

# Copper-Based Reverse ATRP Process for the Controlled Radical Polymerization of Methyl Methacrylate

Kai Pan, Long Jiang, Juan Zhang, Yi Dan

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

Received 2 June 2006; accepted 6 November 2006

DOI 10.1002/app.26246

Published online 27 March 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of copper-based reverse atom transfer radical polymerizations (ATRP) were carried out for methyl methacrylate (MMA) at same conditions (in xylene, at 80°C) using *N,N,N',N'*-tetramethylethylenediamine (TMEDA), *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA), 2,2'-bipyridine, and 4,4'-Di(5-nonyl)-2,2'-bipyridine as ligand, respectively. 2,2'-azobis(isobutyronitrile) (AIBN) was used as initiator. In CuBr<sub>2</sub>/bpy system, the polymerization is uncontrolled, because of the poor solubility of CuBr<sub>2</sub>/bpy complex in organic phase. But in other three systems, the polymerizations represent controlled. Especially in CuBr<sub>2</sub>/dNbpy system, the number-average molecular weight increases linearly with monomer conversion from 4280 up to 14,700. During the whole polymerization, the polydispersities are quite low (in the range 1.07–1.10). The different results obtained from the four systems are due to the

differences of ligands. From the point of molecular structure of ligands, it is very important to analyze deeply the two relations between (1) ligand and complex and (2) complex and polymerization. The different results obtained were discussed based on the steric effect and valence bond theory. The results can help us deep to understand the mechanism of ATRP. The presence of the bromine atoms as end groups of the poly(methyl methacrylate) (PMMA) obtained was determined by <sup>1</sup>H-NMR spectroscopy. PMMA obtained could be used as macroinitiator to process chain-extension reaction or block copolymerization reaction via a conventional ATRP process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 521–526, 2007

**Key words:** reverse atom transfer radical polymerization; ligand; methyl methacrylate; kinetics (polym.)

## INTRODUCTION

Atom transfer radical polymerization (ATRP) is a robust and versatile technique for the synthesis of well-defined polymers with various architectures, such as block,<sup>1–6</sup> graft,<sup>7–10</sup> and star polymers,<sup>11,12</sup> and narrow molecular weight distribution. It can be realized through two different initiation systems—an organic halide catalyzed by a transition-metal complex in its lower oxidation state, that is, normal ATRP; a conventional radical initiator [such as 2,2'-azobis(isobutyronitrile) (AIBN)] catalyzed by a transition-metal species, named reverse ATRP.<sup>13–16</sup> The reverse ATRP has proved to be the better pathway to initiate ATRP.

For ATRP, a suitable catalyst enables the system to establish a dynamic equilibrium between growing radicals and dormant chains rapidly and reduce the contribution of the inevitable radical termination, so it can offers the controlled/"living" character to the po-

lymerization. The catalyst is usually a transition metal complex. Obviously, a ligand in the metal complex plays a crucial role in solubility and stability of a complex, and consequently the concentration of the activator and the deactivator in the system, which has great influence on the control of polymerization. Many ligands were employed in recent years, which give us more choices for ATRP. But different ligands bring different controllability of ATRP. Hence, it is necessary for us to understand deeply the molecular structure of ligands, the complex state of ligands with transition metal, and the influence of the complex on polymerization. So, we chose the common copper as the transition metal and four different structure ligands, at the same conditions, a series of copper-based reverse ATRPs for MMA in xylene at 80°C were carried out, respectively. The different results obtained were discussed based on the steric effect and valence bond theory. It can give us some guidance on choosing the ligand in ATRP.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA) was purchased from Chengdu Kelong Chemical Reagent Factory (Chengdu, China) and distilled under reduced pressure prior to use. CuBr<sub>2</sub> (98.5%), xylene all came from Chengdu Kelong Chemical Reagent Factory (Chengdu, China),

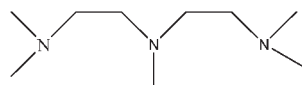
Correspondence to: Y. Dan (danyichenweiwei@163.com).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20374036.

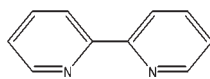
Contract grant sponsor: Research Foundation of Sichuan Province of China; contract grant number: 03JY029-054-1.

Contract grant sponsor: Talent Training Foundation of Sichuan Province of China.

