Room Temperature Atom Transfer Radical Polymerization of Glycidyl Methacrylate Mediated by Copper(I)/*N*-Alkyl-2-pyridylmethanimine Complexes[†]

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ABSTRACT: The homogeneous controlled/"living" free radical polymerization of glycidyl methacrylate (GMA) by atom transfer radical polymerization (ATRP) using Cu(I)X/N-alkyl-2-pyridylmethanimine complexes with various initiators R-X (X = Cl, Br) and solvents was investigated. Most of these systems display characteristics of a living radical polymerization as indicated by (a) linear first-order kinetic plots of $\ln[M]_0/[M]$ vs time, (b) an increase in the number-average molecular weight (M_n) vs conversion, and (c) relatively narrow polydispersities indicating a constant number of propagating species throughout the polymerization with negligible contribution of termination or transfer reactions. The dependence of the rate of polymerization on the concentrations of initiator, ligand, and temperature is presented. We observed comparable rates of polymerization linear increase of molecular weight with conversion and low polydispersities in polar solvents. No polymerization was observed in nonpolar solvents such as toluene and xylene at room temperature. The order of controlled polymerization with different initiator system is CuBr/BPN > CuCl/BPN > CuBr/ClPN, and the polymerization did not proceed with CuCl/ClPN initiator system at room temperature. The high functionality of bromine end groups present in the polymer chains was confirmed by ESI MS analysis. The thermal stability of PGMA prepared by the CuBr/PPMI/BPN initiation system is higher than by the other three systems, indicating the high regioselectivity and the virtual absence of termination reactions in the former case. The ligand alkyl chain length from R = propylto octyl did not affect the rate of polymerization. The molecular weight (M_n) increases linearly with conversion, and these polymers showed narrow polydispersities.

Introduction

"Living" polymerization of vinyl monomers is a route to synthesize a wide range of well-defined polymers. It allows the synthesis of polymers with well-defined compositions, architectures, functionalities, chain topology of macromolecules with narrow molecular weight distribution, targeted number-average molecular weights, specific end groups, etc. Traditionally, this has been accomplished by living ionic polymerization techniques.¹⁻³ However, such polymerization techniques require highpurity monomers, solvents, and reagents, coupled with low temperatures, which thereby makes ionic polymerizations relatively difficult processes. Another major limitation of ionic polymerization is the difficulty in polymerizing monomers containing polar and/or functional groups, e.g., 2-hydroxyethyl methacrylate, (meth)acrylic acid, and glycidyl methacrylate, as they can complicate reaction pathways. Functional monomers can be readily polymerized via free-radical routes. The development of controlled/"living" radical polymerization processes has been the focus of much activity in recent years. In the past decade, the development of controlled/ "living" radical polymerization (CRP) techniques allows the synthesis of polymers using less vigorous conditions. Many controlled polymerization techniques have been proposed, including nitroxide-mediated living radical polymerization (NMRP),⁴ atom transfer radical polymerization (ATRP),^{5,6} reversible addition and fragmentation chain transfer (RAFT),7 and group transfer polymerization (GTP).8

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Transition-metal-mediated atom transfer radical polymerization is a versatile technique for the controlled polymerization of wide variety of functional monomers and has been used successfully to prepare well-defined polymers such as styrene, substituted styrenes,⁹ (meth)acrylates,¹⁰ and acrylonitrile.¹¹ Atom transfer radical polymerization systems using Cu,^{9–11} Ru,⁶ Rh,¹² Ni,¹³ Pd,¹⁴ and iron¹⁵ based transition metals in conjunction with suitable ligands such as substituted and unsubstituted bipyridines, phosphorus-containing ligands, and multidentate amines¹⁶ have been used as catalysts. This living radical polymerization technique tolerates a wide range of functional groups in the monomer, solvent, or initiator. Although ATRP is usually performed in the bulk or in an organic solvent, the efficient polymerization of various hydrophilic monomers in protic media has been demonstrated at ambient temperature¹⁷⁻²¹ and also for hydrophobic monomers²² by using a more powerful catalyst system such as CuBr/Me6-TREN and CuBr/Me₄Cyclam under mild conditions or at room temperature.

