Macromolecular Research, Vol. 13, No. 5, pp 391-396 (2005)

Cu Catalyst System with Phosphorous Containing Bidendate Ligand for Living Radical Polymerization of MMA

Sung Chul Hong

Department of Nano Science and Technology, Sejong University, Seoul 143-747, Korea

Ki Eun Shin and Seok Kyun Noh*

School of Chemical Engineering & Technology, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea

Won Seok Lyoo

School of Textiles, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea

Received May 24, 2005; Revised August 24, 2005

Abstract: The polymerization of methyl methacrylate (MMA) was carried out using CuBr/bidentate phosphorus ligand catalyst systems. MMA polymerization with CuBr/ phosphine-phosphinidene (PP) exhibited high conversion (~80%) in 5 h at 90 °C along with a linear increase of $\ln([M]_0/[M])$ versus time, indicating constant concentration of the propagating radicals during the polymerization. The molecular weight of the prepared PMMA tended to increase with conversion, suggesting the living polymerization characteristic of the system. On the other hand, a large difference between the measured and theoretical molecular weight and a broad molecular weight distribution were observed, implicating possible incomplete control over the polymerization. This may have been caused by the low deactivation rate constant (k_{deact}) of the system. The low k_{deact} would result in irreversible generation of radicals instead of reversible activation/deactivation process of ATRP. Polymerizations performed at different ligand to CuBr ratios and different monomer to initiator ratios did not afford better control over the polymerization, suggesting that the controllability of CuBr/phosphorus ligand system for ATRP is inherently limited.

Keywords: controlled radical polymerization, MMA polymerization, Cu/phosphorus ligand catalyst, bidendate phosphorus ligand for controlled polymerization.

Introduction

Atom transfer radical polymerization (ATRP) has provided one of the most promising synthetic tools for living radical polymerizations (LRP), enabling the polymerization of a wide range of monomers.[1-10] The basis of ATRP is the reversible transfer of a radically transferable atom, typically a halogen atom, from a monomeric or polymeric alkyl (pseudo)halide to a transition metal complex in a lower oxidation state, forming an organic radical and a transition metal complex with a higher oxidation state. By changing metal/ligand combinations, the redox potential and activation/deactivation rate constants of the catalyst system can be altered according to monomer. Various metals such as Mo, Re, Ru, Fe, Rh, Ni, Pd, Cu complexes have been tested in conjunction with nitrogen, phosphorus, cyclopentadienyl, indenyl ligands in ATRP.[10,11]

Phosphorus-based ligands have been used to complex most transition metals like Re,[12,13] Ru,[14,15] Fe,[16-18] Rh,[19,20] Ni[21,22] and Pd[23] for ATRP. PPh_3 is the most popular ligand and has been applied successfully in ATRP. $P(nBu)_3$ also has been used in Ni and Fe systems. Phosphine ligands that are strongly basic and possess a sterically bulky group afforded high catalytic activity and good control over the polymerization. However, so far no reports have been presented for Cu.

In this study, we would like to describe a new polymerization system for ATRP to polymerize MMA. The ligand in our system possesses two phosphorus sites in conjunction with bulky substituents in its structure which can contact with two coordination sites with steric hindrance to make a bond at the metal center to form the active species.[24] It is expected that this structural feature may provide distinctive polymerization behavior for ATRP.

