

Atom-Transfer Radical Polymerization of Methyl Methacrylate with α,α' -Dichloroxylylene/CuCl/ N,N,N',N'',N''' -Pentamethyldiethylenetriamine Initiation System Under Microwave Irradiation

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ABSTRACT: The atom-transfer radical polymerization (ATRP) of methyl methacrylate (MMA), using α,α' -dichloroxylylene as initiator and CuCl/ N,N,N',N'',N''' -pentamethyldiethylenetriamine as catalyst was successfully carried out under microwave irradiation (MI). The polymerization of MMA under MI showed linear first-order rate plots, a linear increase of the number-average molecular weight with conversion, and low polydispersities, which indicated that the ATRP of MMA was controlled. Using the same experimental

conditions, the apparent rate constant (k_p^{aPP}) under MI ($k_p^{aPP} = 7.6 \times 10^{-4} \text{ s}^{-1}$) was higher than that under conventional heating ($k_p^{aPP} = 5.3 \times 10^{-5} \text{ s}^{-1}$). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2189–2195, 2004

Key words: microwave irradiation; atom-transfer radical polymerization (ATRP); methyl methacrylate; α,α' -dichloroxylylene; block copolymers

INTRODUCTION

Atom-transfer radical polymerization (ATRP) has been increasingly used,^{1–3} although a large amount of catalyst, long reaction time, and a high temperature are ordinarily needed to achieve a higher polymerization rate. To solve these problems, a new catalyst system with higher reactivity or additional measures to enhance the reactivity of the present catalyst system are needed. Microwave, as peculiar source of energy, has been widely applied to enhance chemical reactions.^{4–6} The main benefit of performing reactions under microwave irradiation (MI) is the significant rate enhancement; that is, it can enhance the reactivity of reaction system.

Halogen compounds with two reactive carbon-halogen bonds such as α,α' -dihaloxylylenes can be used as bifunctional initiators for metal-catalyzed living-radical polymerizations to prepare telechelic polymers.^{7–9} α,α' -Dibromoxylylene has a higher initiator efficiency than that of α,α' -dichloroxylylene (DCIX),⁸ which is consistent with the lower initiator efficiency of 1-phenylethyl chloride than that of 1-phenylethyl bromide.¹⁰ A possible reason for this phenomenon

was reported by Matyjaszewski et al.¹¹ Compounds that have similar structures, such as 9,10-bis(choromethyl)anthracene (Cl–DMA–Cl) and 9,10-bis(bromomethyl)anthracene (Br–DMA–Br), also have been used as bifunctional initiators in ATRP of methyl methacrylate (MMA),¹² although the initiator efficiency of Cl–DMA–Cl is rather low (12–17%) and the initiator efficiency of Br–DMA–Br is even poorer down to less than 1%. All these show that the initiator efficiency for ATRP of MMA initiated by α,α' -dihaloxylylenes is low.

In this work, we report the ATRP of MMA with the DCIX/CuCl/ N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA) initiation system under microwave irradiation. The purpose of this work was to enhance the polymerization rate, decrease the reaction temperature, and increase the initiator efficiency with the help of microwave irradiation.

EXPERIMENTAL

Apparatus

The self-improved Samsung domestic microwave oven (Model M9D88) is schematically shown as Figure 1. Its irradiation power ranged from 90 to 900 W. The reactor is a two-neck bottle (500 mL) with refluxing solvent (350 mL, *n*-hexane) used for controlling the reaction temperature (72°C), which is slightly higher than the boiling point of the solvent (69°C). A dry sealed glass tube filled with reaction materials was placed into the refluxing solvent to allow polymerization to occur.

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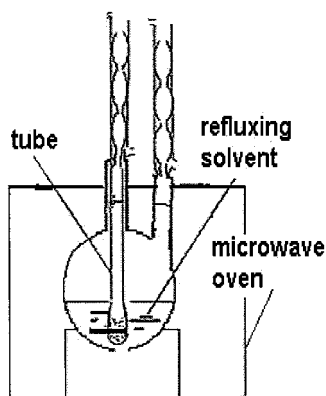


Figure 1 Schematic diagram of the Samsung M9D88 self-improved domestic microwave oven.