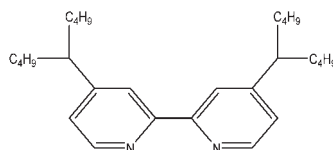
## (A) Aliphatic amines ligand:

N,N,N',N'-teramethylethylenediamine  
(TMEDA)N,N,N',N',N''-pentamethyldiethylenetriamine  
(PMDETA)

## (B) bpy and substituted bpy ligand:



2,2'-bipyridine (bpy)



4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy)

**Scheme 1** Ligands used for the preparation of ATRP catalyst complexes.

and were used directly. 2,2'-Azo-bisobutyronitrile (AIBN) (A.R) was obtained from Beijing Chemical Reagent Factory (Beijing, China) and recrystallized from methanol before used. 2,2'-bipyridine (bpy) (A.R) came from Beijing Shiyong Chemical Reagent Factory (Beijing, China) and used directly. 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) (97%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (99%) came from Aldrich and used as received. *N,N,N',N'*-teramethylethylenediamine (TMEDA) (99%) came from ACROS ORGANICS and used as received.

**Polymerization**

A 150-mL Schlenk flask equipped with a magnetic stirrer was charged with MMA and  $\text{CuBr}_2$ , under the argon protected, the mixture was stirred for 0.5 h. AIBN and ligand were dissolved in xylene and then added to the Schlenk flask. At room temperature and argon atmosphere, the mixture of MMA,  $\text{CuBr}_2$ , AIBN, ligand, and xylene was stirred for 1 h and then placed in a water bath with magnetic stirring at  $80^\circ\text{C}$ . The reactions were carried out under stirred and argon for 3 h. Samples were taken periodically via syringe to monitor the conversion and molecular weight. The monomer conversion was determined gravimetrically, and then the samples were dissolved in acetone and precipitated in methanol, and then dried.

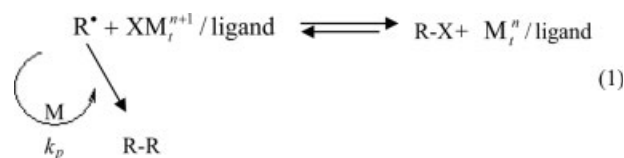
**Characterization**

The monomer conversion was determined gravimetrically. The number-average molecular weight ( $M_n$ ) and polydispersities ( $M_w/M_n$ ) of the obtained polymers were measured at  $35^\circ\text{C}$  by gel permeation chromatography on a waters 2410 instrument using THF as the solvent (1.0 mL/min), calibration with polysty-

rene standards, and Waters Millenium 32 as the data-processing software.  $^1\text{H-NMR}$  spectra were taken at  $25^\circ\text{C}$  on a Bruker ARX400 (400 MHz) spectrometer in  $\text{CDCl}_3$  using tetramethylsilane as internal reference.

**RESULTS AND DISCUSSION**

The key issue to a well-controlled radical polymerization is to maintain a rapid equilibrium between the growing radical and the dormant species. In ATRP or reverse ATRP, such equilibrium can be achieved by using a metal complex that switches between  $n$  and  $n + 1$  oxidation states eq. (1).



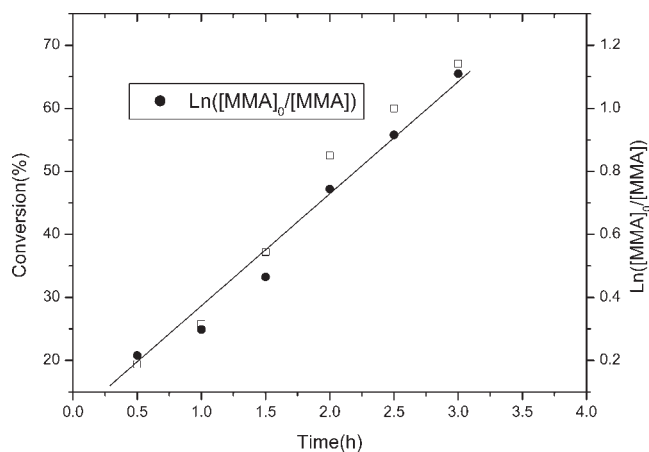
The same principle holds for bulk and solution systems. Since the first requirement for control over the polymerization is to have sufficient concentrations of both the activator (metal complex at the lower oxidation state) and the deactivator (metal complex at the higher oxidation state), the choosing of the proper ligand becomes crucial. To understand the effect of ligand on the polymerization better, we chose two types of ligands with different electronic effect and different solubility, i.e., aliphatic amines (TMEDA, PMEDTA) and bpy and substituted bpy (dNbpy), in our experiments. The molecular structures of the ligands are depicted in Scheme 1. The polymerizations were carried out under the same conditions, a typical reverse ATRP in xylene under the conditions described in Table I.

