

Atom Transfer Radical Bulk Polymerization of Methyl Methacrylate under Microwave Irradiation

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ABSTRACT: Microwave irradiation (MI) was applied to the atom transfer radical bulk polymerization of methyl methacrylate. The influence of the amount of the refluxing solvent used for controlling the polymerization temperature, irradiation power, irradiation time, and initiator concentration on the conversion, molecular weight, and molecular weight distribution of the polymers was studied with a benzyl chloride/cuprous chloride/2,2'-bipyridyl initiation system and compared with the corresponding conventional heating (CH) process. In comparison with CH, the results can be summarized as follows. The polymerization rate for reaching 70% conversion increased 2.6–5.1 times under an irradiation power of 270–630 W. The apparent increasing rate constant was much larger than that with CH and increased with the irradiation power. MI produced a higher polymerization rate and conversion even if the concentration of the initiation system was very low (initial monomer concentration/initial initiator concentration = 200:0.33 mol/mol) and the polydispersity index (DI) was narrower; how-

ever, CH yielded almost no polymers. MI promoted the activities of the catalyst and monomer, and its initiation efficiency was higher than that with CH and increased with the irradiation power. MI obviously played an important role in promoting the polymerization rate of atom transfer radical polymerization (ATRP). MI reduced the concentration of the initiation system and perhaps made ATRP controlled (cf. uncontrolled ATRP with CH); at the same time, it made the DI values of the polymers narrower. In comparison with the initiation efficiencies found with benzyl bromide and 2,2'-azobisisobutyronitrile used as initiators, the initiation efficiency with *p*-toluene sulfonyl chloride used as an initiator was higher; moreover, DI was much narrower (1.17), and the polymerization rate was greater. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1787–1793, 2003

Key words: irradiation; atom transfer radical polymerization (ATRP); living polymerization

INTRODUCTION

Since Gedye and Smith¹ and Giguere and Brayl² reported in 1986 that microwave irradiation (MI) could enhance some organic chemistry reactions, MI applied to enhance chemical reactions has become a hot topic.

Atom transfer radical polymerization (ATRP) is a new technique of living radical polymerization³ that has many advantages and great industrialization prospects in comparison with other living radical polymerizations. However, the main problems of ATRP are the larger amount of catalyst needed and the lower activity of the initiation system. Usually, a higher temperature (ca. 120°C) and a greater catalyst concentration are required for a higher polymerization rate (R_p); this results in a reduced molecular weight (i.e., several thousand to several tens of thousands) much lower than that obtained with the conventional radical po-

lymerization process. The key goals for ATRP are, therefore, to reduce the amount of catalyst needed and to experiment at a lower temperature range of 40–80°C.

Recently, all ATRPs have almost been studied with a conventional heating (CH) method, and so far there has not been any other report about ATRP with MI besides that of our group.⁴ For this reason, MI was applied to ATRP by us, and the polymerization of methyl methacrylate (MMA) was studied with MI in this work. With the help of the thermal effect and no-thermal effect provided by MI, the activities of both the catalyst and monomer were raised, and R_p was then promoted; this allowed the reaction to proceed at a lower temperature, and so the goal of reducing the amount of the catalyst needed and the temperature was reached.

EXPERIMENTAL

Apparatus

A self-improved domestic microwave oven (M9D88, Samsung) is schematically illustrated in Figure 1. Its irradiation power (P) was from 90–900 W. The reactor was a three-necked bottle (1000 mL) with a refluxing

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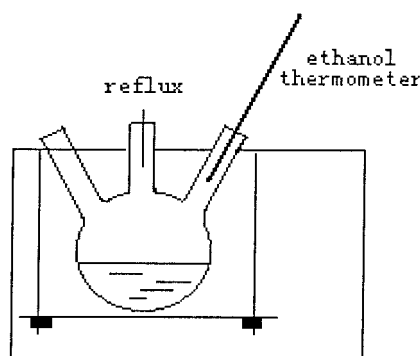


Figure 1 Sketch map of the MI experimental installation.

solvent used for controlling the reaction temperature (the boiling point of the solvent). Dry and sealed glass tubes filled with cuprous chloride (CuCl), benzyl chloride (PhCH_2Cl), 2,2'-bipyridyl (bpy), and MMA were placed in the refluxing solvent so that polymerization could take place.