*Corresponding Author. E-mail: sknoh@yumail.ac.kr

Experimental

Chemicals. Methyl methacrylate (MMA, 99%, Aldrich) and styrene (sty, 99%, Aldrich) were passed through a column filled with neutral alumina, dried over CaH_2, distilled under reduced pressure, and stored in a freezer under nitrogen. CuBr (99+%, Aldrich) was purified by stirring in acetic acid for 5 h followed by washing with ethanol and diethyl ether. Tetrahydrofuran (THF, HPLC grade, Fisher) and toluene (certified grade, Fisher) were freshly distilled from Na/K alloy with benzophenon (99%, Aldrich) and stored under nitrogen. 2-Bromopropionitrile (BrP, $CH_3CHBrCN$, 97%, Aldrich), ethyl 2-bromoisobutyrate (EBB, $(CH_3)_2CBrCO_2C_2H_5$, 99%, Aldrich), methyl 2-bromopropionate (MBP, $CH_3CHBrCO_2CH_3$, 98%, Aldrich), aluminum oxide (Al_2O_3, activated, neutral, Aldrich), 2,2′-bipyridyl (bpy, 99%, Aldrich), 1,3-bis(diphenylphosphino)propane (BPP, 97%, Aldrich), anisole (99%, Aldrich), diphenyl ether (99%, Aldrich) and other solvents were used without further purification. The monomers and solvents were purged by bubbling with dry nitrogen for 1 h immediately before polymerization. Chlorodiphenylphosphine (98%) was freshly distilled before using. Chlorotrimethylsilane (98%) was vacuum transferred from CaH_2. Zinc chloride (98%) was purified by fused under vacuum. 1-Bromo-2,4,6-triisopropyl benzene (98%), phosphorus trichloride (99%), lithium aluminum hydride (95%), *N,N*-dimethylethylenediamine (85%), *tert*-butyldimethylsilyl chloride (97%), 2-bromobenzaldehyde (98%), ammonium chloride (99.5%), and *n*-BuLi (2.5 M in hexanes) were purchased from Aldrich and used without further purification. Concentrated HCl was purchased from DUKSAN.

Synthesis of Phosphine-Phosphinidine Ligand, (2,4,6-(i-Pr)$_3$C$_6$H$_2$)P=(CH)C$_6$H$_4$P(C$_6$H$_5$)$_2$. To a solution of (2, 4, 6-triisopropylphenyl)phosphane (1.63 g, 6.89 mmol) in THF (100 mL) was added *n*- BuLi (3 mL of a 2.5 M solution in hexanes, 7.58 mmol) at -78 °C. The mixture was stirred at -78 °C for 10 min, warmed to room temperature, and stirred for an additional 30 min. *tert*-Butyldimethylsilylchloride (1.14 g, 7.58 mmol) was added at room temperature under N_2 purged. The reaction mixture was stirred at room temperature for 30 min. A solution of diphenylphosphinobenzaldehyde (2 g, 6.89 mmol) in THF (60 mL) was added dropwise at -78 °C. The reaction solution was quickly changed to red color. The solution was stirred at -78 °C for 20 min. Chlorotrimethylsilane (0.66 mL, 7.58 mmol) was added via a syringe at -78 °C, stirred at -78 °C for 10 min, warmed to room temperature and stirred for an additional 1 h. The solvent was evaporated and hexane (100 mL × 2) was added to precipitate LiCl. The mixture was filtered to remove the white solid. Hexane was evaporated to give the ligand as a yellow sticky oil (3.04, 87%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 9.76, 9.66(dd, C=C**H** (J_{P-H}=24 Hz, J_{H-H}=6 Hz)), 8.15-6.78(m, arom., **H**), 3.16(m, 2H (J_{H-H}=6.6 Hz), C**H**$(CH_3)_2$), 2.83(m, 1H (J_{H-H}=6.6 Hz), C**H**$(CH_3)_2$), 1.23(d, 12H (J_{H-H}=6.6 Hz), 4C**H**$_3$), 1.03(d, 6H (J_{H-H}=6.6 Hz), 2C**H**$_3$). ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C) δ: 258.4(d, 1P (J_{P-H}=24 Hz), **P**$(C_6H_5)_2$), -14.5 (s, 1P, **P**CH).

Polymerization. A typical experimental procedure for polymerization is presented as the following. CuBr (0.019 g, 0.135 mmol) and phosphonidine phosphine (PP, 0.1 M in toluene, 1.3 mL, 0.135 mmol) were placed in a 50 mL Schlenk tube followed by degassing under vacuum and backfilling three times with N_2. A measured amount of degassed monomer (MMA, 5.79 mL, 54.1 mmol), toluene (3.2 mL), anisole (1 mL) were then added to the Schlenk flask. After the measured amount of initiator (methyl 2-bromopropionate, MBP, 0.1 M in toluene, 1.3 mL, 0.135 mmol) was added, the reactor was immersed in an oil bath that was preset to a specific reaction temperature (90 °C). Samples were taken from the flask via a syringe at timed intervals to allow kinetic data to be determined. The samples were diluted with THF followed by passing through a column filled with neutral aluminum oxide for gas chromatography (GC) and gel permeation chromatography (GPC) analysis. After a certain polymerization time, the reactor was removed from the oil bath and cooled to room temperature. The polymer solution was diluted with THF, filtered through a column filled with neutral aluminum oxide and kept at room temperature for further analysis.