Haddleton and co-workers developed a catalyst based on Cu(I)X and *N*-alkyl-2-pyridylmethanimine Schiff base ligands for the living-radical polymerization,²³ and the same catalyst was used in an aqueous media without hydrolysis of the ligand.²⁰ The Schiff based ligands are effective for the polymerization of methacrylates^{24,25} in toluene or xylene solutions in conjunction with copper(I) halides and suitable alkyl halide initiators over a range of temperatures (even as low as -15 °C).²⁶ This paper deals with the controlled/"living" radical polymerization of glycidyl methacrylate (GMA) by homogeneous ATRP by using Cu(I)X complexed with various *N*-alkyl-2-pyridylmethanimine ligand as cata-



Figure 1. Effect of initiator concentration on kinetics of homogeneous ATRP of GMA in bulk polymerization at ambient temperature. [GMA]₀ = 7.3 M; [BPN]₀ = 0.097 (**I**), 0.048 (**A**), and 0.029 M (**V**). [CuBr]₀ = [PPMI]₀/2 = 0.058 M.



Poly(glycidyl methacrylate)

lyst and various initiators in bulk and various solvents at an ambient temperature $(30 \ ^\circ C).^{27}$

Experimental Section

Materials. Glycidyl methacrylate (GMA, Aldrich, 97%) was purified by vacuum distillation under reduced pressure and stored in a refrigerator under a nitrogen atmosphere. n-Propylamine (S.D. Fine Chem., India, 98%), n-butylamine (Aldrich, 99.5%), n-hexylamine (Aldrich, 99%), n-octylamine (Aldrich, 99%), pyridine-2-carboxaldehyde (Lancaster, 99%), and cuprous chloride (CuCl, Aldrich, 99+%) were all used as received. Initiators methyl 2-bromopropionate (M 2-BP, Aldrich, 98%), 2-bromopropionitrile (BPN, Aldrich, 97%), 1-phenylethyl bromide (1-PEBr, Aldrich, 97%), and 2-chloropropionitrile (CIPN, Aldrich, 95%) were used as received. Cuprous bromide (CuBr, Fluka, 98%) was purified by washing with glacial acetic acid, followed by absolute ethanol and diethyl ether, and then dried under vacuum at room temperature. The initiator AIBN was recrystallized from ether and was dried at room temperature under vacuum. Diphenyl ether (DPE) was dried over molecular sieves and stored in a nitrogen atmosphere. All other chemicals and solvents were purchased from commercial sources and used after standard purification procedures.

General Procedure for the ATRP of GMA. The ATR polymerization of glycidyl methacrylate was carried out in bulk and in solution. In a typical bulk polymerization, a dry glass tube was charged with CuBr (21.0 mg, 0.146 mmol) and N-(npropyl)-2-pyridylmethanimine (PPMI) (43.2 mg, 0.292 mmol), GMA (2.0 mL, 0.014 mol), and a magnetic stir bar. The tube was fitted with a rubber septum and degassed by three freezepump-thaw cycles. The solution turned dark brown and homogeneous. Initiator 2-bromopropionitrile (12.6 μ L, 0.146 mmol) was added via a degassed syringe, and the solution became progressively more viscous, indicating the onset of polymerization. After various time intervals, the polymer was dissolved in tetrahydrofuran and then filtered through a silica gel column to remove the copper catalyst. The polymer solution was then precipitated by using excess of petroleum ether and dried in a vacuum (time 90 min, 88% conversion, $M_{\rm n,th}$ = 12 500, $M_{n,GPC} = 12$ 150, $M_w/M_n = 1.21$).

