Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization Using Multidentate Amine Ligands

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ABSTRACT: Three multidentate amines, tetramethylethylenediamine (TMEDA), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) have been successfully used as new ligands in the copper mediated atom transfer radical polymerization (ATRP) of styrene, methyl acrylate and methyl methacrylate. All the polymerizations were well controlled with a linear increase of molecular weights (M_n) with conversion and relatively low polydispersities throughout the reactions. Compared to the 2,2′-bipyridine (bipy) based ligands, most multidentate amines are less expensive and the polymerization mixtures are less colored. In particular, the use of the tridentate PMDETA and the tetradentate HMTETA as the ligands resulted in faster polymerization rates for styrene and methyl acrylate than those using bipy as the ligand. This may be in part attributed to the fact that the coordination complexes between copper and the simple amines have lower redox potentials than the copper−bipy complex, resulting in higher rates of activation of the dormant halides. Additional rate effects may originate from the solubilities of the copper(I) and copper(II) complexes. The new ligands are very attractive alternatives to bipy and its derivatives as ligands.

Introduction

Free radical polymerization has been a very important industrial process due to low requirements on monomer and reactant purity, facile copolymerization, and the fact that polymerizations can be conducted in either emulsion or suspension using water as the medium. The significant drawback to these free radical polymerization processes is that polymers with uncontrolled molecular weights and relatively high polydispersities are usually obtained. It has become the focus of extensive research in the past few years to tame the free radical polymerization so that well-defined polymers with low polydispersities and complex architectures can be obtained. Significant progress has been made in the development of such controlled/"living" radical polymerization.[1−11] One such controlled/"living" polymerization system is the transition metal catalyzed, atom transfer radical polymerization (ATRP), a novel controlled/"living" radical process using an alkyl halide as an initiator, and a metal in the low oxidation state with complexing ligands.[4−11] In copper (CuX where $X = Cl^-$ and Br^- with 2,2′-bipyridine as the ligand) mediated ATRP, the polymerization of styrene[7,12] and (meth)acrylates[13,14] has yielded polymers with degrees of polymerization predetermined up to $M_n \approx 10^5$ and $M_w/M_n < 1.5$.

When alkyl-substituted bipy ligands such as 4,4′-di-*n*-heptyl-2,2′-bipyridine (dHbipy) or 4,4′-di-5-nonyl-2,2′-bipyridine (dNbipy) were used, the resulting homogeneous copper ATRP of styrene with 1-phenylethyl bromide (1-PEBr) as the initiator yielded polymers with predetermined molecular weight up to 10^5 and polydispersity as low as 1.05.[7] The detailed kinetic investigation of the ATRP of styrene under such homogeneous conditions showed that the optimum ratio of ligand to copper(I) halide was 2:1, and that ATRP exhibited first-order kinetics with respect to monomer, initiator, and copper(I) halide concentration.[12]

As part of our continuous effort to search for a more efficient and inexpensive catalytic system for ATRP, we decided to study the use of simple amines as ligands for the copper ATRP system. The simple amines are of interest in ATRP for three general reasons. First, most of the simple amines are less expensive, more accessible and more tunable than 2,2′-bipyridine (bipy) ligands. Second, due to the absence of the extensive π-bonding in the simple amines, the subsequent copper complexes are less colored. Third, since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper−bipy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates.[15,16] After extensive investigation of many commercially available simple alkyl amine ligands, we have discovered several new ATRP systems with faster rate, better control, and fewer side reactions for the polymerization of styrene, methyl acrylate and methyl methacrylate, and the results are presented in this paper. The structures of the new amine ligands used in this study are shown in Figure 1. They are tetramethylethylenediamine (TMEDA), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA).

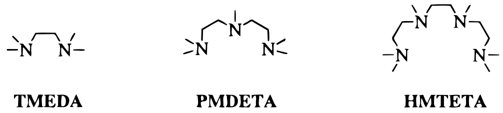

Figure 1. Structures of the amine ligands.