Materials

Methyl methacrylate (MMA, chemically pure; Shanghai Chemical Reagent Co., China) was purified by extracting with 5% sodium hydroxide aqueous solution, washing with water, and drying with sodium sulfate anhydrous overnight, after which it was distilled under vacuum. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (chemically pure; Jiangsu Liyang Jiangdian Chemical Factory, China) was dried with 4-Å molecular sieve and distilled under vacuum. α,α' -Dichloroethylene (DCIX, chemically pure; Jiangsu Jiangdu Sandeli Co., China) was twice recrystallized with ethanol; CuCl (chemically pure; Shanghai Chemical Reagent Co.) was dissolved in HCl, precipitated into a large amount of water, and then dried under vacuum. Tetrahydrofuran (THF, analytical reagent; Shanghai Chemical Reagent Co.), hydrochloric acid

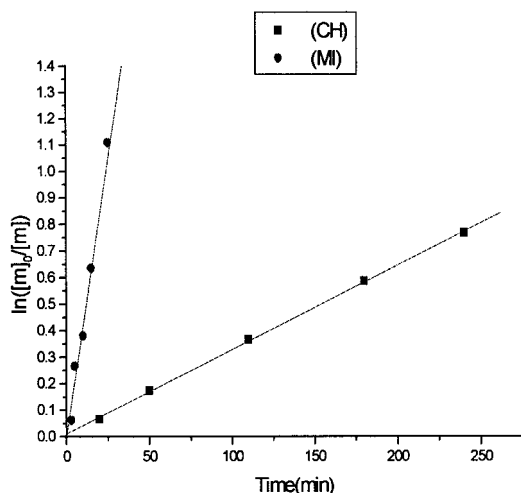


Figure 2 Kinetics of ATRP of MMA under microwave irradiation (MI) and conventional heating (CH). Conditions: $T = 72^\circ\text{C}$; $[\text{MMA}]_0 = 9.46\text{M}$; $[\text{MMA}]_0/[\text{DCIX}]_0/[\text{CuCl}]_0/[\text{PMDETA}]_0 = 400 : 1 : 1 : 3$.

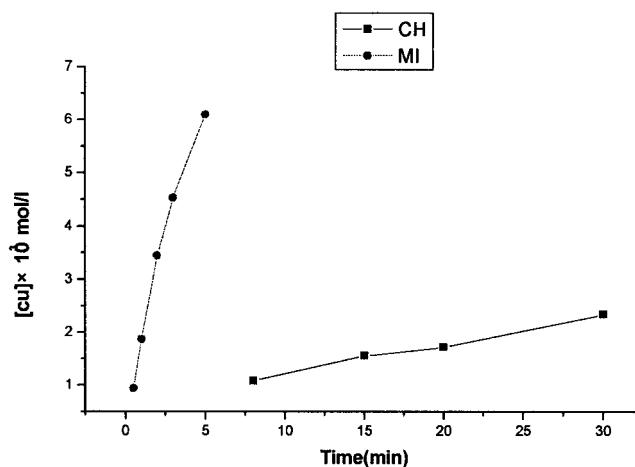


Figure 3 Plots of $[\text{Cu}]$ versus time in solution. Conditions: $[\text{MMA}]_0 = 0.047\text{M}$; $[\text{MMA}]_0/[\text{DCIX}]_0/[\text{CuCl}]_0/[\text{PMDETA}]_0 = 1200 : 1 : 1 : 3$.

(HCl, analytical reagent; Jiangsu Jincheng Chemical Reagent Co., China), and other reagents (chemically pure; Shanghai Chemical Reagent Co.) were used as received.

