Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization Catalyzed by Copper(I) and Picolylamine Complexes

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Received October 29, 1998; Revised Manuscript Received January 20, 1999

ABSTRACT: Two picolyl structure based amines, the tridentate *N,N*-bis(2-pyridylmethyl)octylamine (BPMOA) and the tetradentate tris[(2-pyridyl)methyl]amine, have been successfully synthesized and employed as new ligands in the copper-mediated atom transfer radical polymerization (ATRP) of styrene, methyl acrylate, and methyl methacrylate. Polymerizations showed a linear increase in molecular weight with conversion and relatively low polydispersities throughout the reactions. Compared with the structurally related *N,N,N,N′,N′*-pentamethyldiethylenetriamine, different kinetic behavior was observed when BPMOA was used as the ligand for the copper-mediated ATRP of methyl methacrylate. This is mainly attributed to the solubility difference of the catalyst in these systems. The ready availability of ligands based on the picolyl structure and their easily tunable solubilities as well as steric and electronic properties make them very attractive as new ligands in copper-mediated ATRP.

Introduction

Controlled/"living" radical polymerization has been a field of intensive research in recent years.[1] Significant progress has been made in several areas including nitroxide-mediated stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and most recently, in degenerative transfer[2] by reversible addition-fragmentation chain transfer polymerization.[3] In ATRP, new advances have been aimed toward new metals and new ligands. By following the pioneering work by Sawamoto et al.[4] who used ruthenium, and our group[5] who used copper as the transition metals, alternative systems involving other transition-metal catalysts, such as iron[6,7] or nickel,[8,9] have also been developed. Of all of the transition metals, copper appears to be the most robust because of its versatility; e.g., a variety of monomers can be readily polymerized in a well-controlled fashion. Initially, we reported the use of 2,2′-bipyridine (bpy) as the ligand in copper-mediated ATRP to promote the controlled polymerization of styrene and (meth)acrylic monomers.[5,10] Later, the control of ATRP was further improved, and polydispersities (M_w/M_n) as low as 1.05 were obtained by employing more solubilizing 4,4′-diheptyl-2,2′-bipyridine (dHbpy) or 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) ligands.[11,12] The use of pyridine imines[13] and phenanthroline derivatives[14] as new ligands has also been reported. Recently, we have reported the use of multidentate aliphatic amines as less expensive ligands to promote well-controlled copper-mediated ATRP.[15,16] As part of our ongoing effort to search for new ligands that are readily available and whose structures can easily be varied for tuning, we selected a picolylamine-based structure. In this paper, we report our initial effort in the synthesis of a new class of ligand and its application in copper-mediated ATRP.
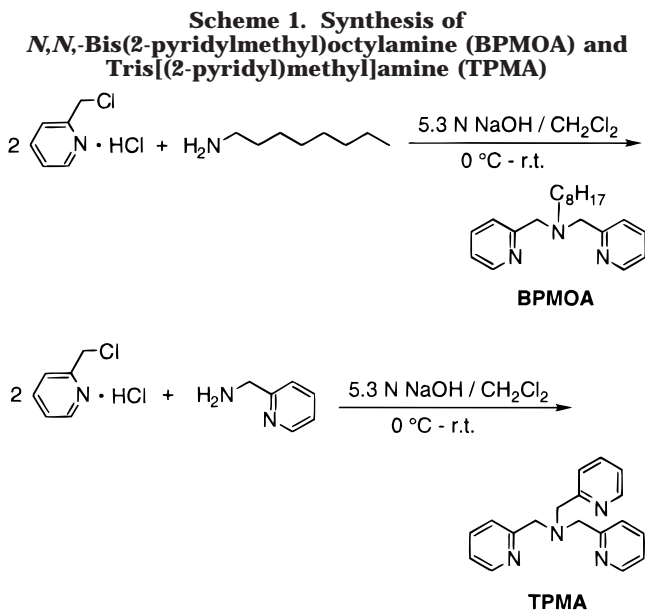
Experimental Section