Materials

MMA (Chemically pure; Shanghai Chemical Reagent Co., Ltd.) was purified by distillation *in vacuo* and stored in a freezer at 5°C . The ligand bpy analytical reagent (AR; Shanghai Chemical Reagent Co., Ltd.) was recrystallized from acetone. The initiator PhCH_2Cl (AR; Shanghai Chemical Reagent Co., Ltd.) was distilled *in vacuo* and stored in a dry, brown bottle. CuCl (AR; Shanghai Chemical Reagent Co., Ltd.) was purified according to a literature procedure.⁵ All other reagents used in this study were analytical grade.

General polymerization procedures

A dry glass tube was filled with CuCl , bpy, PhCH_2Cl , and MMA. Three freeze-pump-thaw cycles were performed, and the tube was sealed *in vacuo* and placed in the self-improved microwave oven with a reflux of CCl_4 at the boiling point (76.8°C) for a certain time with MI, whereas with CH_4 , the tube was placed in an oil bath. The polymerizations were stopped at a desired time by the cooling of the tubes in ice water. Afterward, the tubes were opened, and the contents were transferred and dissolved in acetone.

Characterization

The conversion of the monomer was determined by gravimetry. The molecular weights and molecular weight distributions were measured with a Waters 1515 gel permeation chromatography (GPC) instrument with tetrahydrofuran as a mobile phase and with

a column temperature of 30°C . Polystyrene standards were used to calibrate the columns.

RESULTS AND DISCUSSION

Effect of the amount of the refluxing solvent used for controlling the temperature on the monomer conversion

The irradiation energy provided by an oven can be expressed as follows:

$$E = E_1 + E_2 + E_3 + E_4 \quad (1)$$

where E is the total irradiation energy, E_1 is the irradiation energy absorbed by the refluxing solvent, E_2 is the irradiation energy used for the reaction system, E_3 is the irradiation energy reflected by the system, and E_4 is the irradiation energy consumed by the environment of the system.

As can be seen from Figure 2, the amount of the refluxing solvent used for controlling the temperature had an obvious effect on the conversion of the monomer, and the optimum amount was 400 mL. From eq. (1), we can see that only E_2 was used for the reaction system; therefore, the greater the ratio was of E_2 to E , the faster R_p was, and the higher the monomer conversion was. When a smaller amount of the refluxing solvent was used, the reaction system could not match well with the MI field; then, E_3 increased, and E_2 decreased. If its amount continued increasing, the reaction system could gradually match well with the MI field; E_3 decreased, E_2 increased, and the conversion of the monomer also increased correspondingly. However, when the amount reached a certain value (400 mL in our experiment), because E_3 and E_4 had in-

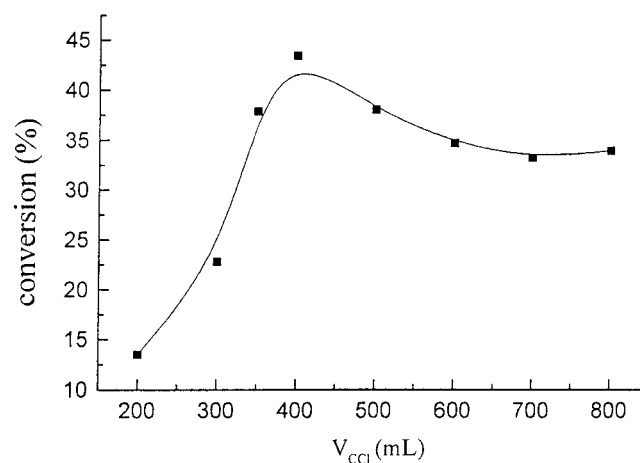


Figure 2 Conversion dependence on the amount of the solvent (CCl_4) used for controlling the temperature (temperature = 76.8°C ; $P = 360$ W; time = 200 min; $[\text{MMA}]_0 = 0.02$ mol; molar ratio $[\text{MMA}]_0:[\text{PhCH}_2\text{Cl}]_0:[\text{CuCl}]_0:[\text{bpy}]_0 = 200:1:1:3$).