**Controllability of MMA polymerization in  $\text{CuBr}_2/\text{TMEDA}$  and  $\text{CuBr}_2/\text{PMEDTA}$  systems**

The radical polymerization of MMA using  $\text{CuBr}_2/\text{TMEDA}$  complex as catalyst was carried out in xylene at  $80^\circ\text{C}$ , the mol ratio of xylene : MMA : AIBN :  $\text{CuBr}_2$  : TMEDA is 1217 : 604 : 1.9 : 1 : 2. From Figure 1 we can see that the conversion of MMA reaches 19.4% within 0.5 h once the polymerization begins and reaches 67.1% after 3 h. The logarithmic conversion data  $\ln([\text{MMA}]_0/[\text{MMA}]_t)$  ( $[\text{MMA}]_0$  and  $[\text{MMA}]_t$  are the concentration of monomer at time 0

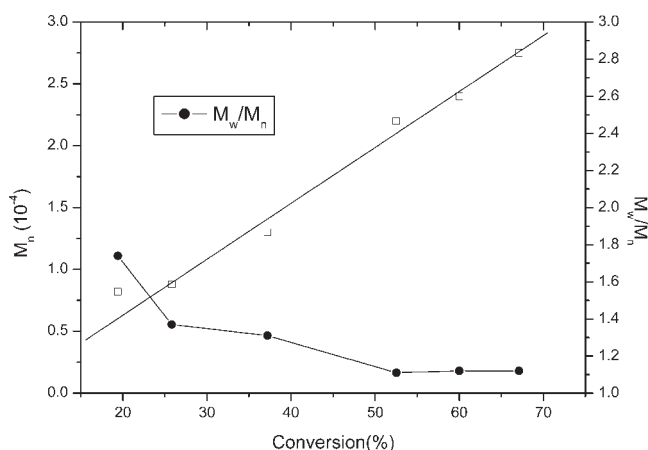
**TABLE I**  
Typical Recipe for Reverse ATRP Process of  
MMA in Xylene System

Monomer	MMA	18 mL or 16.9 g	604 equiv
Solvent	Xylene	42 mL or 36.1 g	1217 equiv
Copper (+2)	$\text{CuBr}_2$	62.5 mg	1 equiv
Ligand	TMEDA	65.3 mg	2 equiv
Initiator	AIBN	84.6 mg	1.9 equiv
Temperature		$80^\circ\text{C}$	

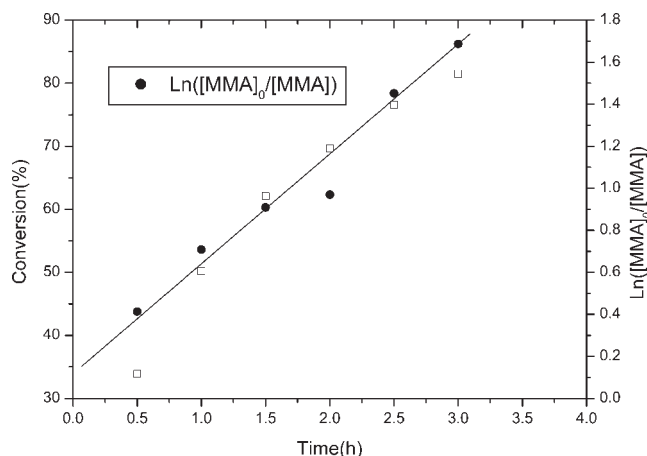


**Figure 1** Time dependence of  $\ln([MMA]_0/[MMA])$  and conversion using  $CuBr_2/TMEDA$  complex as catalyst at  $80^\circ C$  in xylene solution polymerization of MMA.

and  $t$ , respectively) plotted against time is also shown in Figure 1, which shows that the kinetics is first order in the monomer, and the concentration of growing species keeps constant during the polymerization. But the straight line is not through the origin, indicating that the polymerization has an induction period. Figure 2 shows that the experimental molecular weight increases linearly with monomer conversion from 8200 up to 27,500. During the whole polymerization, the polydispersities decline and reaches to 1.11 finally. The sample obtained at 0.5 h represents a high polydispersity ( $M_w/M_n = 1.74$ ). The high polydispersities are due to (1) the irreversible termination reaction that might happen especially at the early stage of the polymerization and (2) the slower establishing of equilibrium between the growing radical and the dormant species. The polymerization at the early stage is uncontrolled. With the carrying out of the polymerization, the polydis-