Experimental Section

Materials. Styrene, methyl acrylate (MA), and methyl methacrylate (MMA) from Aldrich were vacuum distilled over CaH_2 and stored under an argon atmosphere at −15 °C. Anisole (solvent, 99.7%) and ligands tetramethylethylenediamine (TMEDA), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) were obtained from Aldrich and used without further purification. The ligand, 4,4′-di-5-nonyl-2,2′-dipyridyl (dNbipy) was prepared according to the reported procedure.[12] 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 (1-PEBr, 97%),

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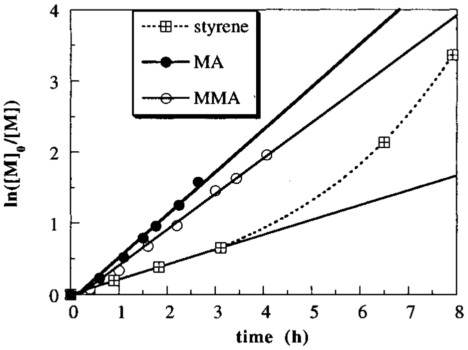

Figure 2. Kinetic plots for the ATRP of styrene, MA, and MMA using TMEDA as the ligand. For styrene: 110 °C; [styrene]$_o$ = 8.7 M (bulk); [1-PEBr]$_o$ = [CuBr]$_o$ = [TMEDA]$_o$/2 = 0.090 M. For MA: 110 °C; [MA]$_o$ = 10.8 M (bulk); [2-EBP]$_o$ = [CuBr]$_o$ = [TMEDA]$_o$/2 = 0.047 M. For MMA: 90 °C; [MMA]$_o$ = 4.62 M (anisole solution); [2-EBiB]$_o$ = [CuBr]$_o$ = [TMEDA]$_o$/2 = 0.023 M.

ethyl 2-bromopropionate (2-EBP, 99%), ethyl 2-bromoisobutyrate (2-EBiB, 98%), and *p*-toluenesulfonyl chloride (*p*-TSCl) were obtained from Aldrich and used without any further purification.

Polymerization. Bulk. To dry glass tubes with CuBr 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 into ice–water. Afterwards, the tubes were opened and the contents dissolved in THF.

Solution. A dry round-bottomed flask was charged with CuBr. 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 temperature. 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) and anisole (for MMA) as internal standards, using a Shimadzu GC-14 gas chromatograph equiped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 Chromatapac. Molecular weights and molecular weight distributions were measured using a Waters 712 WISP autosampler and the following Phenogel GPC columns: guard, linear, 1000 Å, and 100 Å. Polystyrene and poly(MMA) standards were used to calibrate the columns.

Results and Discussion

ATRP Using Tetramethylethylenediamine (TMEDA) as the Ligand. TMEDA is the simplest bidentate fully methylated amine ligand that is commercially available. With TMEDA as the ligand, the reaction mixtures were pale green in color as opposed to the dark red color in the systems based on 2,2′-bipyridine (bipy). The light green color indicated the presense of a small amount of copper(II) halide. The kinetic plots of polymerization with TMEDA as the ligand in ATRP of styrene, methyl acrylate, and methyl methacrylate are presented in Figure 2. The linearity of the semilogarithmic plot of ln([M]$_o$/[M]) vs time for both methyl acrylate and methyl methacrylate indicates the polymerizations were first-order with respect to monomer and that the concentration of the growing radicals remained constant. However, the kinetic plot for styrene showed a significant deviation from first-order kinetics with respect to the monomer at higher conversions, indicative of an increase in the concentration of the propagating radicals. One possible explanation is that as the conversion increased, the concentration of copper(II) halide decreased due to the low solubility of the $CuBr_2$–TMEDA complex. This resulted in an increase in the polymerization rate, as previously reported kinetic investigations showed ATRP generally has a negative order with respect to copper(II) halide concentration.[12,13]

