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New Tridentate Ligands with Mixed Donor Atoms for Cu-Based Atom Transfer Radical Polymerization

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Abstract: 2-Furancarboxaldehyde-2-pyridinylhydrazone (FPH) and 5-methyl-2-furancarboxaldehyde-2-pyridinylhydrazone (MFPH) were synthesized and used as tridentate ligands of copper (I) bromide for the atom transfer radical polymerization of methyl methacrylate (MMA) and styrene. The polymerization of methyl methacrylate achieved high conversion and yielded polymers with a good control of molecular weight and low polydispersity (PDI=1.33). Higher PDI were observed in the polymerization of styrene. Using 1-phenyl ethylbromide (PEBr) and ethyl 2-bromoisobutyrate (EBiB) as model compounds for the polymeric chain ends, the activation rate constants of the new catalytic systems were measured. These results were correlated with the polymerization results and compared with another catalytic system previously reported.

Keywords: atom transfer radical polymerization, copper complex, styrene, methyl methacrylate, activation rate constant, tridentate ligand, mixed donor atoms.

Introduction

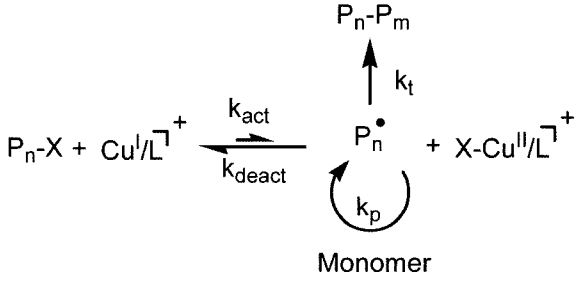
Atom transfer radical polymerization (ATRP) has gained a considerable academic and industrial interest as it can prepare well-defined polymers from a wide range of vinyl monomers under facile reaction conditions.[1,2] The basic concept behind ATRP is the reversible formation of a radical by transfer of a halogen from an alkyl halide to a transition metal catalyst (Scheme I). The success of ATRP depends largely on an appropriate equilibrium and dynamics of the reversible formation of a radical; i.e. the activation process (generation of a radical, k_{act}) and the deactivation process (formation of an alkyl halide, k_{deact}). This equilibrium determines the concentration of radicals and subsequently the rates of polymerization and termination. The dynamics of the exchange reaction determine the level of control in the polymerization.[3]

One of the principal components to determine the described equilibrium and the dynamics in ATRP is the catalyst composed of transition metal and complexing ligands. Consequently, after the discovery of ATRP, intensive research has been carried out to develop new ATRP catalysts and understand their catalytic activities on various combinations of transition metals and ligands. So far many transition metal complexes have been successfully employed in ATRP of styrenes, acrylates, acrylonitriles, and acrylamides. These include various transition metals such as Ti,[4] Mo,[5,6] Ru,[7] Ni,[8] Fe,[2,9-13] and Cu.[13-25]

Among various transition metals, Cu is the most widely used and intensively studied as copper based ATRP catalysts are found superior in terms of activities, versatility, and cost.[1,26] The various ligands have been employed in copper based system, including bipyridine, (substituted) bipyridines,[13,25,27,28] (substituted) terpyridine,[29] pyridineimines,[14,30] linear amines,[9] and branched amines.[31] While nitrogen containing ligands have been extensively studied in copper-complexes as ATRP catalysts, other copper complexes containing sulfur, phosphorous and oxygen ligands or ligands with mixed donor atoms have been relatively unexplored as ATRP catalyst system.

Here, we synthesized furan and pyridinylhydrozone based ligands, 2-furancarboxaldehyde-2-pyridinylhydrazone (FPH) and 5-methyl-2-furancarboxaldehyde-2-pyridinylhydrazone

Scheme I



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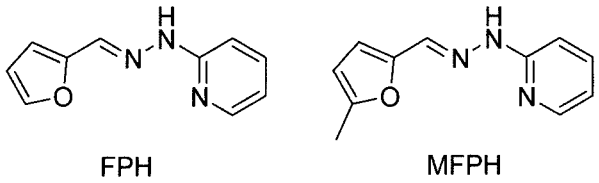


Figure 1. The structures of new tridentate ligands.