Characterization. Conversion of monomer was determined using a *HP* 6890 gas chromatography equipped with a FID detector and a J & W Scientific 30 m DB WAX Megabore column. Anisole was used as an internal standard. Injector and detector temperatures were kept constant at 250 °C. Analysis was run isothermally at 40 °C for 1 min followed by an increase of temperature to 120 °C at the heating rate of 20 °C/min and holding at 120 °C for 1 min, then followed by an increase of temperature to 180 °C at the heating rate of 10 °C/min and holding at 180 °C for 1 min. The molecular weight and molecular weight distribution of polymers were determined by GPC using Waters columns (styragel, HR 5E) equipped with a Waters 515 pump and a Waters 2410 differential refractometer using diphenyl ether as an internal standard. THF was used as an eluent at a flow rate of 1 mL/min. Linear PS standards (1.31×10^3~3.58×10^6 g/mol) were used for calibration. Theoretical molecular weights were calculated through the following eq. (1).

$$M_{n,th.} = ([\text{Monomer}]_0/[\text{Initiator}]_0) \times \text{conversion} \times 100.12\ (\text{MMA MW}) + \text{initiator FW} \quad (1)$$

Results and Discussion

A series of polymerization were carried out following the standard ATRP conditions using different ligands complexed with CuBr (Figures 1 and 2).

Figure 2 shows the semilogarithmic kinetic plot for the polymerization of MMA promoted by CuBr/PP, CuBr/BPP

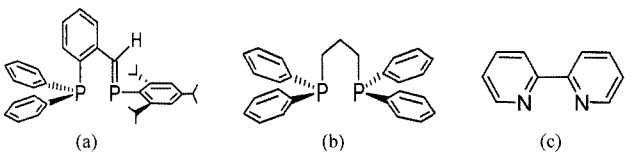

Figure 1. Chemical structures of phosphine-phosphinidine (a, PP), 1,3-bis(diphenylphosphino) propane (b, BPP), and 2,2'-bipyridyl (c, bpy).

or CuBr/bpy. For CuBr/bpy, the conversion of MMA was high (82% in 7 h), generating polymer with M_n of 4.02×10^4 g/mol, which is in good agreement with theoretical molecular weight ($M_{n,th.}$=3.74×10^4 g/mol, Figure 2(b)). Despite of the low solubility of CuBr/bpy in the system, molecular weight distribution exhibited narrow distribution (M_w/M_n ~ 1.3) indicating relatively good control over the polymerization. MMA polymerization with CuBr/PP also exhibited high conversion (~80%) in 5 h (Figure 2(a)). Linear increase of $\ln([M]_0/[M])$ versus time indicates constant concentration of the propagating radicals during the polymerization. Molecular weight also increased with conversion (Figure 2(b)) as well, suggesting living polymerization characteristics. However, the molecular weights of generated polymers were much higher (M_n=1.59×10^5 g/mol at 5 h, Figure 2(b)) than the anticipated theoretical molecular weight ($M_{n,th.}$= 3.18×10^4 g/mol). In addition, molecular weight distributions of the polymers were broad (M_w/M_n ~2.0, Figure 2(b)), indicating lack of appropriate control over the polymerization. This outcome might be occurred by the low deactivation rate constant (k_{deact}) of CuBr/PP for MMA polymerization to give rise to the frequent chain termination reaction. To ascertain a successful catalytic system in living radical polymerization, the catalyst system should provide not only high equilibrium constant (K_{eq}) but also high deactivation rate constant (k_{deact}) to bring the propagating radical back to the dormant species before transfer or termination reactions occur. Polymerization of styrene using the same catalyst system ([Sty]:[CuBr]:[PP]:[MBP]=400:1:1:1 at 110 °C) also afforded polymers (conversion=38% at 9 h) with high molecular weight (M_n= 6.81×10^4 g/mol, $M_{n,th.}$=1.61×10^4 g/mol) and broad molecular weight distribution (M_w/M_n = 2.0), displaying uncontrolled free radical polymerization.