Materials. Styrene, methyl acrylate (MA), and methyl methacrylate (MMA) from Aldrich were vacuum distilled over CaH₂ and stored under an argon atmosphere at −15 °C. Anisole (solvent, 99.7%) was obtained from Aldrich and used without further purification. MMA and anisole were bubbled with dry argon for at least 15 min immediately before polymerization. CuBr (98%, Aldrich) was purified according to the published procedure.[17] The initiators [1-phenylethyl bromide (PEBr; 97%)], ethyl 2-bromopropionate (EBP; 99%), ethyl 2-bromoisobutyrate (EB*i*B; 98%), and *p*-toluene-sulfonyl chloride (*p*TSCl; 98%), were obtained from Aldrich and used without any further purification. The first ligand, tris[(2-pyridyl)methyl]amine (TPMA), was prepared according to the reported procedure.[18] Recrystallization from diethyl ether yielded TPMA (yield: 75%) as a white crystalline solid: mp 85−86 °C; ^{1}H NMR (300 MHz, CDCl₃) δ 8.55 (d, 3H), 7.65 (t, 3H), 7.55 (d, 3H), 7.10 (t, 3H), 3.85 (s, 6H) ppm. The other ligand, *N,N*-bis(2-pyridylmethyl)octylamine (BPMOA), was synthesized in a manner similar to the first but using *n*-octylamine in place of 2-(aminomethyl)pyridine. Purification using activated neutral aluminum oxide chromatography (EtOAc/hexane, $^1/_5$) afforded BPMOA (yield: 85%) as a light yellow oil: ^{1}H NMR (300 MHz, CDCl₃) δ 8.5 (d, 2H), 7.65 (t, 2H), 7.55 (d, 2H), 7.10 (t, 2H), 3.8 (s, 4H), 2.55 (t, 2H), 1.5−1.2 (m, 12H), 0.85 (t, 3H) ppm.

Polymerization. Bulk. To dry glass tubes with copper halide were added, using degassed syringes, amine ligand, degassed monomer, and the initiator. Three freeze−pump−thaw cycles were performed, and the tubes were sealed under vacuum and placed in an oil bath held by a thermostat at the desired temperature. At timed intervals, the polymerizations were stopped by cooling the tubes in ice water. Afterward, the tubes were opened, and the contents were dissolved in THF.

Solution. A dry round-bottom flask was charged with copper halide. The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed amine ligand, monomer, and solvent were added using degassed syringes. After the mixture was allowed to stir at room temperature until it was homogeneous, the initiator was added, and the flask was immersed in an oil bath held by a thermostat at the desired tempera-

Scheme 1. Synthesis of
N,N,-Bis(2-pyridylmethyl)octylamine (BPMOA) and
Tris[(2-pyridyl)methyl]amine (TPMA)

BPMOA

TPMA

ture. At timed intervals, samples were withdrawn from the flask using degassed syringes and added to THF.

Characterization. Monomer conversion was determined from the concentration of residual monomer, with THF (for styrene and MA) or anisole (for MMA) as internal standards, using a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 Chromatopac. Molecular weights and molecular weight distributions were measured using a Waters 712 WISP autosampler and the following PSS columns: guard, 10^5, 1000, and 100 Å. Polystyrene and poly(MMA) standards were used to calibrate the columns. EPR spectra were recorded on a Bruker ESP-300 X-band EPR spectrometer using the reported procedure.[19]

Results and Discussion

ATRP Using N,N-Bis(2-pyridylmethyl)octylamine as the Ligand. BPMOA was synthesized by the coupling of 2-picolyl chloride hydrochloride with the primary amine as shown in Scheme 1 adapting the reported procedure.[18] n-Octylamine was chosen to achieve good solubility of the copper−ligand complex. The reaction is easy to carry out, and the product can be isolated using column chromatography. Yields of the purified product were usually around 85%. A great advantage of this synthetic procedure is its versatility. A large number of primary amines are commercially available, making the tuning of the catalytic properties very straightforward.