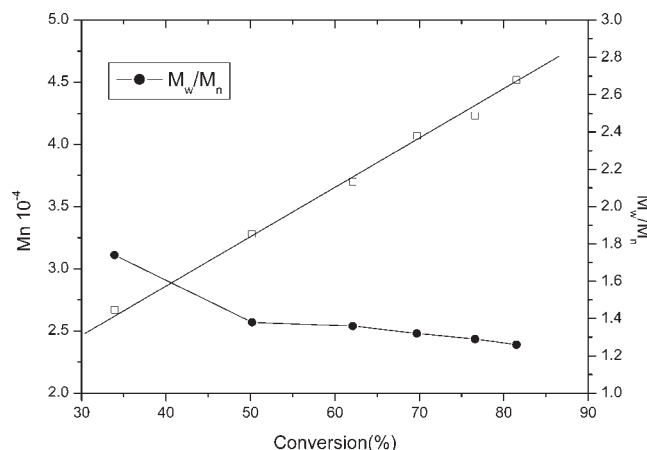
**Figure 2** Dependence of number-average molecular weight and polydispersities of PMMA on conversion using  $CuBr_2/TMEDA$  complex as catalyst at  $80^\circ C$  in xylene solution polymerization of MMA.



**Figure 3** Time dependence of  $\ln([MMA]_0/[MMA])$  and conversion using  $CuBr_2/PMDETA$  complex as catalyst at  $80^\circ C$  in xylene solution polymerization of MMA.

persities decline gradually. Other factors, such as the transferring of radical to solvent or monomer, might influence the control of polymerization, but the rapid establishing of the equilibrium between the growing radical and the dormant species is the key issue in the controlled polymerization.

The radical polymerization of MMA using  $CuBr_2/PMDETA$  complex as catalyst was performed at the same conditions. From Figures 3 and 4 it can be seen that the whole polymerization represents a certain extent control. The kinetics is first order in the monomer and the molecular weight increases linearly with monomer conversion. But the line of the first order plot pass through vertical axis, which means that the concentration of growing radical is high at the beginning, and the monomer conversion has a rapid increasing. As shown in Table II, the polymerization is rapid under same reaction conditions and the polydispersities are higher ( $M_w/M_n = 1.74$ – $1.26$ ).



**Figure 4** Dependence of number-average molecular weight and polydispersities of PMMA on conversion using  $CuBr_2/PMDETA$  complex as catalyst at  $80^\circ C$  in xylene solution polymerization of MMA.

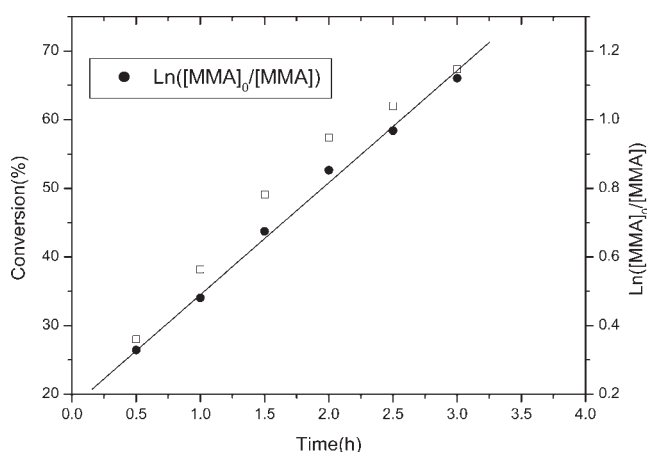
**TABLE II**  
Reverse ATRP of MMA in Xylene at 80°C, [Xylene]/  
[MMA]/[AIBN]/[CuBr<sub>2</sub>-ligand] = 1217/604/1.9/1

Ligand	Time (h)	Conv.	$M_n$	$M_w/M_n$
TMEDA	0	0		
	1.5	0.372	13,000	1.31
	3	0.671	27,500	1.12
PMDETA	0	0		
	1.5	0.621	37,000	1.36
	3	0.815	45,200	1.26