General procedures of polymerizations

Microwave irradiation (MI) process

A dry glass tube was filled with MMA, DCIX, CuCl, and PMDETA. Three freeze–pump–thaw cycles were performed, and the tube was sealed under vacuum and placed into the self-improved microwave oven with reflux of *n*-hexane (MI power = 450 W). The polymerization was stopped at the desired time by cooling the tube in ice water. Afterward, the tube was opened and the contents were dissolved in THF and

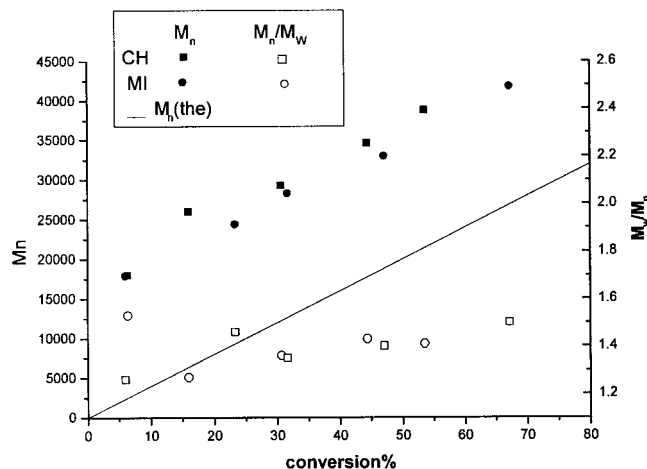


Figure 4 Dependency of M_n and M_w/M_n on conversion for the ATRP of MMA under MI and CH. Conditions are as in Figure 1.

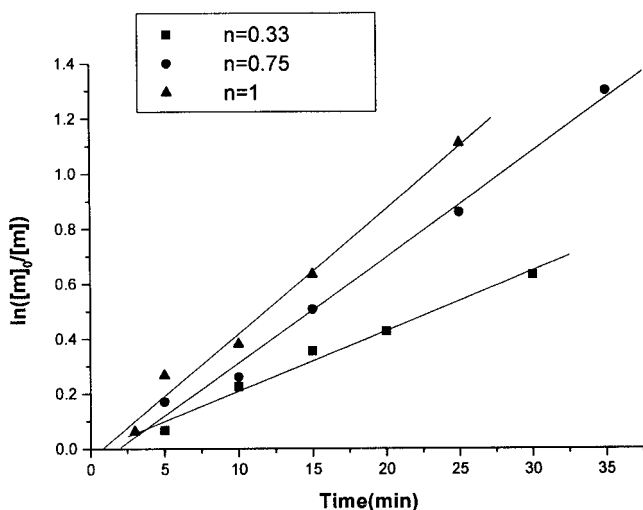


Figure 5 Kinetics of ATRP for the MMA at different initiator concentrations under MI. Conditions: $[M]_0 = 9.46M$; $[MMA]_0/[DCIX]_0/[CuCl]_0/[PMDETA]_0 = 400:n:1:3$ ($n = 0.33, 0.75, 1$).

precipitated into a large amount of methanol/HCl (100/0.05, volume ratio). The dried product was then characterized by gravimetry.

Conventional heating (CH) process

The sealed tube under vacuum was placed in an oil bath held by a thermostat at the desired temperature to polymerize. The other procedures were identical to those under MI.

Characterizations

Conversion of monomer was determined by gravimetry. Molecular weights and molecular weight distributions were measured using a Waters 1515 GPC apparatus (Waters Chromatography Division/Millipore, Milford, MA) with THF as a mobile phase and with column temperature of 30°C. Polystyrene standards were used to calibrate the columns. 1H -NMR spectra were recorded in $CDCl_3$ with an Inova 400-MHz spectrometer (Varian, California) at ambient temperature. The concentration of Cu in the solution of MMA/CuCl/PMDETA was determined by Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometers (Hitachi, Osaka, Japan).

RESULTS AND DISCUSSION

ATRP of MMA with DCIX/CuCl/PMDETA

Heterogeneous polymerization of MMA in bulk catalyzed by CuCl/PMDETA was carried out. Figure 2 shows the kinetic plots of $\ln([M]_0/[M])$ versus time for ATRP of MMA using different polymerization processes (MI and CH). The resulting slopes indicate the polymerizations proceeded with an approximately constant number of active species for the duration of the reaction. According to the slopes of the kinetic plots, the apparent rate constant (k_p^{app}) was calculated. The k_p^{app} under MI ($7.6 \times 10^{-4} s^{-1}$) is much higher than that under CH ($5.3 \times 10^{-5} s^{-1}$), which indicates that applying MI can greatly enhance the rate of polymerization.