In contrast to the dark brown color observed when bpy and its derivatives were used as the ligand for Cu-(I) halides in ATRP, polymerization solutions employing BPMOA were yellow and homogeneous at room temperature. At the reaction temperature, the polymerization solutions of both styrene and MMA gradually turned to green, indicating the formation of copper(II), presumably resulting from radical termination reactions. As the polymerization proceeded, the polymerization solution of styrene became progressively heterogeneous, but that of MMA remained homogeneous, indicative of the lower solubility of the catalyst at lower monomer concentrations for a less-polar monomer. In contrast, the polymerization solutions of MA remained yellow and homogeneous throughout the polymerization.
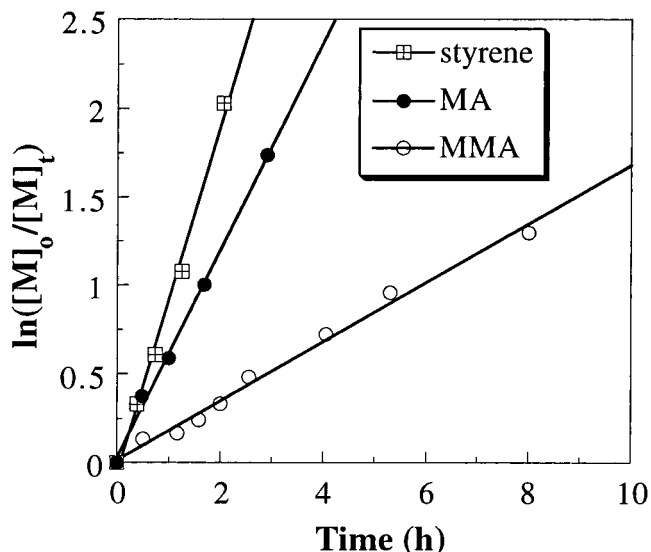

Figure 1. Kinetic plots for copper-mediated ATRP using BPMOA as the ligand. For styrene: 110 °C; $[styrene]_o = 8.7$ M (bulk); $[styrene]_o/[PEBr]_o = 96$; and $[PEBr]_o/[CuBr]_o/[BPMOA]_o = 1/1/1$. For MA: 50 °C; $[MA]_o = 10.8$ M (bulk); $[MA]_o/[EBP]_o = 232$; and $[EBP]_o/[CuBr]_o/[BPMOA]_o = 1/1/1$. For MMA: 50 °C; $[MMA]_o = 4.6$ M (50 vol % in anisole); $[MMA]_o/[EBiB]_o = 200$; and $[EBiB]_o/[CuCl]_o/[BPMOA]_o = 1/1/1$.
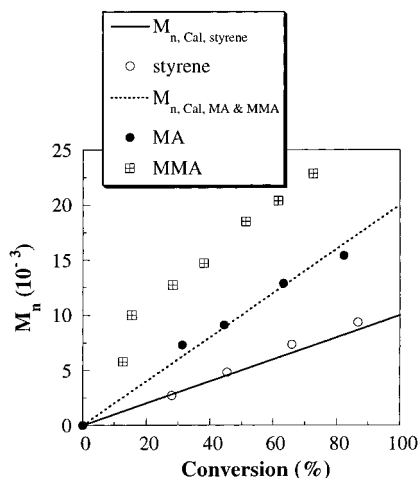

Figure 2. Dependence of molecular weight, $M_{n,SEC}$, on monomer conversion for the copper-mediated ATRP using BPMOA as the ligand. See Figure 1 for conditions.
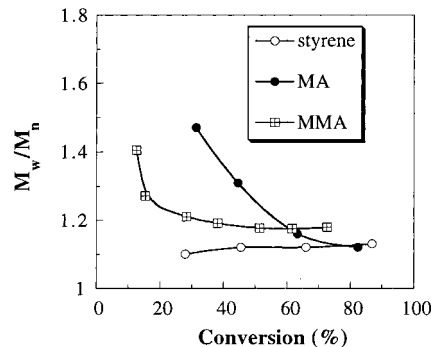

Figure 3. Dependence of polydispersity, M_w/M_n, on monomer conversion for the copper-mediated ATRP using BPMOA as the ligand. See Figure 1 for conditions.