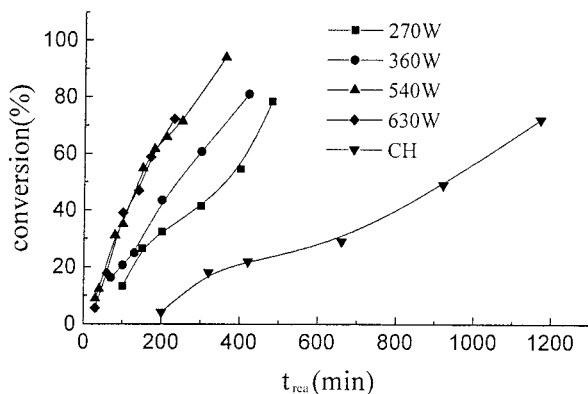


Figure 3 Conversion dependence on t_{rea} (temperature = 76.8°C; $[\text{MMA}]_0 = 0.02$ mol; amount of $\text{CCl}_4 = 400$ mL; molar ratio $[\text{MMA}]_0:[\text{PhCH}_2\text{Cl}]_0:[\text{CuCl}]_0:[\text{bpy}]_0 = 200:1:1:3$).

creased to its counterbalance and E was kept almost constant, if the amount continuously increased again, E_2 decreased with increasing E_1 , and this resulted in a decrease in the conversion. However, the declining extent of conversion was small, about 10%.

Control over the polymerization temperature and the choice of P

The polymerization temperature in this experiment was controlled by a solvent refluxing method. The experiment was carried out at 76.8°C (the boiling point of CCl_4) with CCl_4 with a lower dielectric constant ($\delta = 2.205$) as the solvent of the reflux. The monomer was MMA with a higher polarity ($\delta = 3.5$) so that the irradiation energy provided by the microwave oven could be absorbed by the monomer and reactants as much as possible; this enabled us to investigate the influence of the irradiation energy on the polymerization better. The experimental results showed that the minimum P value of the microwave oven to keep 400 mL of CCl_4 refluxing was 270 W. We also found that when P was greater than 630 W, the solvent refluxed violently, and this resulted in the cracking of the sealed tube. That was why we chose P values from 270 to 630 W.

Effect of the polymerization time on conversion and comparison with CH

The conversion dependence on the reaction time (t_{rea} ; min) under different powers is shown in Figure 3. The monomer conversions increased with t_{rea} , and all conversions with MI were higher than those with CH; the higher P was, the larger the conversion was. This demonstrated that R_p increased with P . Compared with the CH method, the new method with MI had a much higher R_p . Under the minimum P value of 270 W, the polymerization resulted in a conversion of 78.4% for 480 min. With the same temperature and

catalyst ratio, the CH method resulted in a conversion of 72.3% for 1170 min, which was about 2.44 times that obtained with MI. The latter reduced the polymerization time by 59% and also increased the conversion by 6%. Also, according to Figure 3, with a conversion of 70%, 1150 min was needed with CH; comparatively, only 225 min was needed with MI of 630 W, which was 5.1 times R_p of the former. With the same conversion, 240 min was needed for 540 W, which was 4.8 times higher; 350 min was needed for 360 W, which was 3.3 times higher; and only 450 min was needed for the lowest value, 270 W, which was 2.6 times higher. This clearly demonstrated that MI enhanced the polymerization greatly.

Dependence of the conversion on the apparent irradiation energy (E) with different values of P

E supplied to every gram of the monomer by the microwave oven can be expressed as follows:

$$E \text{ (kJ/g)} = (60t_{\text{rea}}) \cdot (P/1000) / M \quad (2)$$

where M is the initial mass of the monomer. As depicted in Figure 4, at the same temperature, ratio of initial concentrations ($[\text{MMA}]_0:[\text{PhCH}_2\text{Cl}]_0:[\text{CuCl}]_0:[\text{bpy}]_0$), and amount of CCl_4 , if the E values were the same, the conversions changed little, even though the P values were different. Moreover, conversion increased linearly with E .