(MFPH) and studied their catalytic activities in Cu-based ATRP of styrene and methyl methacrylate (MMA)(Figure 1). We were interested in how the ligands with mixed coordinating atom, oxygen, and nitrogen, affect the activity of the copper complex compared to the other nitrogen-based ligands previously reported. We studied catalytic activities in the ATRP of methyl methacrylate and styrene using CuBr/FPH and CuBr/MFPH. For critical evaluation of their activities, we also measured the activation rate constants of the catalysts in atom transfer reaction with alkyl halide as a model for polymeric chain ends in ATRP under kinetic isolation condition.

Experimental

Materials. 2-Furaldehyde (Aldrich, 99%), 5-methylfuraldehyde (Aldrich, 99%), 2-hydrazinopyridine (Aldrich, 97%) and 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (Aldrich 98%) was used as received. CuBr (Aldrich 98%) was purified according to literature.[13] 1-Phenylethylbromide (PEBr, Aldrich 97%) and ethyl 2-bromoisobutyrate (EBiB, Aldrich 98%) were vacuum distilled before use. Styrene (Junsei Chemical, 99.5%) and methyl methacrylate (Yukuri Pure Chemical, 99.5%) were distilled over CaH_2 before use. Other solvents were used as received.

Characterization. Monomer conversion was determined using HP 5890 series 2 gas chromatography equipped with HP-101 column (25 m × 0.32 mm × 0.3 μm) and FID detector. Molecular weights were determined by THF GPC calibrated with polystyrene standards and equipped with Agilent 1100 pump, 2 Agilent Plgel Mixed-C columns, and Agilent 1100 RI detector. The consumption of PEBr in the activation rate constant measurement was determined with HPLC. HPLC was performed using a Shimadzu LC 10AD pump, Waters Nova-Pak C18 column (3.9 × 150 mm), Young-Lin M720 absorbance detector (λ = 220 nm) at room temperature by the elution of acetonitrile and water mixture (60:40 vol%). The retention times of TEMPO, PEBr, biphenyl were 1.6, 2.7, and 4.2 min, respectively. The consumption of EBiB in the activation rate constant measurement was determined with GC. The temperature program for GC column was as follows: initial, inlet and detector temperature: 40, 200, and 200 °C, ramp: 20 °C/min. In the case of GC analysis, the retention times of EBiB, Biphenyl and TEMPO were 3.9, 5.4, and 7.4, respectively.

Synthesis of 2-Furancarboxaldehyde-2-pyridinylhydrazone (FPH). 0.38 mL (0.44 g, 0.46×10^{-2} mol) of 2-furaldehyde and 0.50 g (0.46×10^{-2} mol) of 2-hydrazinopyridine in 5.00 mL of ethanol was refluxed for 4 hrs at 80 °C. The solution was cooled, precipitated, washed with ethanol and dried for 12 hrs. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm), 8.14 (d, 1H), 7.74 (s, 1H), 7.65 (t, 1H), 7.50 (s, 1H), 7.39 (d, 1H), 6.80 (t, 1H), 6.62 (d, 1H), 2.49 (m, 1H).

Synthesis of 5-Methyl-2-furancarboxaldehyde-2-pyridinylhydrazone (MFPH). MFPH was prepared with similar procedure as for the synthesis of FPH where 0.27 mL (0.30 g, 0.27×10^{-2} mmol) of 5-methylfuraldehyde was used instead of 2-furaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm), 8.82 (s, 1H), 8.14 (d, 1H), 7.63 (t, 1H), 7.61 (s, 1H), 7.36 (d, 1H), 6.78 (t, 1H), 6.49 (d, 1H), 6.08 (d, 1H), 2.40 (s, 3H).