The effect of addition order of components in polymerization procedure was tested and the results were summarized in Table I. All the experiments afforded polymers having broader molecular weight distributions and higher molecular weights comparing to the theoretical values. These results demonstrate that the poor controllability of CuBr/PP system for MMA polymerization is likely caused by the inherent kinetic characteristics of the catalyst regardless of the reaction variables.

The catalyst system of CuBr with BPP presented polymerization with constant radical concentration (linear increase of $\ln([M]_0/[M])$ in Figure 2(a)). However, the rate of polymerization turned out to be very slow, yielding high molecular weight (M_n=5.53×10^5 at 42% conversion) and broad molecular weight distribution (M_w/M_n ~3.0). This could be interpreted that CuBr/BPP system afforded low k_{act} in conjunction with very low k_{deact} or not all the initiating system was activated during the polymerization

Polymerizations of MMA were conducted at a different ratio of ligand to CuBr and the results were summarized in Figure 3. CuBr complex with 1 equivalent of PP ligand exhibited higher polymerization rate than that with 0.5 equivalent of ligand. Copper complex with 2 equivalent of PP showed much slower polymerization, suggesting existence of side reactions. The molecular weights of polymers increased with conversion. However, the complications from the large difference between the measured and the theoretical molecular weight of the manufactured polymers in addition to their broad molecular weight distributions (M_w/M_n=2.0~ 3.0) were not improved for all [PP]/[Cu] ratios.

Figure 4 summarizes the polymerization results of MMA promoted by CuBr/PP at different $[MMA]_0/[MBP]_0$ ratios.

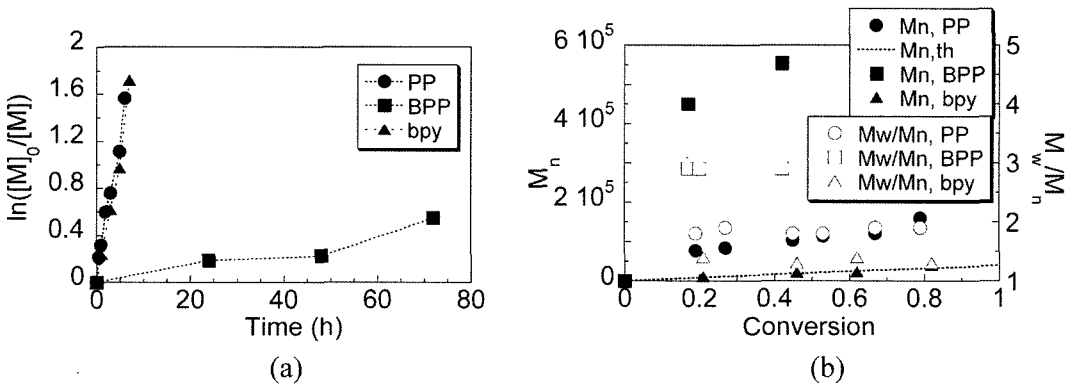

Figure 2. Kinetic plots (a) and evolution of M_n and M_w/M_n vs. conversion (b) for the polymerization of MMA using CuBr with different ligands; CuBr/PP (● or ○), CuBr/BPP (■ or □) and CuBr/bpy (▲ and △): Polymerization conditions: catalyst=CuBr/ligand, $[MMA]_0$: [methyl 2-bromopropionate]$_0$:$[CuBr]_0$:$[ligand]_0$=400:1:1:1, $[MMA]_0$=4.45 mol/L, MMA/toluene/anisole=1/1/0.2 v/v/v, temperature=90 °C.