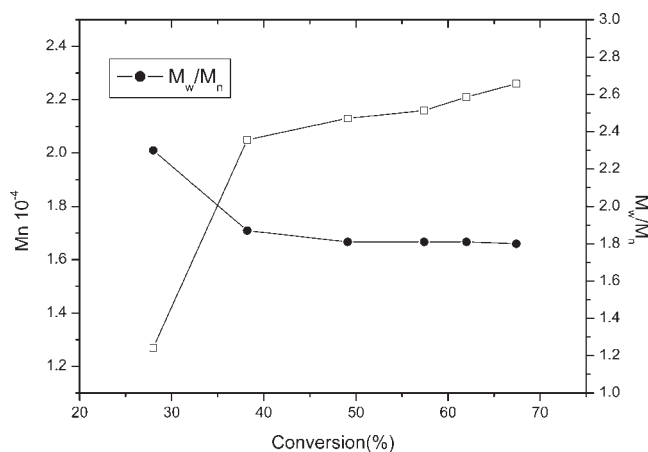
Scheme 1(A) shows the molecular structure of TMEDA and PMDETA. The polymerization system using CuBr<sub>2</sub>/TMEDA as catalyst in xylene was homogeneous, while that using CuBr<sub>2</sub>/PMDETA as catalyst in xylene was not homogeneous and there was a little green dark insoluble substance in the bottom of flask. Compared with the molecular structure of TMEDA and PMDETA, there is one more amine group in PMDETA than in TMEDA. But only two amine groups can complex with CuBr<sub>2</sub>, when the CuBr<sub>2</sub>/PMDETA complexes catch radicals, the amine group that cannot take part in complex would lead to the steric effect. The equilibrium between the growing radical and the dormant species cannot establish rapidly. The CuBr<sub>2</sub>/TMEDA system has not this effect. So the control of polymerization using CuBr<sub>2</sub>/TMEDA as catalyst is better than that using CuBr<sub>2</sub>/PMDETA as catalyst.

#### Controllability of MMA polymerization in CuBr<sub>2</sub>/bpy and CuBr<sub>2</sub>/dNbpy systems

The radical polymerization of MMA using CuBr<sub>2</sub>/bpy complex as catalyst was carried out in xylene using same reaction conditions. Figure 5 shows that the conversion of MMA increases from 28.0% up to



**Figure 5** Time dependence of  $\ln([MMA]_0/[MMA])$  and conversion using CuBr<sub>2</sub>/bpy complex as catalyst at 80°C in xylene solution polymerization of MMA.



**Figure 6** Dependence of number-average molecular weight and polydispersities of PMMA on conversion using CuBr<sub>2</sub>/bpy complex as catalyst at 80°C in xylene solution polymerization of MMA.

67.4% within 3 h. Also, the kinetics is first order in the monomer. Figure 6 shows that the experimental molecular weight increases with monomer conversion. From Figure 6 it can be seen that the molecular weight increasing is not linear with monomer conversion, and the polydispersities are too high ( $M_w/M_n = 2.3$ ) for a controlled radical polymerization. The whole polymerization represents uncontrolled. From the experimental phenomena it can be observed that there was a lot of CuBr<sub>2</sub> insoluble at the bottom of the flask throughout polymerization. The solubility of CuBr<sub>2</sub>/bpy complex in xylene is too low to make the polymerization be controlled.

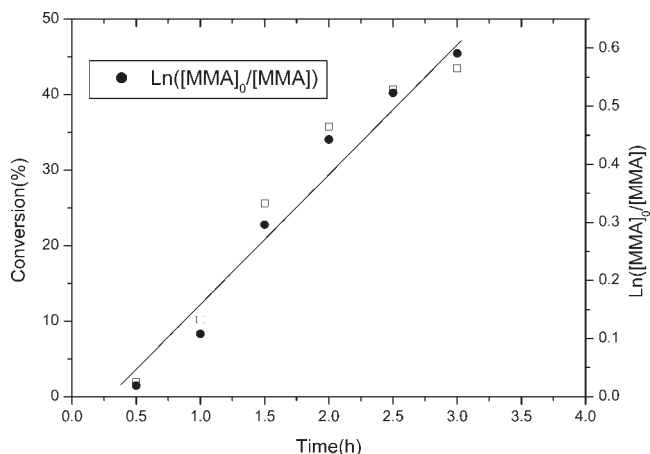
The polymerization using CuBr<sub>2</sub>/dNbpy complex as catalyst was also studied in our previous work<sup>17</sup> and the results are shown in Figures 7 and 8. The system using CuBr<sub>2</sub>/dNbpy as catalyst in xylene was homogeneous. From Figure 7 it can be seen that the conversion of MMA reaches 1.9% within 0.5 h once the polymerization begins, after 3 h, the conversion of MMA reaches 43.5%. The increasing of monomer conversion is obviously slower than in CuBr<sub>2</sub>/bpy system. The logarithmic conversion data  $\ln([MMA]_0/[MMA]_t)$  plotted against time is also shown in Figure 7, which shows the kinetic is first order in the monomer. As shown in Figure 8, a well-controlled polymerization, characterized by a linear correlation between molecular weights and monomer conversion, is realized using this system. During the whole polymerization, the polydispersities are in the range of 1.07–1.10, even for the first sample obtained at 0.5 h.