The results for the polymerization of styrene, MA, and MMA are shown in Figures 1−3. For MMA, the halogen-exchange method was used to gain better control of the polymerization.[20] The linear plots of $\ln([M]_o/[M]_t)$ versus

**Table 1. Copper-Mediated ATRP of MMA Using
N,N,-Bis(2-pyridylmethyl)octylamine as the Ligand[a]**

entry	temp (°C)	initiator	CuX	time (h)	conv (%)	$M_{n,cal}$	$M_{n,SEC}$	M_w/M_n
1	22	EB*i*B	CuBr	3.5	52	10 400	14 600	1.57
2	22	EB*i*B	CuCl	13.7	55	11 000	18 000	1.24
3	50	EB*i*B	CuBr	1.0	44	8 800	13 700	1.46
4	50	EB*i*B	CuCl	2.5	42	8 400	14 500	1.19
5	50	*p*TSCl	CuBr	3.5	43	8 600	14 000	1.22

[a] Conditions: $[MMA]_o$ = 4.6 M (50 vol % in anisole); $[MMA]_o/$
$[initiator]_o$ = 200; $[initiator]_o/[CuX]_o/[BPMOA]_o$ = 1/1/1.

time observed for all three monomers indicated that the concentration of growing radicals remained constant (Figure 1). Molecular weights (M_n) increased linearly with conversion, and the measured molecular weights were close to the calculated values for both styrene and MA polymerizations (Figure 2). Polydispersities for all three monomers remained quite low (M_w/M_n < 1.2) at conversions higher than 50% (Figure 3).

The deviation of the measured molecular weights from the calculated values for MMA (Figure 2) was attributed to the radical termination reactions at the early stage of the polymerization which lowered the apparent initiator efficiency (apparent initiator efficiency $f = M_{n,Cal}/M_{n,SEC}$). In fact, the polymerization of MMA proceeded even at ambient temperature (Table 1, entries 1 and 2). The polydispersity was improved using either the halogen-exchange method (Table 1, entries 2 and 4)[20] or the *p*TSCl/CuBr combination (Table 1, entry 5).[21] The concentration of growing radicals in the mixed halogen system is lower, which not only slows down the polymerization but also reduces the proportion of terminated chains. As a result, the control of the polymerization is improved, and the polydispersity is reduced.

When copper-mediated ATRP of MMA was carried out under the same conditions using another tridentate amine ligand of similar structure, namely *N,N,N,N′,N′*-pentamethyldiethylenetriamine (PMDETA), kinetic curvature was observed at 50 °C, similar to what was previously reported at 90 °C.[15] In contrast, a linear kinetic plot was obtained when BPMOA was used as the ligand (Figure 1). We attribute this different kinetic behavior mainly to the solubility difference of the copper(II) species. In the case of a less solubilizing ligand such as PMDETA, the concentration of the deactivator copper(II) ("persistent radical") in the polymerization solution was lower. This led to the higher radical concentration and the continuous consumption of alkyl halide and the active copper(I) species by radical termination reactions, resulting in a gradual decrease in the polymerization rate. When BPMOA was used as the ligand, the copper(II) species were soluble, and thus led to the reduced polymerization rate and lower radical concentration via better-controlled persistent radical effect. This prevented excessive termination and depletion of alkyl halide and the active copper(I) species.