Polymerization of MMA in the bulk initiated by the $\text{PhCH}_2\text{Cl}/\text{CuCl}/\text{bpy}$ initiation system

The mechanism of ATRP is outlined as Scheme 1. X is Cl or Br, M_t^+ is the transition-metal species, M is the monomer, K_i is the initiation rate constant, k_p is the propagation rate constant, k_{act} is the activation (oxida-

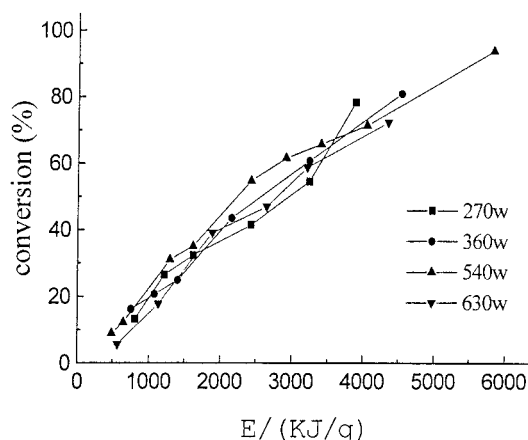


Figure 4 Conversion dependence on E (temperature = 76.8°C; $[\text{MMA}]_0 = 0.02$ mol; amount of $\text{CCl}_4 = 400$ mL; molar ratio $[\text{MMA}]_0:[\text{PhCH}_2\text{Cl}]_0:[\text{CuCl}]_0:[\text{bpy}]_0 = 200:1:1:3$).

TABLE II
Data of Conversion, Molecular weight, Molecular Weight Distribution, and f for ATRP of MMA

CH								
Conversion	18.0	21.8	29.0	49.1				
$M_{n,th}$	3,600	4,360	5,800	9,820				
$M_{n,GPC} (\times 10^4)$	11.7	12.0	13.5	13.5				
DI	1.44	1.45	1.45	1.57				
f (%)	3.1	3.6	4.3	7.3				
MI								
270 W								
Conversion	13.2	26.5	32.3	41.4	54.5	78		
$M_{n,GPC} (\times 10^4)$	5.2	6.8	8.0	8.6	8.9	7.8		
$M_{n,th}$	2,640	5,300	6,460	8,280	10,900	15,600		
DI	1.96	1.56	1.65	1.52	1.72	1.6		
f (%)	5.1	7.8	8.0	9.6	12.2	20.		
360 W								
Conversion	16.2	20.6	43.5	60.7	81.02			
$M_{n,th}$	3,240	4,120	8,700	12,140	16,200			
$M_{n,GPC} (\times 10^4)$	7.3	7.1	7.2	8.1	7.0			
DI	1.45	1.45	1.39	1.51	1.56			
f (%)	4.4	5.9	12.1	15.0	23.2			
540 W								
Conversion	12.2	31.0	35.0	54.7	61.5	65.	71.4	93.9
$M_{n,th}$	2,440	6,200	7,000	10,940	12,300	13,000	14,280	18,780
$M_{n,GPC} (\times 10^4)$	3.1	5.0	5.5	6.0	7.1	7.1	6.6	5.5
DI	1.59	1.70	1.54	1.39	1.59	1.5	1.89	1.65
f (%)	7.8	12.4	12.7	18.3	17.3	18.3	21.7	34.2

[MMA]₀: [PhCH₂Cl]₀: [CuCl]₀: [byp]₀ = 200:1:1:3 (molar ratio), [MMA]₀ = 0.02 mol, temperature = 76.8°C.

biphenyl ether for ATRP of MMA at 110°C with PhCH₂Cl as an initiator.

In comparison with the values found with MI, the polydispersity index (DI = 1.45) with CH was narrower, but $M_{n,GPC}$ was higher, about 110,000–140,000. DI with MI was a little wider than that with CH, from 1.39 to 1.70, but $M_{n,GPC}$ decreased, being less than 90,000. All of this showed that MI could improve the activities of the catalysts and monomers and also increase the f value of PhCH₂Cl. From Table II, it can be seen that the f value of PhCH₂Cl with MI was higher than that with CH with a similar conversion, and it increased with P . However, because of the low efficiency of the initiation, the initiator perhaps did not take part in the reaction wholly, and the slow initiation reaction also caused the forming time of the dormant species (RM_nCl) to be different. All these would cause DI to be wider.⁷

When the conversion was more than 60% (Table II), the molecular weight decreased with the conversion slowly, and this was perhaps the result of the degradation of polymer chains under long-time irradiation.