To further investigate the difference in the apparent rate constants between MI and CH, the concentration

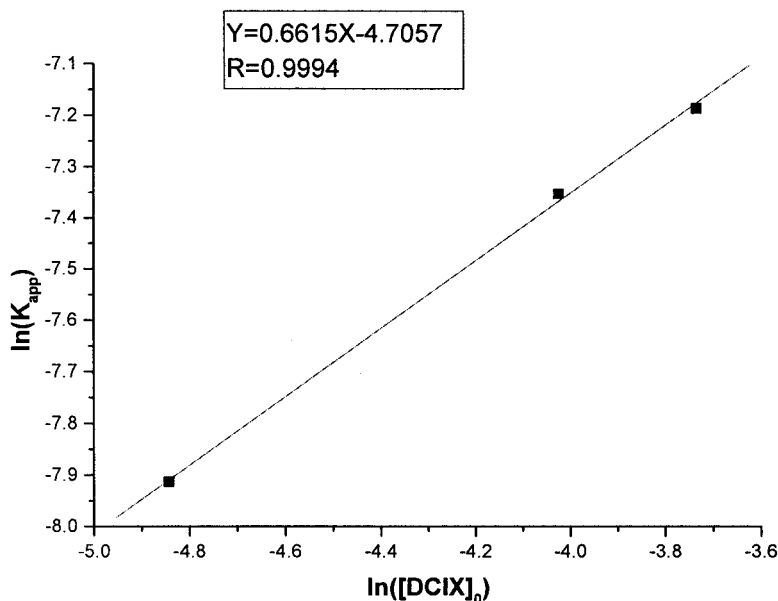


Figure 6 Plot of k_p^{app} versus $\ln[DCIX]_0$ for the ATRP of MMA.

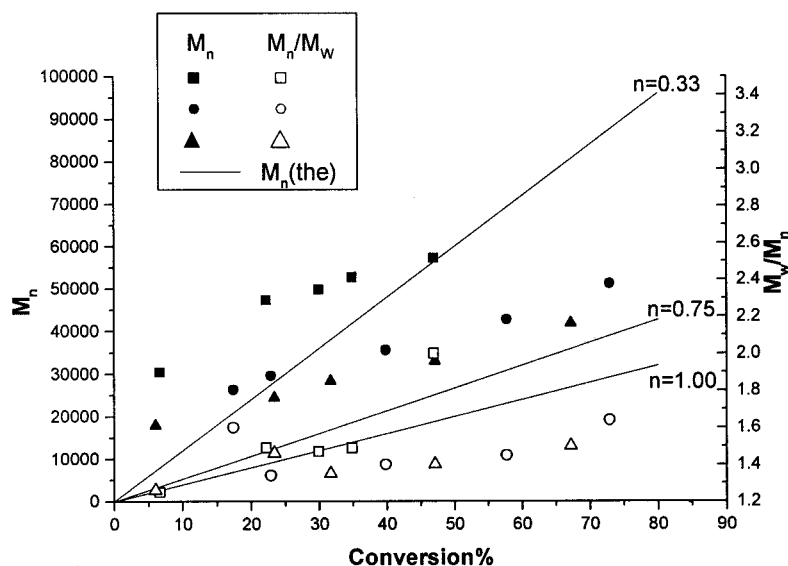


Figure 7 Dependency of M_n and M_w/M_n on conversion for the ATRP of MMA under MI at different initiator concentrations. Conditions are as in Figure 5.

of Cu in the solution of this heterogenous system was determined; the results (Fig. 3) show that the concentration of Cu under MI is higher than that under CH within the same time. MI increases the dissolution of CuCl in the system; this may be one of the reasons that applying MI to polymerization can enhance the rate of polymerization.

Plots of number-average molecular weight (M_n) and molecular weight distributions (M_w/M_n) versus conversion are shown in Figure 4. It is clear that M_n increases with increasing conversion. Molecular weight distributions under the MI process range from 1.2 to 1.5, and under the CH process range from 1.2 to 1.6. The $M_{n(\text{GPC})}$ values under both MI and CH processes are higher than theoretical values, indicating low initiator efficiency; a similar phenomenon was reported by other researchers.^{8,10,12} However, the initiator efficiency under the MI process (0.14–0.64) is slightly higher than that under the CH process (0.14–0.53) at the same monomer conversion.

