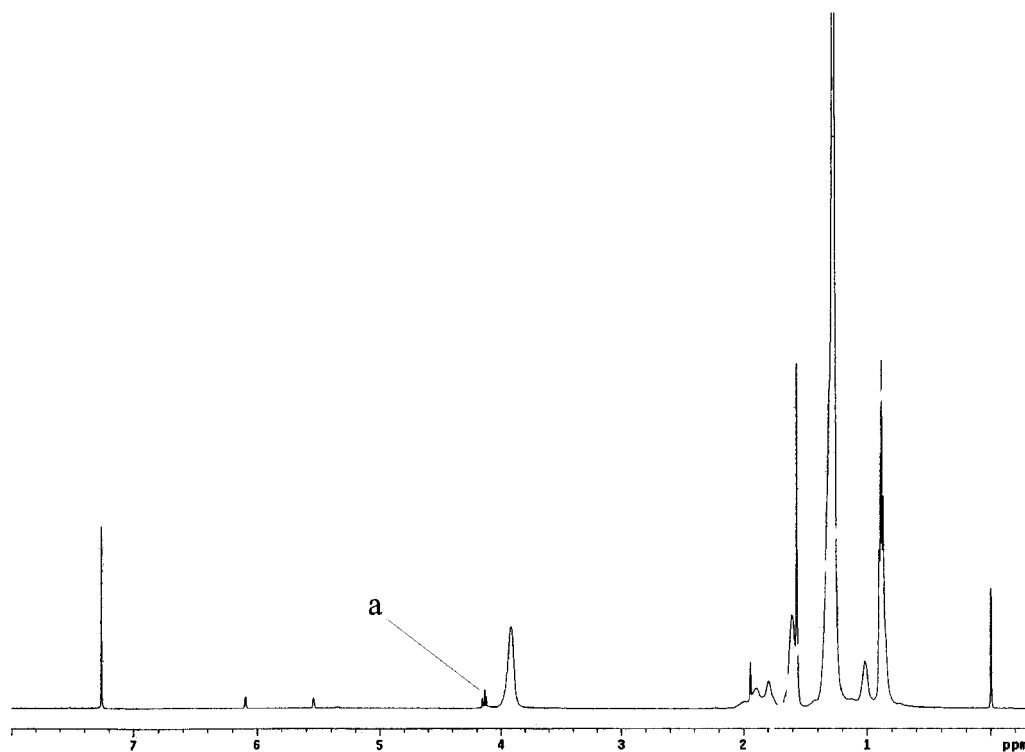


Figure 10 Dependence of  $k_p^{\text{app}}$  on the concentration of CuCl for ATRP of LMA in toluene at 110°C ([LMA]<sub>0</sub> = 2.63M; [EBrB]<sub>0</sub> = 0.0132M; [CuCl]<sub>0</sub> = [PMDETA]<sub>0</sub>/3; slope = 1.30).



**Figure 11** GPC curves of PLMA: (a) after chain extension and (b) before chain extension ( $[LMA]_0/[macroinitiator]_0/[CuCl]_0/[PMDETA]_0 = 161:1:1:3$ ;  $V_{DMF}/V_{LMA} = 1:1$ ; polymerization temperature =  $110^\circ C$ ).



**Figure 12**  $^1H$ -NMR spectrum of PLMA prepared with EBrB/CuCl/PMDETA as the initiation system in toluene at  $110^\circ C$ .



### Chain-extension reaction and end-group characterization

According to the mechanism of ATRP, if there is a halogen atom at the end of the polymer chain, the macroinitiator should be able to initiate the polymerization of a fresh feed of LMA in the presence of the ATRP catalyst, CuCl/PMDETA. Experimentation confirms this hypothesis, as shown in Figure 11 by chromatograms of isolated poly(lauryl methacrylate) (PLMA; synthesized with EBrB/CuCl/PMDETA) and the final polymer obtained after a 46.0% conversion of an additional crop of the monomer with the CuCl/PMDETA catalyst.  $M_n$  increases to 46,800 from 24,900, but  $M_w/M_n$  (1.73) of the final polymer is broader than that (1.22) of the macroinitiator. Furthermore, the  $^1\text{H-NMR}$  spectrum in Figure 12 shows a signal (a in Fig. 12) at 4.14 ppm corresponding to the lauryl ester group at the chain end. These demonstrate the quantitative presence of a halogen atom at  $\omega$  of the chain.

### CONCLUSIONS

ATRP of LMA in a solvent initiated by EBrB/CuCl/PMDETA has been investigated. The rate of polymerization follows a first order with respect to the monomer, a 0.56 order with respect to the concentration of the initiator, and a 1.30 order with respect to the concentration of the Cu(I) catalyst. The rate of polymerization in DMF is faster than that in other solvents (acetonitrile, anisole, benzene, and toluene) discussed in this article, and the molecular weight distributions in anisole and acetonitrile are a little narrower than those in others.  $\Delta H_{\text{eq}}^0$  (7.65 kcal mol $^{-1}$ ) for LMA with this initiation system is much lower than for MA and MMA, as reported by Matyjaszewski.

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