Effect of the different initiator concentrations on ATRP of MMA

Table III shows that the conversion decreased with the initiator concentration with MI, but R_p and the conversion (40.2%) were still higher, even for [MMA]: [phCH₂Cl] = 200:0.33, and the DI was also narrower (1.55). At the same time, under these conditions, the rate was very slow with CH, and almost no polymer formed. DI decreased with the concentration of the initiator, although the conversion decreased. Compared with CH, MI could increase R_p and decrease the polymerization time. The main problems for the in-

TABLE III
Effect of Different Initiator Concentrations on ATRP

[MMA] ₀ /[PhCH ₂ Cl] ₀ (molar ratio)	CH Conversion (%)	MI, CCl ₄ = 400 mL; P = 360 W			
		Conversion (%)	$M_{n,th}$	$M_{n,GPC}$	DI
200:1	3.12%	62.4	12,499	253,490	1.98
200:0.5	0	52.2	20,917	57,650	1.71
200:0.4	0	43.2	21,641	95,790	1.49
200:0.33	0	40.2	24,125	124,570	1.55

Temperature = 76.8°C: [MMA]₀ = 0.04 mol: [PhCH₂Cl]₀: [CuCl]₀: [bpy]₀ = 1:1:3 (molar ratio): time = 180 min.

TABLE IV
Conversion and M_n at a Lower Initiator Concentration

Conversion (%)	$M_{n,th}$	$M_{n,GPC}$	f (%)	DI
9.9	3,981	73,070	5.4	1.82
20.5	8,202	87,890	9.3	1.48
27.8	11,137	103,090	10.8	1.48
39.7	15,911	108,240	14.7	1.47

[MMA]₀: [PhCH₂Cl]₀: [CuCl]₀: [bpy]₀ = 200:0.5:0.5:1.5 (molar ratio); P = 540 W, CCl₄ = 400 mL, temperature = 76.8°C.

dustrialization of ATRP lie in the low activity and large amount of the initiator needed. Maybe MI could resolve these problems. Of course, there would be still a lot of work to do in this field.

Table IV shows that $M_{n,GPC}$ increased with conversion, and the largest $M_{n,GPC}$ value was about 108,000 for a corresponding conversion of only 39.7% with [M]₀: [I]₀ = 200:0.5. In contrast to Table II, the changing trends for the number-average molecular weight (M_n) and DI with conversion are similar. However, the great difference between the tables is that the concentration of the initiator in Table IV ([M]₀: [I]₀ = 200:0.5) is lower than that in Table II ([M]₀: [I]₀ = 200:1), the latter twice that of the former, but the minimum $M_{n,GPC}$ value is about 73,000 in Table IV and 31,000 in Table II for a similar conversion. Therefore, because of the degradation of the polymer chains, the conversion became lower when M_n reached its largest value at a lower concentration of the initiator, but the corresponding largest M_n was much larger than that at a higher concentration of the initiator.

Effect of other initiation systems on ATRP of MMA

p-Toluene sulfonyl chloride (*p*-TsCl), benzyl bromide (PhCH₂Br), and 2,2'-azobisisobutyronitrile (AIBN) were used as initiators of ATRP of MMA under conditions with MI and CH, respectively. The results are shown in Table V.

p-TsCl used as an initiator

Higher f values and the lowest DI value (1.17) were reached, and the polymerization could proceed at a higher rate. The conversion of the monomer reached 52.3% for 120 min with MI, which was 29% higher, and the f value was 18% higher; also, the DI was narrower in comparison with that from CH (only a 37.4% conversion for 150 min). When we prolonged t_{rea} to 300 min with CH, we obtained a conversion similar to that from MI, but the DI of the latter was still narrower than that of the former. These results show that MI has good prospects for applications in ATRP.