Effect of concentration of initiator on polymerization

Figure 5 shows the kinetics of polymerization at different initiator concentrations under MI. The polymerizations are approximately first-order kinetics with respect to the initiator concentrations, which indicates that the number of active species in the polymerization process is constant, and the transfer and termination reactions can be negligible. Figure 6 shows that the relation between the apparent rate constant (k_p^{app}) and the initiator concentration is first-order linear, and that k_p^{app} linearly increases with increasing initiator concentration. The variations of molecular weights

and molecular weight distributions with monomer conversion are shown in Figure 7. The molecular weights increase linearly with the conversion. Almost all the molecular weight distributions range in value from 1.2 to 1.5, which shows that the polymerizations are controlled. However, at low initiator concentration ($[\text{MMA}]_0/[\text{DCIX}]_0 = 400 : 0.33$), the molecular weight distribution is broad ($M_w/M_n > 2.0$) when the conversion is over 45%. The same trends, that molecular weight distributions become slightly broader, can be seen at other initiator concentrations.

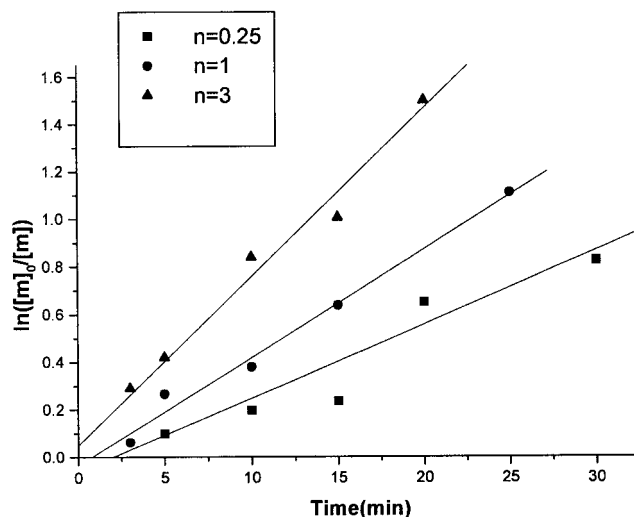


Figure 8 Kinetics of ATRP for the MMA at different catalyst concentrations under MI. Conditions: $[\text{M}]_0 = 9.46\text{M}$; $[\text{MMA}]_0/[\text{DCIX}]_0/[\text{CuCl}]_0/[\text{PMDETA}]_0 = 400 : 1 : n : 3n$ ($n = 0.25, 1, 3$).

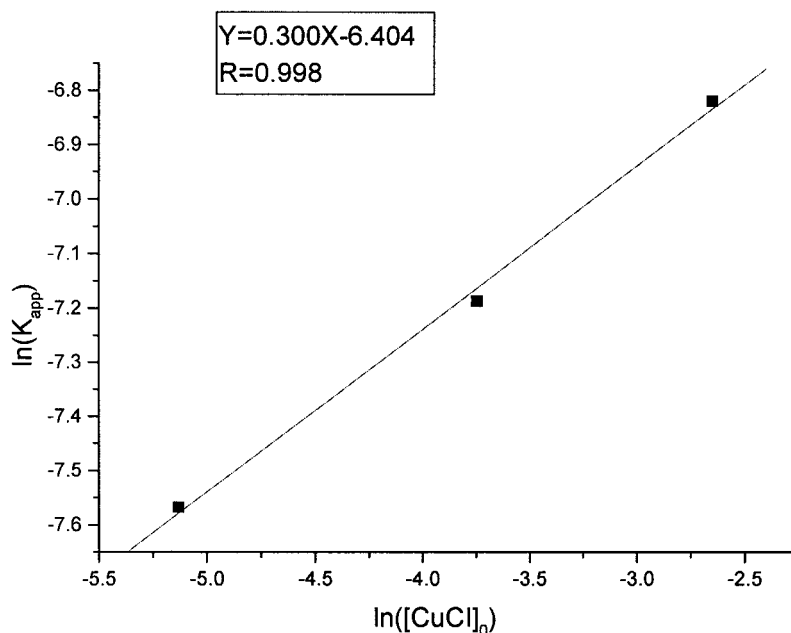


Figure 9 Plot of k_p^{app} versus $\ln[CuCl]_0$ for the ATRP of MMA.