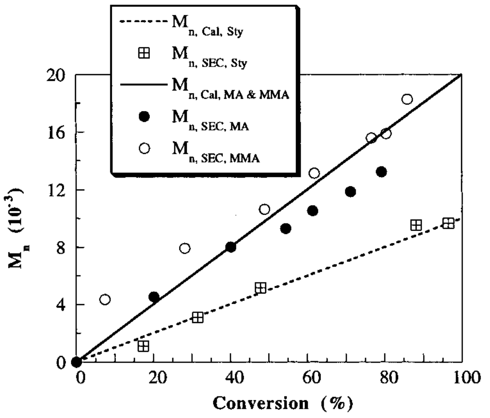

Figure 3. Dependence of molecular weight, M_n, on monomer conversion for the ATRP of styrene, MA, and MMA using TMEDA as the ligand. See Figure 2 for conditions.

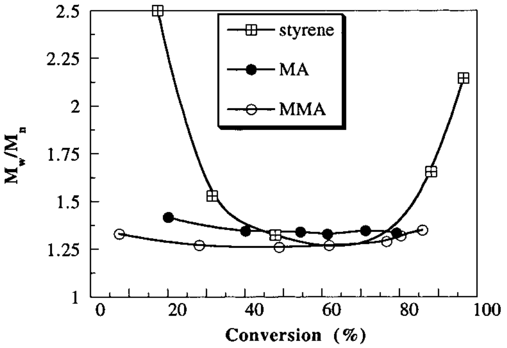

Figure 4. Dependence of molecular weight distribution, M_w/M_n, on monomer conversion for the ATRP of styrene, MA, and MMA using TMEDA as the ligand. See Figure 2 for conditions.

Compared to bipy or substituted bipy derivatives, TMEDA as the ligand resulted in a slower polymerization rate.[12−14] It is possible that steric effects from the methyl groups on the nitrogens make the resulting copper(I)–TMEDA complex less effective to abstract halogen atoms to form radicals. The molecular weights (M_n) increased linearly with conversion indicating a controlled radical process (Figure 3); however, the polydispersities (M_w/M_n) for all three polymerizations showed significantly higher values than those obtained using bipy or its derivatives as the ligands (Figure 4). For styrene, there was an increase in polydispersity at higher conversions, possibly due to the decrease in the copper(II) halide concentration in the solution, since the copper(II) halide is the deactivating reagent in ATRP.

ATRP Using *N,N,N′,N′,N″*-Pentamethyldiethylenetriamine (PMDETA) as the Ligand. When this tridentate amine ligand was employed in ATRP, the rate of polymerization showed a significant increase for both styrene and methyl acrylate, as compared to the corresponding bipy systems.[12,13] The kinetic plots for the polymerization of styrene, methyl acrylate and methyl methacrylate are shown in Figure 5. The linear kinetic plots for styrene and methyl acrylate indicate the constant concentration of the growing radicals. For

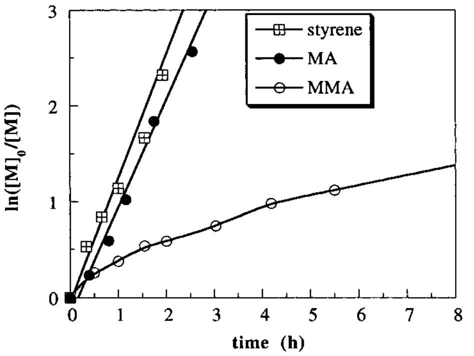

Figure 5. Kinetic plots for the ATRP of styrene, MA, and MMA using PMDETA as the ligand. For styrene: 110 °C; [styrene]$_o$ = 8.7 M (bulk); [1-PEBr]$_o$ = [CuBr]$_o$ = [PMDETA]$_o$ = 0.090 M. For MA: 90 °C; [MA]$_o$ = 10.8 M (bulk); [2-EBP]$_o$ = [CuBr]$_o$ = [PMDETA]$_o$ = 0.047 M. For MMA: 90 °C; [MMA]$_o$ = 4.62 M (anisole solution); [2-EBiB]$_o$ = [CuBr]$_o$ = [PMDETA]$_o$ = 0.023 M.