The polymerization of MA using either PMDETA or BPMOA as the ligand was followed by electron paramagnetic resonance (EPR) studies. As shown in Figure 4, the EPR signals of both catalytic systems are quite similar, indicating that similarities existed in the structure of copper(II) species. However, the total amount of copper(II) (both soluble and insoluble in solution) generated in the polymerization when the less solubilizing PMDETA was used as the ligand was about 2 times higher than that when BPMOA was employed
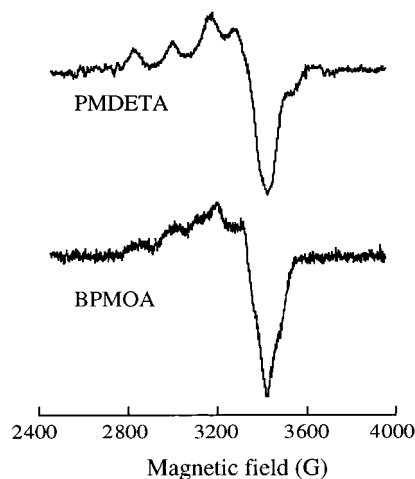

Figure 4. EPR spectra of copper-mediated ATRP of MA using PMDETA and BPMOA as the ligands. Reaction conditions: 50 °C; $[MA]_o$ = 10.8 M (bulk); $[MA]_o/[EBP]_o$ = 232; and $[EBP]_o/[CuBr]_o/[ligand]_o$ = 1/1/1.
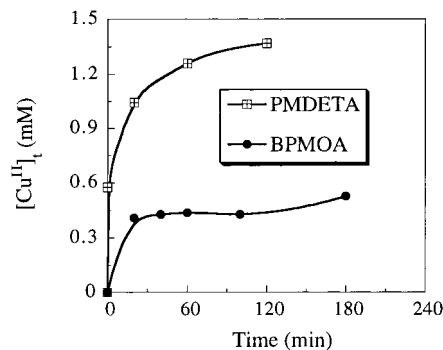

Figure 5. Plots of time dependence of the concentration of copper(II) species for ATRP of MA using PMDETA and BPMOA as the ligands. See Figure 4 for conditions.

**Table 2. Copper-Mediated ATRP Using
Tris[(2-pyridyl)methyl]amine as the Ligand**

entry	monomer	temp (°C)	time (h)	conv (%)	$M_{n,cal}$	$M_{n,SEC}$	M_w/M_n
1[a]	styrene	110	4.0	79	7 900	8 600	1.07
2[b]	MA	50	0.9	79	15 800	15 200	1.05
3[c]	MMA	50	1.0	<5	<1 000	10 500	1.12

[a] Conditions: $[styrene]_o$ = 8.7 M (bulk); $[styrene]_o/[PEBr]_o$ = 96; $[PEBr]_o/[CuBr]_o/[TPMA]_o$ = 1/0.2/0.2. [b] $[MA]_o$ = 10.8 M (bulk); $[MA]_o/[EBP]_o$ = 232; $[EBP]_o/[CuBr]_o/[TPMA]_o$ = 1/0.2/0.2. [c] $[MMA]_o$ = 4.6 M (50 vol % in anisole); $[MMA]_o/[EB*i*B]_o$ = 200; $[EB*i*B]_o/[CuBr]_o/[TPMA]_o$ = 1/1/1.

as the ligand (Figure 5). These results support the assumption that a more solubilizing ligand can result in better-controlled persistent radical effects and reduce the amount of radical termination reactions.