Polymerization Method. Monomer (St: 5.54 mL, 0.48×10^{-1} mol, or MMA: 5.35 mL, 0.05 mol) and anisole were transferred into a deoxygenated Schlenk flask via syringes. After 2 freeze-pump-thaw cycles, ligand (FPH: 4.68×10^{-2} g, 0.25 mmol or MFPH: 5.03×10^{-2} g, 0.25 mmol), and CuBr (3.59×10^{-2} g, 0.25 mmol) were added to the Schlenk flask. After 3 more freeze-pump-thaw cycles, the Schlenk flask was placed in an oil bath thermostatted at the desired temperature (St: 110 °C, MMA: 90 °C). At timed intervals, 0.20 mL aliquot of the reaction mixture was taken and diluted in THF for GC analysis and filtered through a short alumina column to remove catalyst for GPC analysis.

Activation Rate Constant Measurement. 4.0 mL of acetonitrile was transferred into a deoxygenated Schlenk flask. After 3 times of freeze-pump-thaw cycles, 0.20 mmol of TEMPO (3.12×10^{-2} g), 0.10 mmol of the ligand and 0.10 mmol of CuBr (1.44×10^{-2} g) was added to the frozen solution followed by 2 more freeze-pump-thaw cycles. The Schlenk flask was put in oil bath at 35 °C and the mixture was stirred for 30 min. Then, 1.0 mL of deoxygenated PEBr (1-phenylethyl bromide) or EBiB (ethyl 2-bromoisobutyrate) stock solution (each 5.0×10^{-3} M in acetonitrile) was added to the Schlenk flask via a degassed syringe. A sample was taken without delay for the reference, and other samples were taken at timed intervals. The taken samples were passed through a short alumina column to quench the reaction by removing the copper catalyst.

Results and Discussion

To evaluate the catalytic activities of new tridentate ligands, FPH and MFPH with CuBr as ATRP catalysts, we investigated the polymerization of methyl methacrylate (MMA) and styrene. Typically one equivalent of tridentate ligands such as *N,N,N',N',N''*-pentamethyldiethylenetriamine[9] and terpyridine[29] relative to copper halide is used to form copper catalyst in ATRP. In our study, the polymerization was conducted with one equivalent of FPH and MFPH relative to copper bromide and in a molar ratio of 200:1:1:1 (for

Table I. ATRP of MMA and St Using CuBr / FPH or CuBr / MFPH

Monomer	Ligand	Time(h) / Temp. (°C)	Conv. (%)	$M_{n(th)}$[a]	$M_{n(GPC)}$[b]	M_w/M_n[b]
MMA[c]	FPH	15 / 90	72	14,600	18,500	1.30
MMA[c]	MFPH	15 / 90	72	14,600	15,300	1.33
styrene[d]	FPH	13 / 110	30	6,100	4,800	2.07
styrene[d]	MFPH	15 / 110	67	13,600	10,000	1.77

[a] $M_{n(th)}$=conversion × ([monomer]$_0$/[initiator]$_0$) × $M_{monomer}$ + $M_{initiator}$. [b]Obtained by GPC calibrated with polystyrene standards. [MMA]$_0$:[Initiator]$_0$:[Cu(I)Br]$_0$:[Ligand]$_0$=200:1:1:1. [d][styrene]$_0$:[Initiator]$_0$:[Cu(I)Br]$_0$:[Ligand]$_0$=193:1:1:1.

MMA) and 193:1:1:1 (for styrene) (monomer: initiator: CuBr: ligand). Ethyl 2-bromoisobutyrate and 1-phenylethyl bromide was used as an initiator for MMA and styrene polymerization, respectively. Table I summarizes the results of the polymerization of MMA and styrene with copper bromide/FPH and CuBr/MFPH.