Characterization. Conversion was determined by gravimetry. Molecular weights and molecular weight distributions



Figure 2. Plot of M_n and M_w/M_n as a function of monomer conversion on differing ratios of monomer:initiator for bulk ATRP of GMA at ambient temperature. [GMA]₀ = 7.3 M; [BPN]₀ = 0.097 (**I**), 0.048 (**A**), and 0.029 M (**V**). [CuBr]₀ = [PPMI]₀/2 = 0.058 M (solid lines indicate $M_{n,th}$ values corresponding to the [M]/[I]₀ ratios).



Figure 3. Dependence of the apparent rate constant of propagation (k^{app}) on the initiator concentration for homogeneous ATRP of GMA in bulk at ambient temperature. [GMA]₀ = 7.3 M; [CuBr]₀ = [PPMI]₀/2 = 0.058 M.



Figure 4. Semilogarithmic kinetic plot for ATR polymerization of GMA in different solvents at an ambient temperature. $[GMA]_0 = 3.65 \text{ M}; [BPN]_0 = [CuBr]_0 = [PPMI]_0/2 = 0.036 \text{ M} (monomer:solvent = 50\% v/v).$

were measured by gel permeation chromatography (GPC). The GPC setup consisted of a Waters 515 LC pump and a Waters 410 differential refractive index detector, with four Ultrastyragel columns (guard, 103, 104, 105 Å). Calibration was based on linear polystyrene standards. The GPC eluent was HPLC grade THF at a flow rate of 1.0 mL/min. The instrument was set at 40 °C before starting the analysis. ¹H NMR spectra were recorded in CDCl₃ solvent using a Bruker MSP 300 spectrometer operating at 300 MHz. The Fourier transform infrared (FT-IR) spectra of the ligands were recorded with a Nicolet Impact 400 spectrometer on solution cast onto KBr disks. (Representative ¹H, ¹³C NMR, and FT-IR spectra of polymer and ligands are given in the Supporting Information.) Electrospray ionization mass spectrometry of the polymer was analyzed by a Hewlett-Packard 1100 MSD mass spectrometer. Thermogravimetric analysis was carried out on a Seiko model SSC 5200H system attached to a thermogravimetry/dynamic thermal analysis module at a heating rate of 20 °C/min in a nitrogen atmosphere (flow rate 100 mL/min).

Results and Discussion

Poly(glycidyl methacrylate) (Scheme 1) is of great interest since the pendant oxirane ring could be opened



Figure 5. Dependence of molecular weight (filled symbols) and molecular weight distributions (open symbols) as a function of monomer conversion for ATRP of GMA at an ambient temperature in different solvent systems. $[GMA]_0 = 3.65 \text{ M}$; $[BPN]_0 = [CuBr]_0 = [PPMI]_0/2 = 0.036 \text{ M}$ (monomer:solvent = 50% v/v).



Figure 6. Semilogarithmic kinetic plot for the bulk polymerization of GMA at ambient temperature using three different initiation systems. $[GMA]_0 = 7.3 \text{ M}$; $[initiator]_0 = [CuBr]_0 = [PPMI]/2 = 0.073 \text{ M}$.

and a wide range of functionalities could be introduced with subsequent reactions. The homopolymerization and copolymerization of GMA are reported by controlled polymerization techniques, such as ATRP,^{27,28} GTP,⁸ and NMRP.²⁹

The kinetic plot of $\ln[M]_0/[M]$ vs time for homogeneous bulk ATRP of GMA catalyzed by CuBr/PPMI initiated by 2-bromopropionitrile at three different initiator concentrations is shown in Figure 1. The straight lines passing through the origin show that the polymerization proceeded with an approximately constant number of active species present throughout the polymerization, and therefore the contribution of termination reactions could be negligible. As expected, the apparent rate constant of polymerization (k^{app}) decreased with decreasing initiator concentration, as determined from the kinetic slopes. The molecular weight evolution, $M_{\rm n}$, and molecular weight distribution, M_w/M_n , as a function of monomer conversion are shown in Figure 2. The molecular weights determined by GPC against linear polystyrene standards generally agreed with the theoretical lines calculated from the degree of polymerization



Figure 7. Dependence of number-average molecular weight and polydispersities on monomer conversion in the bulk polymerization of GMA at ambient temperature using three different initiation systems. $[GMA]_0 = 7.3 \text{ M}$; $[initiator]_0 =$ $[CuBr]_0 = [PPMI]/2 = 0.073 \text{ M}$.