Table I. Polymerization of MMA Promoted by CuBr/PP at Different Addition Order of Components[a]

Expt. No.	addition order	time (h)	conv.[b] (%)	M_n ($\times 10^3$)	$M_{n,th}$ ($\times 10^3$)	M_w/M_n
1	CuBr/PP/MMA/solvent stir for 5 min → add MBP → 90 °C bath	3	56	63.8	5.2	1.7
2	CuBr/PP/MBP/solvent stir for 24 h at 90 °C → add MMA	4	27	189.7	2.8	1.9
3	CuBr/PP/solvent stir for 27 h at 90 °C → add MMA/MBP	4	52	90.8	5.4	2.0
4	CuBr/PP/2 solvent stir for 21 h at 90 °C → add MMA/MBP	4	44	78.9	4.6	1.8

[a]Polymerization conditions: For expt. No. 1, 2, 3: catalyst = CuBr/PP, initiator = methyl 2-bromopropionate (MBP), $[MMA]_0:[MBP]_0:[CuBr]_0:[PP]_0 = 100:1:1:1$, $[MMA]_0$ = 4.45 mol/L, MMA/toluene/anisole = 1/1/0.2 v/v/v, temperature = 90 °C. For expt No. 4: catalyst = CuBr/PP, initiator = methyl 2-bromopropionate (MBP), $[MMA]_0:[MBP]_0:[CuBr]_0:[PP]_0 = 100:1:1:1$, $[MMA]_0$ = 3.06 mol/L, MMA/toluene/anisole = 1/2/0.2 v/v/v, temperature = 90 °C. [b]Conversion determined by GC.

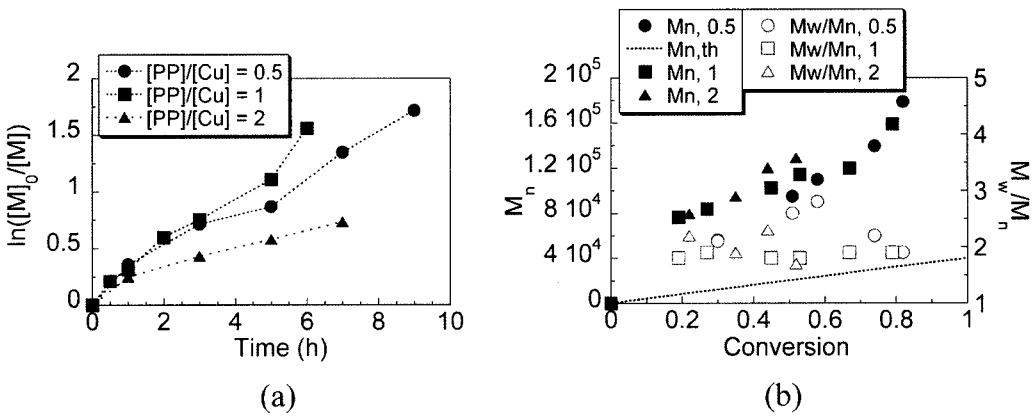

Figure 3. Kinetic plots (a) and evolution of M_n and M_w/M_n vs. conversion (b) for the polymerization of MMA at different PP to CuBr ratios; [PP] : [CuBr] = 0.5 (● or ○), 1 (■ or □) and 2 (▲ and △): Polymerization conditions : catalyst = CuBr/PP, $[MMA]_0$: [methyl 2-bromopropionate]$_0$: $[CuBr]_0 = 400:1:1$, $[MMA]_0$ = 4.45 mol/L, MMA/toluene/anisole = 1/1/0.2 v/v/v, temperature = 90 °C.