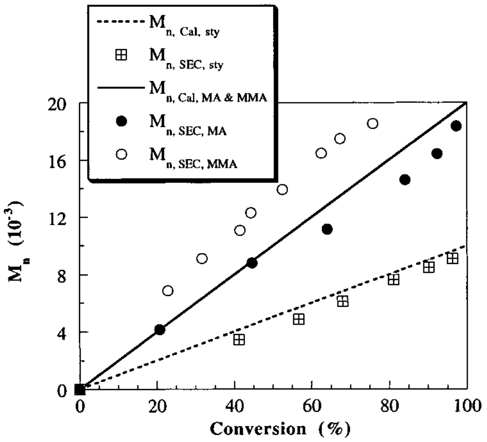

Figure 6. Dependence of molecular weight, M_n, on monomer conversion for the ATRP of styrene, MA, and MMA using PMDETA as the ligand. See Figure 5 for conditions.

methyl methacrylate, however, curvature of the kinetic plot was observed.

The higher polymerization rate of PMDETA as the ligand is partially attributed to the lower redox potential of the copper(I)−PMDETA complex than the copper(I)-bipy complex, which shifts the equilibrium from the dormant species toward the active species resulting in the generation of more radicals in the system. As in the case where TMEDA was used as the ligand, the reaction mixtures using PMDETA as the ligand were pale green in color. In contrast to when TMEDA or bipy was used as the ligand, a copper(I) to PMDETA ratio of 1:1 was sufficient to achieve maximum rates and control of polymerization. The M_n values increased linearly with conversion (Figure 6) with low polydispersities throughout the polymerization (Figure 7). Thus, a well-controlled radical process, comparable to bipy as the ligand, but with faster polymerization rates was achieved. The low polydispersities can be ascribed to the less sterically hindered copper(II)−PMDETA complex which facilitates the deactivation process.

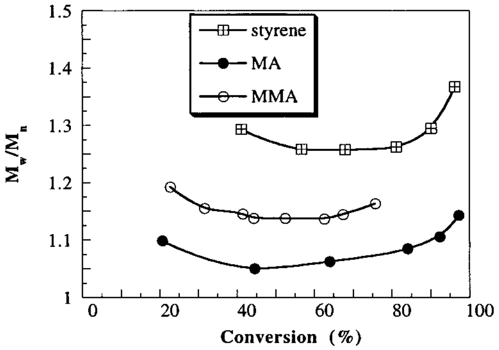

Figure 7. Dependence of molecular weight distribution, M_w/M_n, on monomer conversion for the ATRP of styrene, MA, and MMA using PMDETA as the ligand. See Figure 5 for conditions.

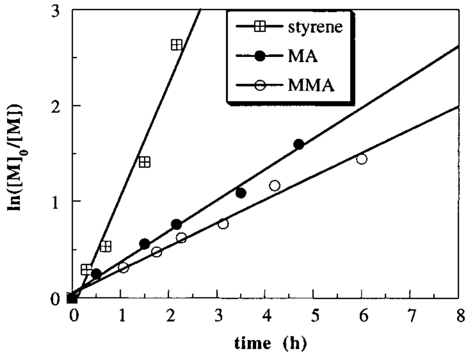

Figure 8. Kinetic plots for the ATRP of styrene, MA, and MMA using HMTETA as the ligand. For styrene: 110 °C; [styrene]$_o$ = 8.7 M (bulk); [1-PEBr]$_o$ = [CuBr]$_o$ = [HMTETA]$_o$ = 0.090 M. For MA: 90 °C; [MA]$_o$ = 10.8 M (bulk); [2-EBP]$_o$ = [CuBr]$_o$ = [HMTETA]$_o$ = 0.047 M. For MMA: 90 °C; [MMA]$_o$ = 4.62 M (anisole solution); [p-TSCl]$_o$ = [CuBr]$_o$ = [HMTETA]$_o$ = 0.023 M.