Figure 8. Semilogarithmic kinetic plots for the bulk ATRP of GMA at an ambient temperature using Cu(I)X/XPN initiation systems, where X = Cl or Br. $[GMA]_0 = 7.3$ M; $[XPN]_0 = [CuBr]_0 = [PPMI]_0/2 = 0.073$ M.

as predicted by the initial ratio of monomer:initiator. The experimental molecular weight ($M_{n,GPC}$) values were very close to theoretical lines ($M_{n,th}$), indicating that BPN was an efficient initiator for ATR polymerization of GMA. The molecular weights increased linearly with monomer conversion, and low polydispersities $M_w/M_n < 1.35$ were observed for all polymerizations. Polydispersities slightly increased with increasing [M]/[I]₀ ratio (Figure 2).

Plotting $\ln k^{app}$ vs $\ln[\text{initiator}]$ elucidated the dependence of the rate of polymerization on the initiator concentration. For this system, the slope of the line indicated an apparent 0.8 order with respect to initiator and (Figure 3) differs slightly from the first-order dependence of the rate on the initiator concentration.

Different solvents were investigated for the ATRP of glycidyl methacrylate using the CuBr/PPMI catalyst system initiated by BPN at room temperature (30 °C) with a monomer concentration of 50% (v/v) for all reactions. The first-order kinetic plots of the polymerizations are shown in Figure 4. All solvents showed a



Figure 9. Dependence of molecular weights (open symbols) and polydispersities (filled symbols) on monomer conversion for bulk ATRP of GMA at an ambient temperature using Cu-(I)X/XPN initiation systems, where X = Cl or Br (solid line represents $M_{n,th}$ values). [GMA]₀ = 7.3 M; [XPN]₀ = [CuBr]₀ = [PPMI]₀/2 = 0.073 M.



Figure 10. First-order kinetic plots for the polymerization of GMA with various *N*-(*n*-alkyl)-2-pyridylmethanimine ligands. $[GMA]_0 = 7.3 \text{ M}; [BPN]_0 = [CuBr]_0 = [ligand]_0/2 = 0.097 \text{ M}.$

slower rate of polymerization than the bulk polymerization. The polymerization of GMA in diphenyl ether (DPE) medium proceeds at a much faster rate compared to the other polar solvents such as methyl ethyl ketone (MEK), methanol, and anisole. The polymerizations did not occur in nonpolar solvents such as toluene and xylene even after 24 h. The plots of M_n and M_w/M_n as a function of monomer conversion for different polymerization systems are shown in Figure 5. In the case of bulk and diphenyl ether solution polymerization systems experimental molecular weights $(M_{n,GPC})$ follow the theoretical line and narrow polydispersities were observed ($M_w/M_n < 1.3$), whereas in other polar solvents such as MEK, anisole, and methanol, molecular weights are higher than the predicted theoretical values. This indicates inefficient initiation in the polar solvents presumably caused by a slower deactivation, resulting in slightly higher polydispersities $M_{\rm w}/M_{\rm n} < 1.5$.

Three different initiators were examined for bulk ATRP of GMA such as 2-bromopropionitrile, methyl 2-bromopropionate, and 1-phenylethyl bromide along with CuBr/PPMI catalyst system at room temperature, and the obtained results are shown in Figures 6 and 7. The polymerization of GMA proceeds with first-order