Figure 2 shows the result of MMA polymerization at 90 °C in 50% anisole solution with CuBr/FPH and CuBr/MFPH as catalysts. Both catalysts were not completely soluble in the polymerization media and the copper complex with

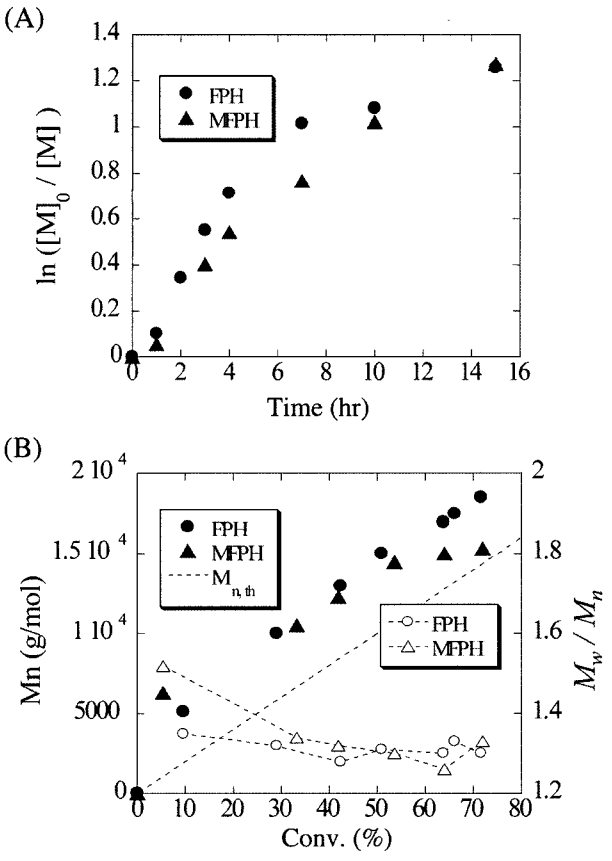


Figure 2. Results of MMA polymerization for the copper-mediated ATRP using FPH and MFPH as the ligand (A) First-order kinetic plots and (B) Evolution of M_n and M_w/M_n with conversion, MMA : 90 °C, [MMA]$_0$=4.76 M (50% anisole solution), [EBiB] =[CuBr]=[ligand]=2.34 × 10^{-2} M, anisole=5.35 mL.

MFPH showed slightly better solubility than that of the copper complex with FPH. The solubility of the catalysts in ATRP is important in controlling polymerization as the deactivator, here Cu(II) complex, should be sufficiently soluble to maintain the appropriate rate of deactivation.[13] To improve the solubility of catalysts, the introduction of long alkyl chain to the ligands has been studied and led to the improvement of polymerization control, especially in lowering molecular weight distribution (PDI).[13] In our study, the methyl substituents increased the rate activation through electron donating effect as discussed later but did not significantly improve the solubility of catalysts.

The conversion of the polymerization with both catalytic systems reached 72% in 15 hrs with narrow molecular weight distribution (PDI = 1.3). The first order kinetic plot (ln([M]$_o$/[M]) vs. time) in the polymerization of MMA with CuBr/FPH and CuBr/MFPH showed curvature, suggesting continuous bimolecular radical termination occurs during the polymerization. As polymerization proceed, the number average molecular weights, M_n, increase linearly and the polydispersity, M_w/M_n decrease with conversion as shown in Figure 2(B) and Figure 3. Thus well-controlled polymerization of MMA with CuBr/FPH and CuBr/MFPH were achieved. One thing to note is that the GPC chromatograms in Figure 3 show the significant tailing in low molecular region, which again suggest continuous termination of growing polymeric radicals during the polymerization.