Effect of concentration of catalyst on polymerization

Figure 8 shows the kinetic plots of $\ln[M]_0/[M]$ versus time for ATRP of MMA catalyzed by CuCl/PMDETA initiated by DCIX at various catalyst concentrations. The polymerization processes are approximately first-order kinetics with respect to the catalyst concentrations. The result shows that the apparent rate constant increases with increasing concentration of CuCl; fur-

thermore, a plot of k_p^{app} versus $\ln[CuCl]_0$ shows clearly that the rate of polymerization follows a linear order with respect to the concentration of the CuCl (Fig. 9).

The effects of the concentration of catalyst (CuCl/PMDETA) on molecular weights and molecular weight distributions are shown in Figure 10. The molecular weights increase with increasing conversion, and the molecular weight distributions are less than 1.5. However, at low concentrations of catalyst

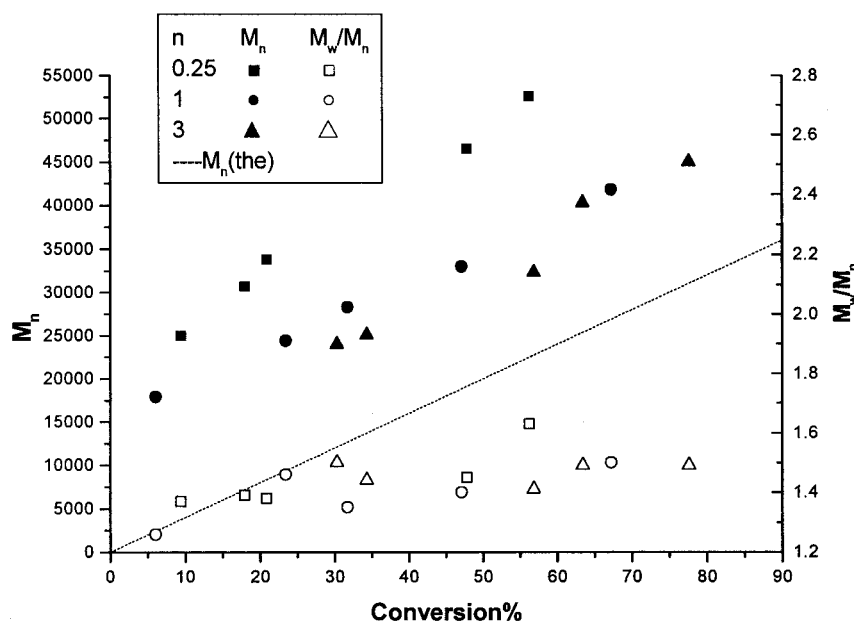


Figure 10 Dependency of M_n and M_w/M_n on conversion for the ATRP of MMA under MI at different catalyst concentrations. Conditions are as in Figure 8.

TABLE I
Effect of Different Catalysts and Polymerization Processes on ATRP of MMA^a

Catalyst	Time (min)	Conversion (%)	$M_{n(th)}$	$M_{n(GPC)}$	PDI	f
CuCl	180 (CH)	44.4	17,700	34,600	1.43	0.51
	15 (MI)	47.1	18,800	33,000	1.40	0.57
CuBr	180 (CH)	53.1	21,200	46,000	1.45	0.46
	15 (MI)	66.8	26,700	34,700	1.44	0.77
CuSCN	110 (CH)	26.8	10,700	41,500	1.46	0.26
	15 (MI)	28.6	11,400	28,400	1.50	0.40

^a $[MMA]_0/[DCIX]_0/[Catalyst]_0/[PMDETA]_0 = 400:1:1:3$;
 $T = 72^\circ\text{C}$.