time/ min				
	$M_{n,GPC}$	$M_{\rm w}/M_{\rm n}$	% conv	$k^{ m app} imes 10^{-4}~(m s^{-1})$
15	1580	1.19	19.0	2.415
30	3130	1.17	35.0	
45	4150	1.20	46.2	
60	4920	1.18	57.3	
90	6980	1.20	73.0	
15	1870	1.23	20.6	2.568
30	3730	1.25	37.0	
45	4910	1.20	47.8	
60	5980	1.24	59.5	
90	7650	1.22	75.5	
15	1855	1.18	20.0	2.380
30	3490	1.17	35.6	
45	4680	1.21	45.7	
60	5590	1.19	57.0	
90	7120	1.19	72.5	
15	1780	1.16	19.0	2.368
30	3650	1.15	35.0	
45	4680	1.10	45.7	
60	5885	1.12	56.5	
90	7350	1.13	72.3	
	min 15 30 45 60 90 15 30 45 60 90 15 30 45 60 90 15 30 45 60 90	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 1. Effect of Alkyl Chain Length in N-Alkyl-2-pyridylmethanimine Ligands on the Atom Transfer Radical Polymerization of GMA in Bulk at RT^a

^{*a*} [GMA]₀ = 7.3 M; [BPN]₀ = $[CuBr]_0 = [ligand]_0/2 = 0.097$ M.

kinetics with respect to monomer concentration for BPN and M 2-BP initiation systems, whereas 1-PEBr showed significant curvature in the first-order kinetic plot, which indicates that termination is detectable as shown in Figure 6. The number-average molecular weight $(M_{\rm n})$ increases linearly with monomer conversion, which indicates constant concentration of growing chains present throughout the reaction. In BPN initiator, the $M_{n,GPC}$ values follow the theoretical line, whereas in the M 2-BP system a higher value than theoretical line indicates inefficient initiation caused by slow deactivations. In the 1-PEBr/CuBr initiation system, the rate of initiation is much slower than propagation, resulting an inefficient initiation. Consequently, deviation of molecular weights from the theoretical line and higher polydispersities were also observed.

2-Halopropionitriles (XPN, X = Br or Cl) are good initiators for copper-based ATR polymerization of methacrylates and acrylonitrile. Comparison between the initiation systems CuBr/BPN and CuCl/ClPN shows that CuBr/BPN gave better control of the polymerization, $M_{n,GPC}$ values are very close to the theoretical line, and low polydispersities were observed throughout the polymerization, which indicates an efficient activation/ deactivation process. On the other hand, no polymerization was observed in the CuCl/ClPN system at room temperature. The results of mixed halide/initiator system for ATRP of GMA are shown in Figures 8 and 9. In the mixed halide initiation systems, CuCl/BPN gave better control of polymerization and the $M_{n,GPC}$ values followed the theoretical line, whereas the CuBr/ClPN system showed a significant curvature in a first-order kinetic plot; poor control of molecular weight and molecular weight distribution was observed (Figure 9). The results imply that the mixed halide system CuCl/ BPN should give faster initiation and slower propagation and therefore better control of molecular weight and lower polydispersities, whereas the CuBr/ClPN initiation system gave essentially uncontrolled polymerization, which was attributed to the strong C-Cl bond and inefficient initiation.³⁰ In the mixed halide system the presence of a chlorine originating from either the initiator or the catalyst becomes the $\dot{\omega}$ -terminus of the



Figure 11. Plot of k^{app} vs equivalents of PPMI used for bulk ATRP of GMA using CuBr/PPMI as the catalyst at room temperature. [GMA]₀ = 7.3 M; [BPN]₀ = [CuBr]₀ = 0.048 M.



Figure 12. Plot of $\ln k_p^{\text{app}}$ vs 1/T for ATRP of GMA. [GMA]₀ = 7.3 M; [BPN]₀ = [CuBr]₀ = [ligand]₀/2 = 0.097 mM.

polymer, leading to the lowering of the rate of polymerization compared to the CuBr/BPN initiation system.