The polymerizations of styrene with CuBr/FPH and CuBr/MFPH were performed using 1-phenyl ethyl bromide (PEBr) as an initiator at 110 °C (Figure 4). The rate of styrene polymerization was slower than that of MMA polymerization. While the curvature of first order kinetic plots in the polymerization with CuBr/FPH and CuBr/MFPH was observed, M_n increased with conversion following theoretical molecular weights. The molecular weight distributions were broader and PDI remained over 1.5 during the polymerization.

While the polymerization results provide information about the apparent activity of the catalysts in ATRP, it is rather difficult to critically evaluate the activity of the catalysts only based on polymerization kinetics due to the complexities of ATRP process. In ATRP, in addition to the catalyst activity, many parameters affect the overall poly-

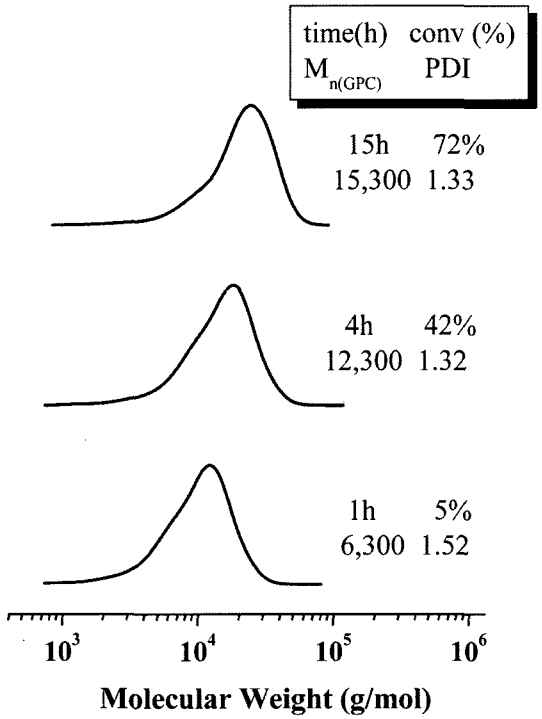


Figure 3. GPC traces of MMA polymerization using MFPH as ligand.

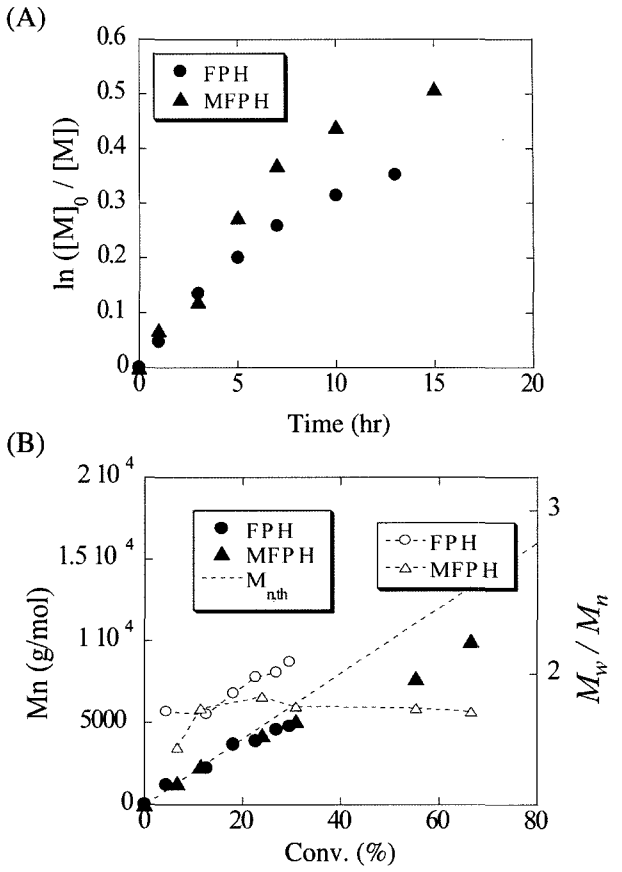
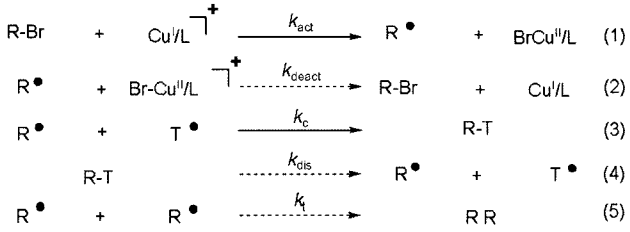