PhCH₂Br used as an initiator

A comparison of entries 5 and 6 in Table V shows that for the same t_{rea} value, the conversion with MI was 17.7% higher than that with CH, and the DI (1.22) of the former was also narrower than that (1.84) of the latter. The f value with MI was almost 10% higher than that with CH. Even though we reduced the irradiation time to 20 min, the conversion of the monomer could still reach 4.3%.

AIBN used as an initiator

When [M]₀: [I]₀ was 200:1 (entry 7), the DI was wider, and ATRP was out of control. However, when we lowered the concentration of the initiator, that is, [M]₀: [I]₀ = 200:0.5 (entry 8), the DI was narrower (1.43). Comparing it with the results from CH, we knew that in the same period of time (20 min), the conversion and f value were almost 6% higher than those with CH, and the DI (1.43) was narrower than that (1.60) with CH.

When we finished the polymerization with MI, we could change the uncontrolled ATRP into controllable ATRP by reducing the concentration of the initiator, and the DI became narrower. Moreover, Table IV shows that although the conversion decreased while

TABLE V
Data of Conversion and Molecular Weight by Different System for the ATRP of MMA

Entry	System	Method	Time (min)	Conversion		DI	f (%)	
				(%)				
1	<i>p</i> -TsCl	MI	120	52.3	10,469	17,120	1.17	55.5
2	<i>p</i> -TsCl	CH	150	23.1	4,626	10,560	1.39	37.4
3	<i>p</i> -TsCl	CH	300	56.1	11,229	24,430	1.23	43.4
4	PhCH ₂ Br	MI	20	4.3	851	20,810	1.31	4.0
5	PhCH ₂ Br	MI	100	52.1	10,426	43,230	1.22	26.4
6	PhCH ₂ Br	CH	100	34.3	6,868	33,920	1.84	16.1
7	AIBN	MI	20	78.1	15,633	35,160	2.49	48.5
8	AIBN	MI	20	25.5	10,216	109,890	1.43	11.7
9	AIBN	CH	20	19.6	7,857	111,160	1.60	5.3

P = 540 W; amount of CCl₄ = 400 mL 1–7 [MMA]₀: [I]₀: [CuCl]₀: [bpy]₀ = 200:1:1:3 (molar ratio); 8 and 9 [MMA]₀: [I]₀: [CuCl]₀: [bpy]₀ = 200:0.5:1:3 (molar ratio).

the concentration of the initiator was reduced, the DI was narrower.

CONCLUSIONS

1. The optimum amount of the refluxing solvent used for controlling the temperature of MI was 400 mL. P was moderate, between 270 and 630 W. Under the same polymerization conditions and with the same value of E , nearly the same conversion of the monomer was obtained. The conversion was in direct proportion to E .
2. R_p with MI was notably faster than that with CH. When P was 270–630 W and the conversion was 70%, R_p with MI could be 2.7–5.1 times that with CH. This showed that MI could promote ATRP.
3. We plotted the kinetic curve of the polymerization with MI. $\ln([M]_0/[M]_t)$ was directly proportional to t_{rea} over a very wide range of monomer conversions. The reaction showed first-order kinetics. At the same temperature and ratio, k_p^{APP} from MI was much larger than that from CH and increased with increasing P . This also showed that MI could promote ATRP.
4. The polymer had a narrower DI (ca. 1.45) but a higher M_n value with CH; by contrast, it had a wider DI (ca. 1.39–1.7) but a lower M_n value with MI. This showed that MI could enhance the ac-

tivities of both the initiator and monomer and also increase the f value of PhCH_2Cl , which was higher than that from CH. $M_{n,\text{GPC}}$ decreased but f increased with P .

5. MI yielded a higher R_p value, a higher conversion, and a narrower molecular weight distribution (DI = 1.55) when the initiator system was very low ($[\text{MMA}]_0/[\text{PhCH}_2\text{Cl}]_0 = 200:0.33$). Under the same conditions, CH yielded little polymer. Decreasing the concentration of the initiator by MI may change an uncontrolled ATRP into a controllable ATRP and make the molecular weight distribution narrower.
6. In contrast to PhCH_2Br and AIBN used as initiators, $p\text{-TsCl}$ had some advantages, such as a high f value, a narrow molecular weight distribution, and a high R_p value.

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