Compared with the above two systems, the solubility of complex as catalyst in xylene is the key issue to influence the control of polymerization. Scheme 1(B) shows the molecular structure of bpy and dNbpy. When the  $-\text{CH}(\text{C}_4\text{H}_9)_2$  group is introduced to bpy

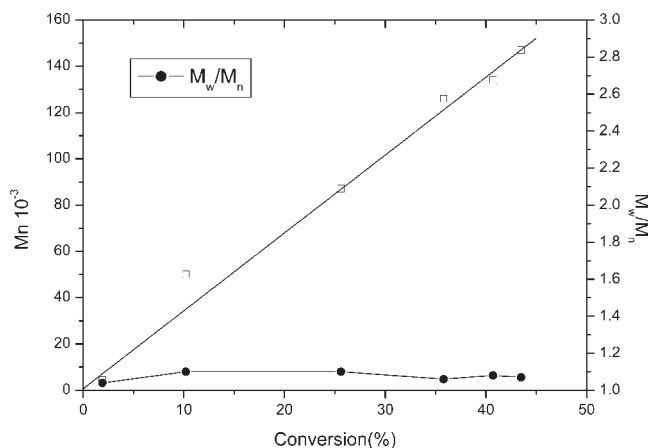


(dNbpy), the solubility of complex in xylene is much improved, so the control of the polymerization is much improved. If choosing a suitable solvent which can well solve the  $\text{CuBr}_2/\text{bpy}$  complex, a controlled polymerization also can be obtained.

The above results show that the different solubility of complex will bring different control of ATRP. But if the systems are all homogeneous, the electronic effect of ligand molecular would play the crucial role on the control of polymerization. The polymerization system of MMA using  $\text{CuBr}_2/\text{TMEDA}$  complex as catalyst and using  $\text{CuBr}_2/\text{dNbpy}$  complex as catalyst are homogeneous. From the Figures 1,2 and Figures 7,8 it can be seen that the control of polymerization in  $\text{CuBr}_2/\text{dNbpy}$  system is better than in  $\text{CuBr}_2/\text{TMEDA}$  system. Scheme 2 shows the electronic effect of complexes formed with TMEDA and dNbpy as ligands. The molecular structure of bpy is a big conjugated system of bonds, the  $\pi$  electrons will spread themselves as a group over a large section of the molecular. In the big conjugated system of bonds, the density of electrons is high and the electrons can flow freely. The  $-\text{CH}(\text{C}_4\text{H}_9)_2$  group is a electron donating group, the introducing of  $-\text{CH}(\text{C}_4\text{H}_9)_2$  group not only make  $\text{CuBr}_2/\text{dNbpy}$  complex easily dissolve in xylene but also make electrons flow freely from dNbpy to Cu atom. Whatever dNbpy complex with  $\text{Cu}^{+1}$  or  $\text{Cu}^{+2}$ , the electron donating effect reduce the oxidation state (the oxidation state is not the valence state) of Cu atom and make the complex ( $\text{Cu}^{+1}$  or  $\text{Cu}^{+2}$ ) more stable. So the equilibrium between the growing radical and the dormant species can be rapid established and the control of polymerization is easily to be realized. The four  $-\text{CH}_3$  groups are also electron donating groups in TMEDA molecular, but the bonds formed are  $\text{sp}^3$  hybrid bonds. The flowing of electrons from



**Figure 7** Time dependence of  $\ln([MMA]_0/[MMA])$  and conversion using  $\text{CuBr}_2/\text{dNbpy}$  complex as catalyst at  $80^\circ\text{C}$  in xylene solution polymerization of MMA.