Figure 4. Results of styrene polymerization for the copper-mediated ATRP using FPH and MFPH as the ligand (A) First-order kinetic plots and (B) Evolution of M_n and M_w/M_n with conversion, styrene: 110 °C, $[styrene]_0 = 7.98$ M, [PEBr] = [ligand] = 4.14×10^{-2} M, anisole (internal standard) = 0.50 mL.



Scheme II. Model reaction for measurements of the activation rate constant.

merization kinetics. These parameters include the concentration of persistent radical, i.e. transition metal catalyst in high oxidation state in ATRP, the solubility of the catalysts in lower and higher oxidation state, the type and concentration of the initiator, solvent and so forth. For example, a catalyst that activates faster relatively to its rate of deactivation generates a high concentration of radicals, which then terminate and yield high Cu(II) concentration at the early stage of the polymerization. Then, high concentration of Cu(II) reduced the rate of the polymerization, resulting in low apparent catalytic activity for catalysts with high activity. Therefore, to critically evaluate the catalyst activity in ATRP, it is necessary to determine the activation rate constants for atom transfer reaction.

The activation rate constants can be directly measured using the reported method (Scheme II).[32] The radicals generated by halogen transfer to the copper complex (1) were scavenged with TEMPO ($T^\bullet$). In the presence of a large excess of TEMPO (10 times with respect to the alkyl halide), it was expected that nearly all the alkyl radicals were trapped with TEMPO to form the corresponding alkyl-TEMPO adduct (3). Under these conditions, the rate of activation should be the same as the rate of consumption of R-Br. An excess amount of catalyst (20 times with respect to R-Br) was used to provide pseudo-first-order kinetic conditions. The first-order kinetic plot of the consumption of R-Br was almost linear (Figure 5), indicating that the change in concentration of the catalyst was relatively small during the reaction while reactions 2 and 4 did not contribute significantly.

The activation rate constants for EBiB and PEBr were measured as they can be models for the polymeric chain ends in ATRP of MMA and styrene, respectively. From the slopes of the first kinetic plot (Figure 5), the activation rate constants can be calculated. The activation rate constants

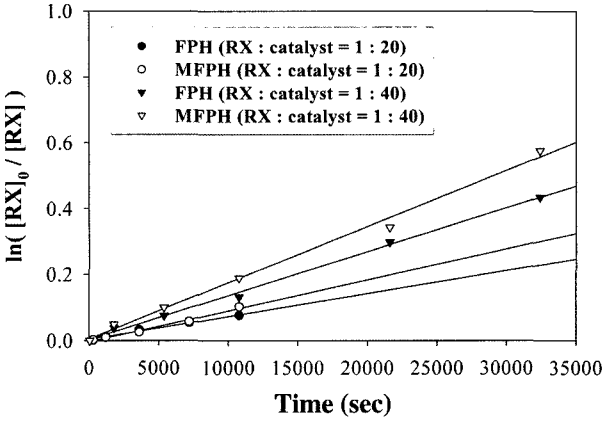


Figure 5. First-order kinetic plots in activation rate constant measurement using PEBr $[PEBr]_0=1.0\times10^{-3}$ M, $[Cu(I)Br]_0=[ligand]_0=2.0\times10^{-2}$ M, $[TEMPO]_0=4.0\times10^{-2}$ M, $[biphenyl]_0=1.0\times10^{-3}$ M for RX : catalyst = 1:20 and $[Cu(I)Br]_0=[ligand]_0=4.0\times10^{-2}$ M, $[TEMPO]_0=8.0\times10^{-2}$ M, $[biphenyl]_0=1.0\times10^{-3}$ M for RX : catalyst = 1:40 in acetonitrile at 35 °C.

measured in this study and previously reported are summarized in Table II. The activation rate constants were measured at 35 °C in acetonitrile which makes homogeneous catalyst solution.