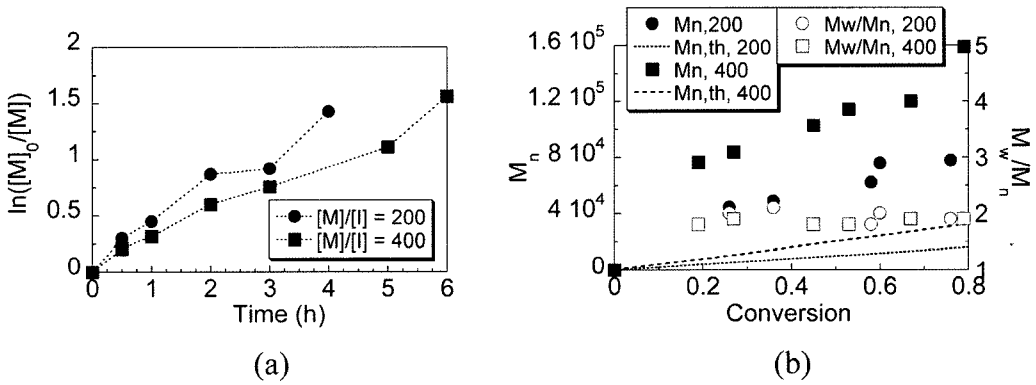

Figure 4. Kinetic plots (a) and evolution of M_n and M_w/M_n vs. conversion (b) for the polymerization of MMA at different monomer to initiator mole ratios; [MMA]/[methyl 2-bromopropionate] = 200 (● or ○) and 400 (■ or □): Polymerization conditions: catalyst = CuBr/PP, [methyl 2-bromopropionate]$_0$: $[CuBr]_0$: $[PP]_0 = 1:1:1$, $[MMA]_0$ = 4.45 mol/L, MMA/toluene/anisole = 1/1/0.2 v/v/v, temperature = 90 °C.

The conversion increased linearly with time (Figure 4(a)). The molecular weight (M_n) of the polymers was determined not only by conversion but also by $[MMA]_0/[MBP]_0$ (Figure 4(b)). Polymers with higher molecular weight were obtained with higher $[MMA]_0/[MBP]_0$. Molecular weight distribution remained constant (M_w/M_n~2.0).

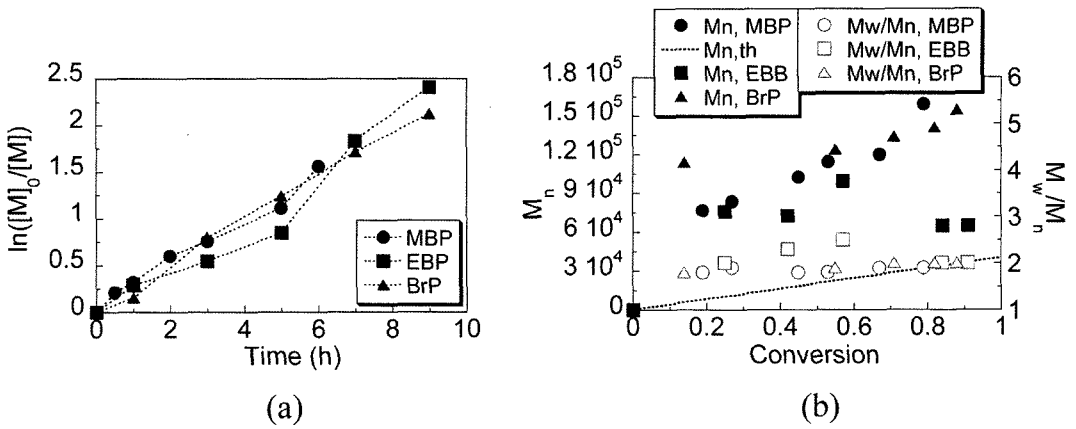

Figure 5. Kinetic plots (a) and evolution of M_n and M_w/M_n vs. conversion (b) for the polymerization of MMA with different initiators; initiator = methyl 2-bromopropionate (MBP, ● or ○), ethyl 2-bromoisobutyrate (EBB, ■ or □) and 2-bromopropionitrile (BrP, ▲ and △): Polymerization conditions: catalyst = CuBr/PP, [MMA]:[initiator]$_0$:[CuBr]$_0$:[PP]$_0$=400:1:1:1, [MMA]$_0$= 4.45 mol/L, MMA/toluene/anisole = 1/1/0.2 v/v/v, temperature = 90 °C.

Introduction of a different initiator did not affect either the rate of polymerization (Figure 5(a)) or molecular weight distribution (M_w/M_n ~2.0, Figure 5(b)). This clearly represented that the characteristics of the polymerization were governed principally by the catalyst system. Different from MBP initiator, use of EBB or BrP initiator resulted in large molecular weight jump at the early stage of polymerization. Presumably, EBB and BrP are better initiator than MBP to form more radicals at the beginning of polymerization. Faster initiation and slow deactivation may lead to high but constant molecular weight probably due to the increased termination events between radicals.