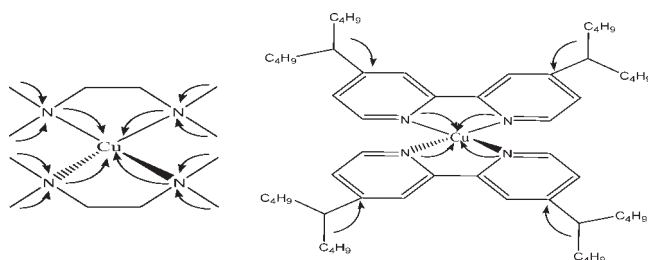


**Figure 8** Dependence of number-average molecular weight and polydispersities of PMMA on conversion using  $\text{CuBr}_2/\text{dNbpy}$  complex as catalyst at  $80^\circ\text{C}$  in xylene solution polymerization of MMA.

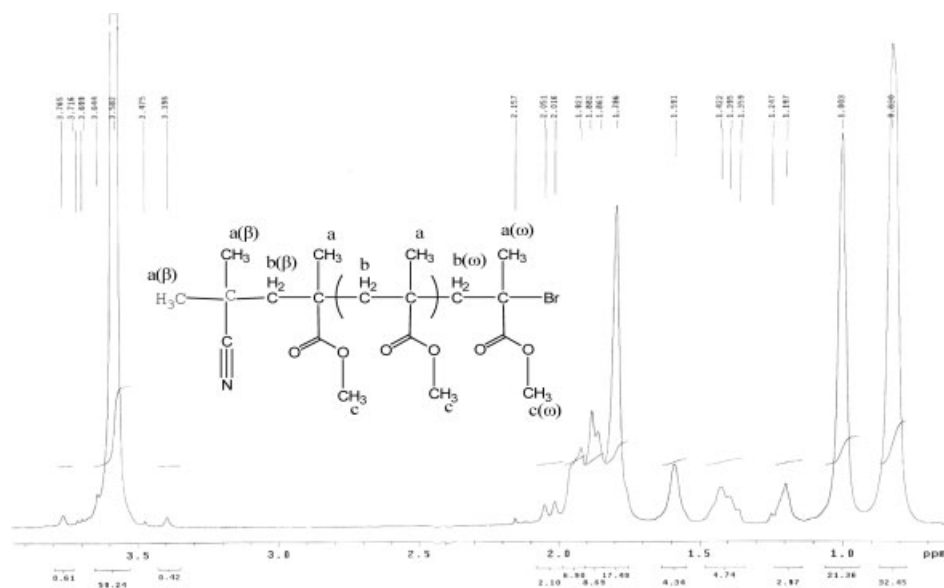
TMEDA to Cu atom is limited. Compared with dNbpy molecular, the stability of complex (TMEDA with  $\text{Cu}^{+1}$  or  $\text{Cu}^{+2}$ ) is poor. The establishing of the equilibrium between the growing radical and the dormant species is slower, which influences the control of polymerization directly. The ligand with conjugated system of bonds and electron donating groups is fit for a homogeneous ATRP.

### End group analysis

End group analysis of the resultant poly(methyl methacrylate) (PMMA) obtained from  $\text{CuBr}_2/\text{TMEDA}$  system was carried out by  $^1\text{H-NMR}$  spectroscopy. Figure 9 shows a representative  $^1\text{H-NMR}$  spectrum of the well-defined PMMA. The spectrum is the same as that reported by Chen and Qiu.<sup>15</sup> The signals at 0.89–1.20, 1.80–1.92, and 3.58 ppm are assigned to the protons of methyl groups [peak a] of  $-\text{C}(\text{CH}_3)(\text{COOCH}_3)$ , methylene groups [peak b] of  $-\text{CH}_2-$ , and methoxy groups [peak c] of  $-\text{C}(\text{CH}_3)(\text{COOCH}_3)$ , respectively. These results suggest that the chains of the PMMA only have methyl groups and methylene groups. The



**Scheme 2** Structure of complexes formed with TMEDA and dNbpy as ligands.



**Figure 9**  $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ , 400 MHz) of PMMA ( $M_n = 27,500$  and  $M_w/M_n = 1.11$ ) synthesized with the AIBN/ $\text{CuBr}_2$ /TMEDA system in xylene at  $80^\circ\text{C}$ .

signals at 1.36–1.42 ppm [peak a( $\beta$ )] are for the methyl groups, and the signal at 2.16 ppm [peak b( $\beta$ )] is for the methylene protons. It indicates that one end group of the PMMA chain is a  $\alpha$ -isobutyronitrile group ( $-\text{C}(\text{CN})(\text{CH}_3)_2$ ). In particular, the signal at 3.77 ppm [peak c( $\omega$ )] is for the protons of the methoxy group, that at 2.02–2.05 ppm [peak b( $\omega$ )] are for the methylene protons, and that at 1.25 ppm [peak a( $\omega$ )] exhibits the characteristic chemical shifts of the terminal MMA unit capped with an  $\omega$ -end bromine. Thus, a  $\omega$ -end bromine atom end group is just another end group.