$([MMA]_0/[CuCl]_0/[PMDETA]_0 = 400:0.25:0.75)$, the initiator efficiency is lower. For example, at conversion 47%, the initiator efficiency is 0.41 ($[MMA]_0/[CuCl]_0/[PMDETA]_0 = 400:0.25:0.75$), whereas the other ($[MMA]_0/[CuCl]_0/[PMDETA]_0 = 400:1:3$) is 0.57. The reason may be that the lower concentration of catalyst cannot efficiently turn the active species into a dormant species, and many more side reactions occur.

Effect of different catalysts on polymerization

Table I shows the effect of different catalysts (CuCl, CuBr, CuSCN) on polymerization under MI and CH

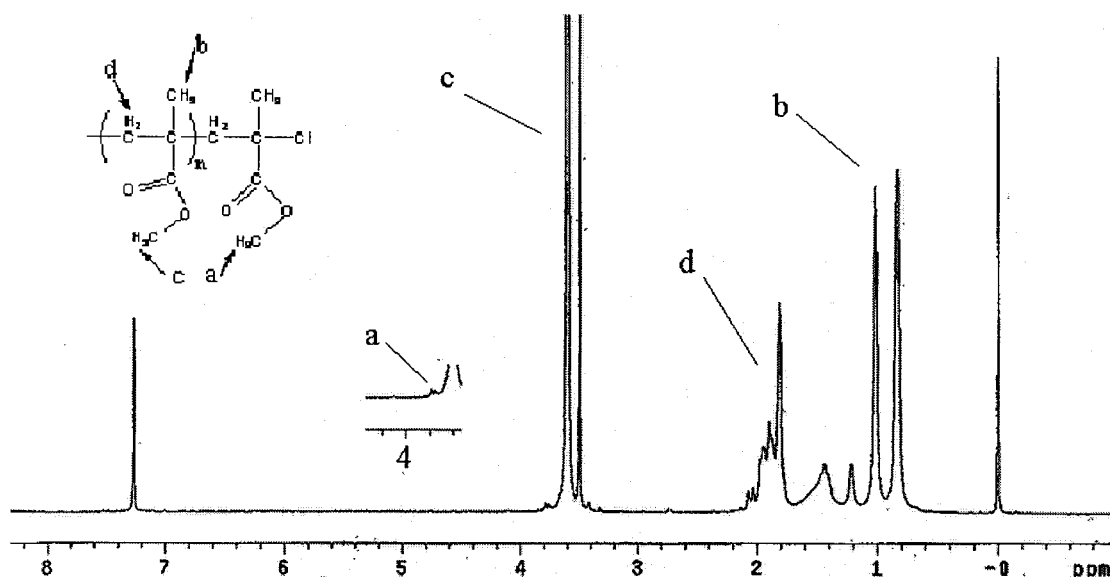


Figure 11 $^1\text{H-NMR}$ spectrum of PMMA initiated with DCIX/CuCl/PMDETA system.

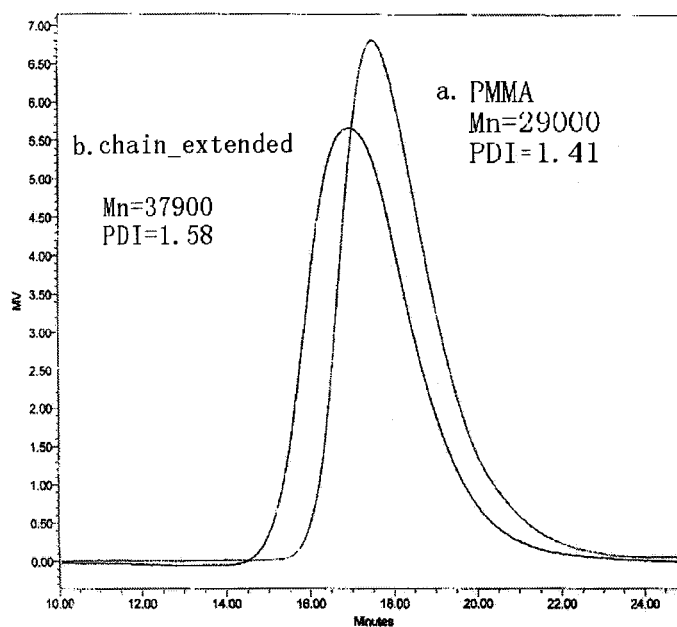


Figure 12 GPC curves of PMMA (a) before and (b) after chain extension with MMA.