For both PEBr and EBiB, the activation rate constants of CuBr/MFPH are larger than those of CuBr/FPH. The enhanced activation rate of CuBr/MFPH can be explained by the electron donating effect of methyl substituents in furan moiety. The activation rate constants of CuBr/MFPH and CuBr/FPH are several orders of magnitude smaller than those of CuBr/dNbpy and CuBr/PMDETA, two widely used ATRP catalysts. These differences in the activation rate constants are rather unexpected, because the polymerization rates with new tridentate ligands are relatively fast and comparable with those with dNbpy and PMDETA. Considering the smaller activation rate constants and the relatively fast polymerization rates of new catalysts, the deactivation rate constants of the new catalyst are expected to be small. This interpretation is consistent with the observations in the polymerization; the curvature in the first order kinetic plot in the polymerization, broader molecular weight distribution and the existence of low molecular tailing in GPC chromatograms.

Table II. Activation Rate Constants for PEBr and EBiB with Different CuBr Complexes, $[PEBr]_0=[EBiB]_0=[biphenyl]_0=1.0\times10^{-3}$ M, $[Cu(I)Br]_0=[ligand]_0=2.0\times10^{-2}$ M, or 4.0×10^{-2} M $[TEMPO]_0=4.0\times10^{-2}$ M in Acetonitrile at 35 °C

RX	Complex	k_{act} [$M^{-1}s^{-1}$]
PEBr	CuBr / FPH	0.345×10^{-3} ($\pm0.005\times10^{-3}$)
PEBr	CuBr / MFPH	0.45×10^{-3} ($\pm0.02\times10^{-3}$)
PEBr[a]	CuBr / 2dNbpy	0.085
PEBr	CuBr / PMDETA	0.135 ($\pm$0.005)
EBiB	CuBr / FPH	0.233×10^{-2} ($\pm0.005\times10^{-2}$)
EBiB	CuBr / MFPH	0.32×10^{-2} ($\pm0.02\times10^{-2}$)
EBiB[a]	CuBr / 2dNbpy	0.60
EBiB[a]	CuBr / PMDETA	1.7

[a] K. Matyjaszewski, H.-j. Paik, P. Zhou, and S. J. Diamanti, *Macromolecules*, **34**, 5125 (2001).

Conclusions

We studied catalytic activities in the copper-mediated ATRP of MMA and styrene using FPH and MFPH, new tridentate ligands with mixed donor atom. The polymerization of MMA with new catalytic system reached high conversion yielding polymers with a good control of molecular weight and low polydispersity (PDI=1.33). Higher PDI were observed in the polymerization of styrene. Activation rate constant measurement for PEBr and EBiB has allowed to properly evaluate the catalytic activity of CuBr/FPH and CuBr/MFPH and understand the polymerization results.