The alkyl chain length in the Schiff base ligands can be easily varied by appropriate choice of primary amine reacting with pyridine-2-carboxaldehyde. Figure 10 shows the first-order kinetic plots of bulk polymerization of GMA with four different N-alkyl-2-pyridylmethanimine ligands ranging from *n*-propyl to *n*-octyl, and very similar rates of polymerization were observed for all the reactions. The nature of the alkyl group dramatically affects the solubility of the copper complexes in a range of solvents, especially at ambient temperature. Normally, when the length of the alkyl group is increased, the system becomes more soluble in nonpolar solvents. But in more polar monomers such as MMA and GMA, the shorter alkyl chain ligands are more soluble, and when the concentration of the monomer in the reactions is increased, the solubility of the copper complexes is also increased. In all polymerizations, the $M_{\rm n}$ increases linearly with monomer conversion, and the polydispersity index remains relatively narrow; the same is shown in Table 1. $M_{n,GPC}$ values are slightly lower than the predicted values. These results suggest



Figure 13. (a) ESI MS spectrum of PGMA prepared by CuBr/BPN/PPMI initiation system. (b) Expanded ESI MS spectrum.

that the variation of alkyl chain length from *n*-propyl to *n*-octyl has no appreciable changes in the rate of polymerization.

The dependence of the rate of polymerization in the homogeneous ATRP of GMA with catalyst concentration was also investigated. Figure 11 shows the dependence of the apparent rate constant of polymerization as a function of [ligand]:[CuBr] ratio. The optimum ratio is found to be 2:1 with the rate of polymerization increasing significantly as ligand concentration is raised to this value, but beyond this concentration the rate of polymerization is slightly decreased. These reactions are usually carried out with 2 times molar excess of Schiff base ligand with respect to Cu(I)X. Because the Cu(I) prefers a tetrahedral geometry, which can be achieved with two bidendate ligands. However, further increasing the ligand concentration, coordination of the ligand to the metal center may hinder the activity of the catalyst,



Figure 14. Comparison of (a) TG and (b) DTG curves for PGMA prepared by five different initiation systems. Reaction conditions: $[GMA]_0 = 7.3 \text{ M}$; $[XPN]_0 = [CuBr]_0 = [PPMI]_0/2 = 0.073 \text{ M}$.

resulting in a slight decrease in the rate of polymerization.

The temperature dependence on the reaction rates was determined by the Arrehenius parameters for the apparent first-order rate constants (ln k^{app}). The Arrhenius plot for the CuBr/PPMI/BPN-catalyzed polymerization of GMA is shown in Figure 12. The apparent activation energy (E_a) calculated for the CuBr/PPMI/BPN initiation system is 86.35 kJ/mol. Such an apparent activation energy is higher than that reported for the homogeneous dNbpy/CuBr ATRP system (50 kJ/mol)³¹

End-Group Analysis of PGMA-Br. End-group analysis of ATRP polymers is important because polymer chains with halogen end groups act as a macroinitiator. It can be reactivated in the presence of the ATRP

catalyst system to initiate the polymerization of the second monomer to form a block, graft, star polymers, etc., depending on the position and number of initiation sites. The existence of chain end functionality was confirmed using ESI MS (Figure 13a,b). A series corresponding to the bromo-terminated PGMA with a sodium cation [m = 55 + n(142.16) + 79/81 + 23; for n= 7, m = 1152/1154] and the major series match the molecular weight of the polymer, which is doubly charged with two sodium cations [m = 55 + n(142.16)]+ 79/81 + 23 + 23/2; for n = 13, m = 1014/1016]. The entire range of ESI mass spectrum is given in Figure 13a. The doubly charged species is more intense than the singly charged species. The obtained ESI mass spectrum indicated that there was no significant loss of end group. The results suggest that high functionality of the bromine end groups is present in PGMA. The expanded ESI MS region is shown in Figure 13b. This is also a supporting evidence for the observed high thermal stability of PGMA-Br prepared by CuBr/BPN, suggesting virtually the absence of termination reactions.