The resulting PMMA, with a  $\omega$ -end bromine atom in the chain end, can be used as a macroinitiator for chain extension or block copolymerization using a conventional ATRP process.

## CONCLUSIONS

A series of copper-based reverse ATRP processes were carried out for MMA in xylene at  $80^\circ\text{C}$ . The polymerizations of  $\text{CuBr}_2$ /TMEDA system and  $\text{CuBr}_2$ /dNbpy system are homogeneous, and the polymerizations of  $\text{CuBr}_2$ /PMDETA system and  $\text{CuBr}_2$ /bpy system are not homogeneous. Among the polymerizations, a controlled polymerization (low polydispersity and linear increasing of molecular weight with monomer conversion) can be obtained in  $\text{CuBr}_2$ /TMEDA system,  $\text{CuBr}_2$ /PMDETA system, and  $\text{CuBr}_2$ /dNbpy system, especially in  $\text{CuBr}_2$ /dNbpy system. The control of polymerization in  $\text{CuBr}_2$ /bpy system is poor. The results are due to the poor solubility of  $\text{CuBr}_2$ /bpy complex in xylene. Compared with the  $\text{CuBr}_2$ /TMEDA system and  $\text{CuBr}_2$ /dNbpy system, the control of polymerization is better in  $\text{CuBr}_2$ /dNbpy system. Because the molecule of dNbpy is a big conju-

gated system of bonds, it is easy to stable the complex when dNbpy complex with  $\text{Cu}^{+1}$  or  $\text{Cu}^{+2}$ . So the equilibrium between the growing radical and the dormant species can be rapid established and a well-controlled polymerization can be easy obtained.

Also, we chose the  $\text{CuBr}_2$ /TMEDA system and analyzed the resulting PMMA. A well-defined PMMA with  $\omega$ -end bromine atom in the chain end was obtained. It can be used as a macroinitiator for chain extension or block copolymerization using a conventional ATRP process.

## References

1. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
2. Yuan, J. Y.; Pan, C. Y. *Eur Polym J* 2002, 38, 1565.
3. Jankova, K.; Hvilsted, S. *Macromolecules* 2003, 36, 1753.
4. Kizhakkedathu, J. N.; Kumer, K. R.; Goodman, D.; Brooks, D. E. *Polymer* 2004, 45, 7471.
5. Dayananda, K.; Ramakrishnan, A.; Dhamodharan, R. *J Macromol Sci Pure Appl Chem A* 2005, 42, 471.
6. Zhang, Y.; Im, S.C.; Huang, J. Y.; Matyjaszewski, K.; Pakula, T. *Macromol Chem Phys* 2005, 206, 33.
7. Zhang, Z. B.; Ying, S. K.; Shi, Z. Q. *Polymer* 1999, 40, 1341.
8. Liu, Y.; Klep, V.; Zdyrko, B.; Luzinov, L. *Langmuir* 2004, 20, 6710.
9. Karavia, V.; Deimede, V.; Kallitsis, J. K. *J Macromol Sci Pure Appl Chem A* 2004, 41, 115.
10. Hester, J. F.; Banerjee, P.; Won, Y.-Y.; Akthakul, A.; Acar, M. H.; Mayes, A. M. *Macromolecules* 2002, 35, 7652.
11. Wang, X. S.; Luo, N.; Ying, S. K. *Polymer* 1999, 40, 4515.
12. Strandman, S.; Luostarinen, M.; Niemela, S.; Rissanen, K.; Tenhu, H. *J Polym Sci Part A: Polym Chem* 2004, 42, 4189.
13. Qin, D. Q.; Qin, S. H.; Chen, X. P.; Qiu, K. Y. *Polymer* 2000, 41, 7347.
14. Qin, D. Q.; Qin, S. H.; Qiu, K. Y. *J Appl Polym Sci* 2001, 81, 2237.
15. Chen, X. P.; Qiu, K. Y. *Macromolecules* 1999, 32, 8711.
16. Li, M.; Matyjaszewski, K. *Macromolecules* 2003, 36, 6028.
17. Pan, K.; Jiang, L.; Zhang, J.; Dan, Y. *J Appl Polym Sci*, to appear.