Conclusions

Cu/phosphorous ligand complexes were prepared and applied to ATRP. MMA polymerization with CuBr/ phosphine-phosphinidine (PP) exhibited high conversion (~ 80%) in 5 h along with linear increase of ln([M]$_0$/[M]) versus time, indicating constant concentration of the propagating radicals. Molecular weight increased with conversion, suggesting living polymerization characteristic of the system. However, large discrepancy between measured and theoretical molecular weight of the produced polymers and broad molecular weight distribution imply incomplete control over the polymerization, probably due to low deactivation rate constant (k_{deact}) of the system for MMA polymerization. Unfortunately polymerizations performed under a variety of reaction conditions did not afford better control over the polymerization, suggesting inherently limited controllability of CuBr/PP system for MMA polymerization.

Acknowledgements. This study was supported by grant No. RTI04-01-04 from the Regional Technology Innovation of the Ministry of Commerce, Industry, and Energy (MOCIE).

References

(1) K. Matyjaszewski, *ACS Symposium Series; Controlled Radical Polymerization*, American Chemical Society, Washington, DC, 1998.
(2) K. Matyjaszewski, *ACS Symposium Series; Controlled/Living Radical Polymerization: progress in ATRP, NMP, and RAFT*, American Chemical Society, Washington, DC, 2000.
(3) B. Moon and M. Kang, *Macromol. Res.*, **13**, 229 (2005).
(4) W. Xu, X. Zhu, Z. Cheng, J. Chen, and J. Lu, *Macromol. Res.*, **12**, 32 (2004).
(5) M. Sawamoto and M. Kamigaito, *Chemtech*, **29**, 30 (1999).
(6) J.-S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, **117**, 5614 (1995).
(7) K. Matyjaszewski, *Chem. Eur. J.*, **5**, 3095 (1999).
(8) T. E. Patten and K. Matyjaszewski, *Acc. Chem. Res.*, **32**, 895 (1999).
(9) T. E. Patten and K. Matyjaszewski, *Adv. Mater.*, **10**, 901 (1998).
(10) K. Matyjaszewski and J. Xia, *Chem. Rev.*, **101**, 2921 (2001).
(11) M. Kamigaito, T. Ando, and M. Sawamoto, *Chem. Rev.*, **101**, 3689 (2001).
(12) H. Uegaki, Y. Kotani, M. Kamigaito, and M. Sawamoto, *ACS Symposium Series; Living radical polymerization of acrylates with rhenium(V)-based initiating systems: ReO2I(PPh3)2/ Alkyl Iodide*, American Chemical Society, Washington, DC, 2000.
(13) Y. Kotani, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **32**, 2420 (1999).
(14) M. Kato, M. Kamigaito, M. Sawamoto, and T. Higashimura, *Macromolecules*, **28**, 1721 (1995).
(15) F. Simal, A. Demonceau, and A. F. Noels, *Angew. Chem. Int. Ed.*, **38**, 538 (1999).
(16) K. Matyjaszewski, M. Wei, J. Xia, and N. E. McDermott, *Macromolecules*, **30**, 8161 (1997).
(17) T. Ando, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **30**, 4507 (1997).

(18) G. Moineau, P. Dubois, R. Jerome, T. Senninger, and P. Teyssie, *Macromolecules*, **31**, 545 (1998).
(19) V. Percec, B. Barboiu, A. Neumann, J. C. Ronda, and M. Zhao, *Macromolecules*, **29**, 3665 (1996).
(20) G. Moineau, C. Granel, P. Dubois, R. Jerome, and P. Teyssie, *Macromolecules*, **31**, 542 (1998).
(21) H. Uegaki, Y. Kotani, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **30**, 2249 (1997).
(22) H. Uegaki, Y. Kotani, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **31**, 6756 (1998).
(23) P. Lecomte, I. Drapier, P. Dubois, P. Teyssie, and R. Jerome, *Macromolecules*, **30**, 7631 (1997).
(24) D. J. Bauer, C. Like, and O. Telzer, *J. Organomet. Chem.* **626**, 106 (2001).