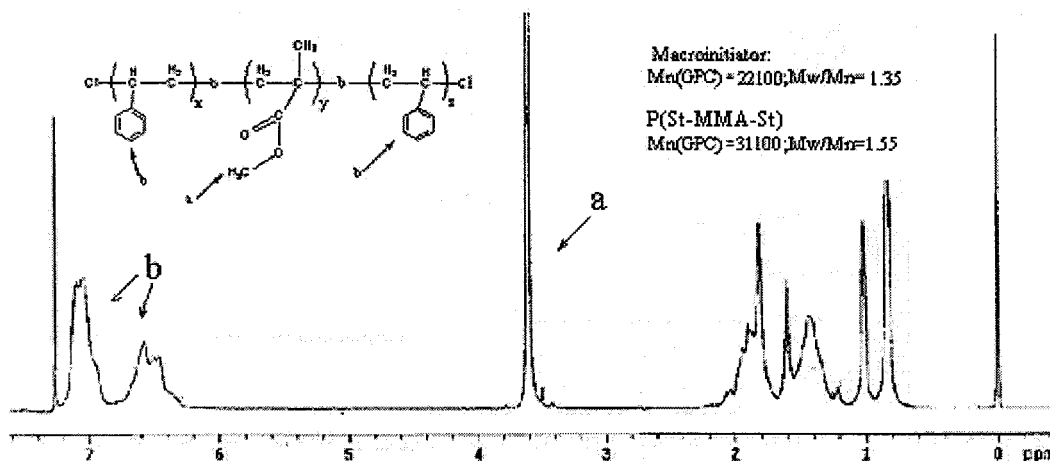


Figure 13 $^1\text{H-NMR}$ spectrum of prepared poly(St-MMA-St).

conditions. It may be observed that for all catalyst systems MI can enhance the polymerization rate and the initiator efficiency compared with CH. The molecular weight distributions are controlled less than 1.50.

End group analysis, chain extension, and block polymerization with styrene

The structure of chain ends of prepared PMMA was analyzed by $^1\text{H-NMR}$ spectroscopy. Figure 11 presents the $^1\text{H-NMR}$ spectra of PMMA. The signals at 0.83–1.21 ppm are assigned to the protons of methyl groups of $-\text{C}(\text{CH}_3)(\text{COOCH}_3)$, the signals at 1.44–2.07 ppm are attributed to the methylene group of $-\text{CH}_2-$, and the peaks at 3.60 ppm correspond to methoxy groups in the main chain. The signal at 3.78 is for the methoxy group next to the halogen chain end.

An additional method toward verifying the functionality of a polymer prepared by ATRP is as a macroinitiator for the same or other monomers. The chain-extension polymerization of MMA with PMMA [$M_n(\text{GPC}) = 29,000$, $M_w/M_n = 1.41$] as the macroinitiator was successfully performed. As is shown in Figure 12, the molecular weight of the chain extended. However, the molecular weight distribution (1.58) is a little broader than that of the macroinitiator (1.41) because a small part of the macroinitiator probably remains unreacted. The chain-extension polymerization further verifies the active nature of the precursor chain end.

Styrene was used as a second monomer to obtain an ABA-type block polymer. Macroinitiator PMMA [$M_n(\text{GPC}) = 22,100$, $M_w/M_n = 1.35$] successfully blocked with St, and obtained P(St-MMA-St) polymer. The $^1\text{H-NMR}$ spectrum of P(St-MMA-St) block polymer is shown in Figure 13.

CONCLUSIONS

ATRP of MMA was successfully carried out using DCIX/CuCl/PMDETA as an initiator system under microwave irradiation. Applying MI to the ATRP of MMA can significantly enhance the rate of polymerization, and slightly increase the initiator efficiency. In addition, by determining the Cu concentration in the polymerization system, an additional explanation was posited as to why MI can enhance the polymerization rate.

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