ATRP Using Tris[(2-pyridyl)methyl]amine (TPMA) as the Ligand. Recently, we have reported the controlled ATRP of acrylates at ambient temperature using as the catalyst CuBr complexed by a tripodal aliphatic amine, tris[2-(dimethylamino)ethyl]amine (Me_6TREN).[16] When 2-picolyl chloride hydrochloride was reacted with 2-(aminomethyl)pyridine (Scheme 1), a new tripodal ligand containing three pyridines, tris[(2-pyridyl)methyl]amine (TPMA), was synthesized. Recently it has been shown that the CuCl/TPMA complex can act as a very efficient catalyst in inter- and intramolecular atom transfer radical additions.[22] Table 2 displays the results of the ATRP of styrene, MA, and
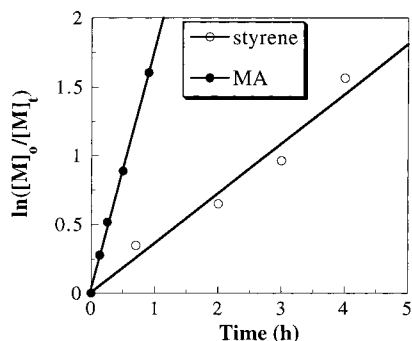
Figure 6. Kinetic plots for the copper-mediated ATRP of styrene and MA using TPMA as the ligand. For styrene: 110 °C; $[\text{styrene}]_o = 8.7$ M (bulk); $[\text{styrene}]_o/[\text{PEBr}]_o = 96$; and $[\text{PEBr}]_o/[\text{CuBr}]_o/[\text{TPMA}]_o = 1/0.2/0.2$. For MA: 50 °C; $[\text{MA}]_o = 10.8$ M (bulk); $[\text{MA}]_o/[\text{EBP}]_o = 232$; and $[\text{EBP}]_o/[\text{CuBr}]_o/[\text{TPMA}]_o = 1/0.2/0.2$.
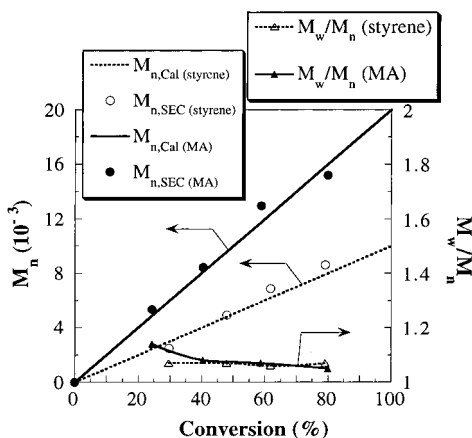

Figure 7. Dependence of molecular weight, $M_{n,SEC}$, and polydispersity, M_w/M_n, on monomer conversion for copper-mediated ATRP of styrene and MA using TPMA as the ligand. See Figure 6 for conditions.

MMA using CuBr/TPMA as the catalyst. Even with a catalyst-to-initiator ratio of 0.2, well-controlled polymerizations were obtained with measured molecular weights close to the calculated values and low polydispersities ($M_w/M_n < 1.1$) for both styrene and MA. For MMA, a very low apparent initiator efficiency ($f < 0.1$) was obtained, presumably due to the irreversible termination reactions as a result of the large number of radicals generated at the beginning of the polymerization, under these reaction conditions.

The kinetic plots with CuBr/TPMA as the catalyst for the ATRP of styrene and MA are presented in Figure 6. The linearity of the semilogarithmic plots of $\ln([\text{M}]_o/[\text{M}]_t)$ versus time indicates that the polymerization was first-order with respect to monomer and that the concentration of growing radicals remained constant for both monomers. The M_n values increased linearly with conversion with low polydispersities throughout the polymerizations (Figure 7).

Conclusions

In conclusion, two new picolyl structure based amines, the tridentate *N,N*-bis(2-pyridylmethyl)octylamine and

the tetradentate tris[(2-pyridyl)methyl]amine,[23] have been successfully employed as new ligands in the copper-mediated atom transfer radical polymerization of styrene, methyl acrylate, and methyl methacrylate. Polymerizations showed a linear increase of molecular weights with conversion and relative low polydispersities throughout the reactions. The different kinetic behavior between the new ligand and the similar structure PMDETA for the polymerization of MMA was attributed to the solubility difference of the catalyst. The straightforward ligand synthesis combined with the large number of amines that are readily available makes picolyl structure based amines very attractive as new ligands in copper-mediated ATRP. Further studies concerning the electronic tuning and other structural variations of the catalyst are in progress.

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MA981694N