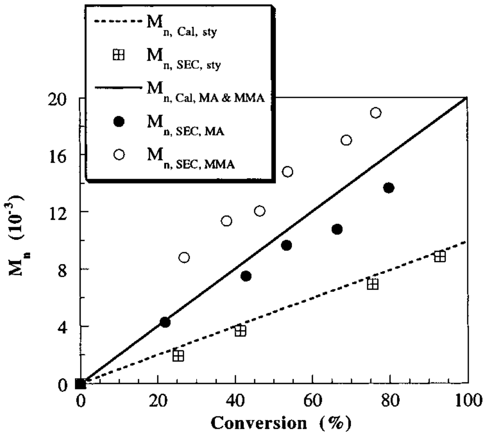

Figure 9. Dependence of molecular weight, M_n, on monomer conversion for the ATRP of styrene, MA, and MMA using HMTETA as the ligand. See Figure 8 for conditions.

ATRP Using 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) as the Ligand. Similar to when PMDETA was employed as the ligand, a copper(I) to HMTETA ratio of 1:1 was sufficient to achieve maximum rates and control of polymerization. The reaction mixtures were slightly green in color. The linear kinetic plots displayed in Figure 8 indicate a constant concentration of the growing radicals and that the reactions were first order with respect to monomer concentrations. Polymerizations for all three monomers showed well-controlled characteristic with M_n increasing linearly with conversion (Figure 9) and low polydispersities (Figure 10) throughout the reactions.

Conclusions

In conclusion, three mutidentate linear amines have been successfully employed as new ligands in the copper mediated atom transfer radical polymerization of styrene, methyl acrylate, and methyl methacrylate. All the polymerizations showed a linear increase of molecular

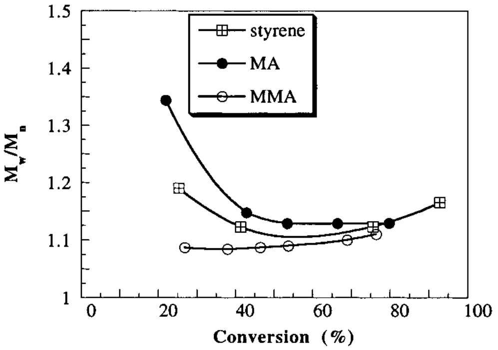

Figure 10. Dependence of molecular weight distribution, M_w/M_n, on monomer conversion for the ATRP of styrene, MA, and MMA using HMTETA as the ligand. See Figure 8 for conditions.

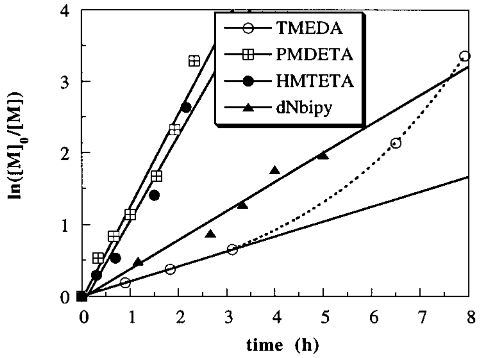

Figure 11. Effect of different ligands on the rate of ATRP of styrene in bulk at 110 °C: $[\text{styrene}]_o = 8.7$ M; $[\text{1-PEBr}]_o = [\text{CuBr}]_o = 0.090$ M; $[\text{TMEDA}]_o = 0.18$ M; $[\text{dNbipy}]_o = 0.18$ M; $[\text{PMDETA}]_o = 0.090$ M; $[\text{HMTETA}]_o = 0.090$ M.

weights with conversion and low polydispersities throughout the reactions. In particular, as shown in Figure 11, the use of the tridentate PMDETA and the tetradentate HMTETA as the ligands resulted in faster polymerization rates than those using bipy as the ligand, in part due to the fact that the coordination complexes between copper and simple amines have lower redox potentials than the copper-bipy complex.[15,16] However, the precise correlation between the observed rates and polydispersities with the ligand structures should also include steric constraining effects as well as solubilities which are currently being studied. The ready availability of these ligands makes them very attractive alternatives to bipy and its derivatives as the ligands.

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