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References

(1) K. Matyjaszewski and J. Xia, *Chem. Rev.*, **101**, 2921 (2001).
(2) M. Kamigaito, T. Ando, and M. Sawamoto, *Chem. Rev.*, **101**, 3689 (2001).
(3) H. Fischer, *Chem. Rev.*, **101**, 3581 (2001).
(4) Y. A. Kabachii, S. Y. Kochev, L. M. Bronstein, I. B. Blagodatskikh, and P. M. Valetsky, *Polym. Bull.*, **50**, 271 (2003).
(5) J. A. M. Brandts, P. van de Geijn, E. E. van Faassen, J. Boersma, and G. Van Koten, *J. Organomet. Chem.*, **584**, 246 (1999).
(6) E. Le Grognec, J. Claverie, and R. Poli, *J. Am. Chem. Soc.*, **123**, 9513 (2001).
(7) M. Kato, M. Kamigaito, M. Sawamoto, and T. Higashimura, *Macromolecules*, **28**, 1721 (1995).
(8) C. Granel, P. Dubois, R. Jerome, and P. Teyssie, *Macromolecules*, **29**, 8576 (1996).
(9) J. Xia and K. Matyjaszewski, *Macromolecules*, **30**, 7697 (1997).
(10) M. Teodorescu, S. G. Gaynor, and K. Matyjaszewski, *Macromolecules*, **33**, 2335 (2000).
(11) V. C. Gibson, R. K. O'Reilly, W. Reed, D. F. Wass, A. J. P. White, and D. J. Williams, *Chem. Comm.*, 1850 (2002).
(12) V. C. Gibson, R. K. O'Reilly, D. F. Wass, A. J. P. White, and D. J. Williams, *Macromolecules*, **36**, 2591 (2003).
(13) K. Matyjaszewski, T. E. Patten, and J. Xia, *J. Am. Chem. Soc.*, **119**, 674 (1997).
(14) D. M. Haddleton, C. B. Jasieczek, M. J. Hannon, and A. J. Shooter, *Macromolecules*, **30**, 2190 (1997).
(15) B. Göbelt and K. Matyjaszewski, *Macromol. Chem. Phys.*,

201, 1619 (2000).
(16) S. C. Hong and K. Matyjaszewski, *Macromolecules*, **35**, 7592 (2002).
(17) P. Kubisa, *Prog. Polym. Sci.*, **29**, 3 (2004).
(18) T. Sarbu and K. Matyjaszewski, *Macromol. Chem. Phys.*, **202**, 3379 (2001).
(19) J. Xia, T. Johnson, S. G. Gaynor, K. Matyjaszewski, and J. DeSimone, *Macromolecules*, **32**, 4802 (1999).
(20) J. Xia and K. Matyjaszewski, *Macromolecules*, **32**, 2434 (1999).
(21) J. Xia, X. Zhang, and K. Matyjaszewski, *Macromolecules*, **32**, 3531 (1999).
(22) K. Matyjaszewski, B. Göbelt, H.-j. Paik, and C. P. Horwitz, *Macromolecules*, **34**, 430 (2001).
(23) G. H. Li and C. G. Cho, *Macromol. Res.*, **10**, 339 (2002).
(24) W. Xu, X. Zhu, Z. Cheng, J. Chen, and J. Lu, *Macromol. Res.*, **12**, 32 (2004).
(25) Y.-W. Lee, S. M. Kang, K. R. Yoon, Y. S. Chi, I. S. Choi, S.-P. Hong, B.-C. Yu, H.-j. Paik, and W. S. Yun, *Macromol. Res.*, **13**, 356 (2005).
(26) T. Pintauer and K. Matyjaszewski, *Coord. Chem. Rev.*, **249**, 1155 (2005).
(27) S. Perrier, S. P. Armes, X. S. Wang, F. Malet, and D. M. Haddleton, *J. Polym. Sci. Polym. Chem.*, **39**, 1696 (2001).
(28) T. E. Patten, J. Xia, T. Abernathy, and K. Matyjaszewski, *Science*, **272**, 866 (1996).
(29) G. Kickelbick and K. Matyjaszewski, *Macromol. Rapid Comm.*, **20**, 341 (1999).
(30) J. M. Goodwin, M. M. Olmstead, and T. E. Patten, *J. Am. Chem. Soc.*, **126**, 14352 (2004).
(31) J. Xia, S. G. Gaynor, and K. Matyjaszewski, *Macromolecules*, **31**, 5958 (1998).
(32) K. Matyjaszewski, H.-j. Paik, P. Zhou, and S. J. Diamanti, *Macromolecules*, **34**, 5125 (2001).