Thermal Stability of PGMA. The thermal stability of polymer is in direct relationship with the polymer structure, and therefore one could expect desirable information on the regioselectivity and the extent of termination reactions during the polymerization process.^{13,32} Figure 14a shows the TG spectra of PGMA synthesized via five different initiating systems: (1) by conventional free-radical polymerization (FRP) using AIBN initiator ($M_n = 91\ 850$, $M_w/M_n = 1.49$);³³ (2) by ATRP (a) CuBr/BPN ($M_n = 6800$, $M_w/M_n = 1.30$), (b) CuBr/ClPN ($M_n = 15~750, M_w/M_n = 1.76$), (c) CuCl/ClPN $(M_{\rm n} = 19 560, M_{\rm w}/M_{\rm n} = 2.14),^{34}$ and (d) CuCl/BPN $(M_{\rm n} = 2.14),^{34}$ = 8100, M_w/M_n = 1.35). The DTG spectra of PGMA synthesized via five different initiating systems is shown in Figure 14b. PGMA produced by CuCl/BPN displays a three-step degradation corresponding to (a) head-tohead linkage (around 80-190 °C), (b) chain-end initiation from the vinylidine ends (around 190-237 °C), and (c) a random scission with in the polymer chain (around 237–377 °C) (Figure 14b). The first two steps (a, b) are more pronounced than in PGMA prepared from CuBr/ BPN, indicating the termination reactions resulting in head-to-head linkages and vinylidene end groups. Thermal degradation of PGMA synthesized by ATRP with the CuBr/PPMI/BPN initiation system shows a single step degradation around 400 °C, originating only from random scission of polymer chain. This polymer is about 80 °C more stable than the PGMA produced by the FRP method. This result further indicates the absence of abnormal linkages, such as head-to-head, and vinylidene end groups. Therefore, this confirms the high regioselectivity and complete absence of termination reactions when using the CuBr/BPN system, whereas the other three combinations such as CuCl/ClPN, CuCl/ BPN, and CuBr/ClPN show three-step degradations like FRP, indicating head-to-head and vinylidene linkages present in the polymer chains. This suggests that the GMA polymerization by ATRP other than CuBr/BPN systems shows the extent of termination reactions during the polymerization.

Conclusions

A range of Schiff base ligands, initiators, and solvents in conjunction with Cu(I)X have been shown to be effective for the homogeneous controlled atom transfer radical polymerization of glycidyl methacrylate at room temperature. Kinetic results showed an apparent 0.8 order dependence of the rate of polymerization on the concentration of initiator, and there is slight deviation from the first-order kinetics. Bulk and diphenyl ether solution polymerization show a better control of polymerization with quite narrow polydispersities. No polymerization in nonpolar solvents, deviation from theoretical molecular weight, and slightly higher polydispersities were observed in polar solvents at room temperature. BPN and M 2-BP show a better control of polymerization with faster initiation and slower propagation, and 1-PEBr shows a curvature in first-order kinetic plot and uncontrolled molecular weight was observed, indicating that termination was taking place. The mixed halide system CuCl/BPN gave faster initiation, slower propagation, and therefore better control of molecular weight and polydispersities. The use of the CuBr/ClPN initiation system essentially proceeds through an uncontrolled polymerization, which is likely due to the strong C-Cl bond and inefficient initiation. The variation of alkyl chain length from *n*-propyl to *n*-octyl does not seem to have an effect on the rate of polymerization and at least 2 mol equiv ligand to copper salt being required for optimum rate of polymerization. Increase in ligand concentration slightly decreases the rate of polymerization. ESI MS suggests that there was no significant loss of bromine end groups present in the polymer chain, and doubly charged species were more intense than singly charged species. The TG spectra of PGMA indicate that the CuBr/PPMI/BPN system show an absence of head-to-head, vinylidene end groups, and high thermal stability compared to the mixed halide initiation system and free radical polymerization.

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Supporting Information Available: The preparation and characterization of ligands (FT-IR, ¹H and ¹³C NMR), polymers (¹H NMR, TG/DTA), and kinetic results. This material is available free of charge via the Internet at http:// pubs.acs.org.

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- $[PPMI]_0/2 = 0.073 \text{ M at } 90 \text{ °C}.$

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