Controlled/“Living” Radical Polymerization of Glycidyl Methacrylate at Ambient Temperature

R. Krishnan and K. S. V. Srinivasan*

Polymer Division, Central Leather Research Institute, Adyar, Chennai- 600 020, India

Received August 31, 2002
Revised Manuscript Received January 13, 2003

Research on controlled/“living” radical polymerization has grown rapidly in recent years. Several new methods have been developed to gain control over the predictable molecular weights, low polydispersities, functionalities, architectures, and well-defined compositions.[1−6] One of the most successful systems is the transition-metal-mediated living radical polymerization known as atom transfer radical polymerization (ATRP). ATRP has a tolerance to wide variety of functional groups on the monomers and has been applied successfully for the preparation of well-defined polymers such as styrene, substituted styrenes,[7] (meth)acrylates,[8] and acrylonitrile.[9] Atom transfer radical polymerization systems using Cu,[4,7−9] Ru,[6] Rh,[10] Ni,[11] Pd,[12] and iron[13] based transition metals in conjunction with suitable ligands such as substituted and unsubstituted bipyridines, phosphorus-containing ligands, multidentate amines, etc.,[14] are used as catalysts. Generally, ATRP is carried out at higher temperature in bulk, aqueous, or nonaqueous media. But recent literature reported that ATRP is particularly effective for hydrophilic monomers[16−19] in aqueous media and also for the hydrophobic monomers[15] by using more powerful catalyst systems, such as CuBr/Me$_6$-TREN and CuBr/Me$_4$Cyclam under mild conditions or at room temperature. Schiff-based ligands are efficient for the ATRP of methacrylates as developed by Haddleton and co-workers,[20] and it is also possible to use as a catalyst in aqueous media without hydrolysis of the ligand.[19]

ATRP has also been applied to a wide variety of functionalized monomers[16,17] to prepare well-defined polymers. Matyjaszewski et al.[21] reported the homopolymerization of glycidyl acrylate (GA) at 90 °C using MBP/CuBr/dNbipy as a catalytic system. Other controlled polymerizations such as anionic or cationic polymerization were difficult to polymerize epoxy ring containing monomers without affecting the oxirane ring.

This paper reports the controlled/“living” radical polymerization of glycidyl methacrylate (GMA) by ATRP at ambient temperature. Poly(glycidyl methacrylate) (PGMA) is of great interest, since the pendant oxirane ring can be opened and a range of functionalities could be introduced with subsequent reactions. Well-defined PGMA has been synthesized by using copper(I) bromide complexed by *N*-(*n*-propyl)-2-pyridylmethanimine ligand as catalyst and 2-bromopropionitrile (BPN) as an initiator in bulk and various solvents at an ambient temperature.

The ATRP of GMA was carried out in diphenyl ether as a solvent initiated with three different concentrations of initiator (BPN) relative to monomer in conjunction with *N*-(*n*-propyl)-2-pyridylmethanimine−copper(I) bromide complex at ambient temperature.[22] The first-order kinetic plots of the polymerization were linear to monomer conversion (Figure 1a), indicating that the number of active species remained constant throughout the polymerization. Relatively straight kinetic lines in the semilogarithmic plots were obtained suggesting the faster initiation with negligible termination. Generally, the rate of polymerization decreases with increasing the ratio of $[M]_0/[I]_0$. The close correlation between the $M_{n(th)}$ with $M_{n(GPC)}$ indicated that BPN was an efficient initiator for the polymerization of GMA at ambient temperature. The measured number-average molecular weight, $M_{n(GPC)}$, and the molecular weight distribution, M_w/M_n, as a function of monomer conversion are shown in Figure 1b. A linear increase of $M_{n(GPC)}$ vs conversion indicated that the polymerization proceeded in a controlled/“living” process with a negligible amount of termination. The molecular weights of polymers determined by GPC against linear polystyrene standards agreed well with the theoretical values as calculated using eq 1.

Table 1. Solution Polymerization of GMA in Different Solvents at Ambient Temperature[a]

solvent	time (min)	conv (%)	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n
diphenyl ether	210	75.6	16 100	9 400	1.25
anisole	240	83.0	17 700	7 200	1.38
ethyl methyl ketone	180	85.7	18 270	10 300	1.48
methanol	145	81.0	17 270	9 100	1.49
water	20	93.0	19 830	17 500	2.3
methanol/water (50% v/v)	30	91.0	19 400	17 600	2.6

[a] ATRP conditions: [GMA]/[BPN]/[CuBr]/[PPMI] = 150/1/0.5/1 in 50 vol % solvent.

$$M_n(\text{cal}) = [\text{GMA}]_0/[\text{BPN}]_0 \times \text{MW}_{\text{GMA}} \times \text{conversion} \quad (1)$$

The observed deviation of experimental M_n values, from the theoretical line at higher $[M]_0/[I]_0$ ratio, could be due to either transfer of some active chains or some deviation due to the differences in the hydrodynamic volumes of the PGMA vs the linear polystyrene standards.[15,21,22] The low polydispersities ($M_w/M_n < 1.3$) were observed throughout the polymerization, indicating a fast and dynamic exchange between the active and the dormant species with copper complexes acting as a reversible halogen atom transfer agent.

Well-defined PGMA could be prepared at ambient temperature in various polar solvents such as anisole, diphenyl ether,[23] methanol, etc. (Table 1). We have observed controlled molecular weights and low polydispersities ($M_w/M_n < 1.5$) in polar solvents, whereas in an aqueous media and methanol/water (50% v/v) showed a faster rate of polymerization with higher conversions (<93%) within short reaction times (<20 min), and the polymerization was not controlled resulting in a broader molecular weight distribution ($M_w/M_n < 2.6$) of the final polymers. In the case of methacrylic monomers, it has been reported that the propagation rate constant (k_p) in water is significantly higher than in nonaqueous media.[24] The higher polydispersity observed could be due to the insolubility of the resulting polymer in aqueous media and the possible existence of higher concentration of propagating radicals in the polymeri-

---

* Corresponding author: phone +91-044-24422059; fax +91-044-24911589; e-mail srinivasan1@hotmail.com.

10.1021/ma025637c CCC: $25.00

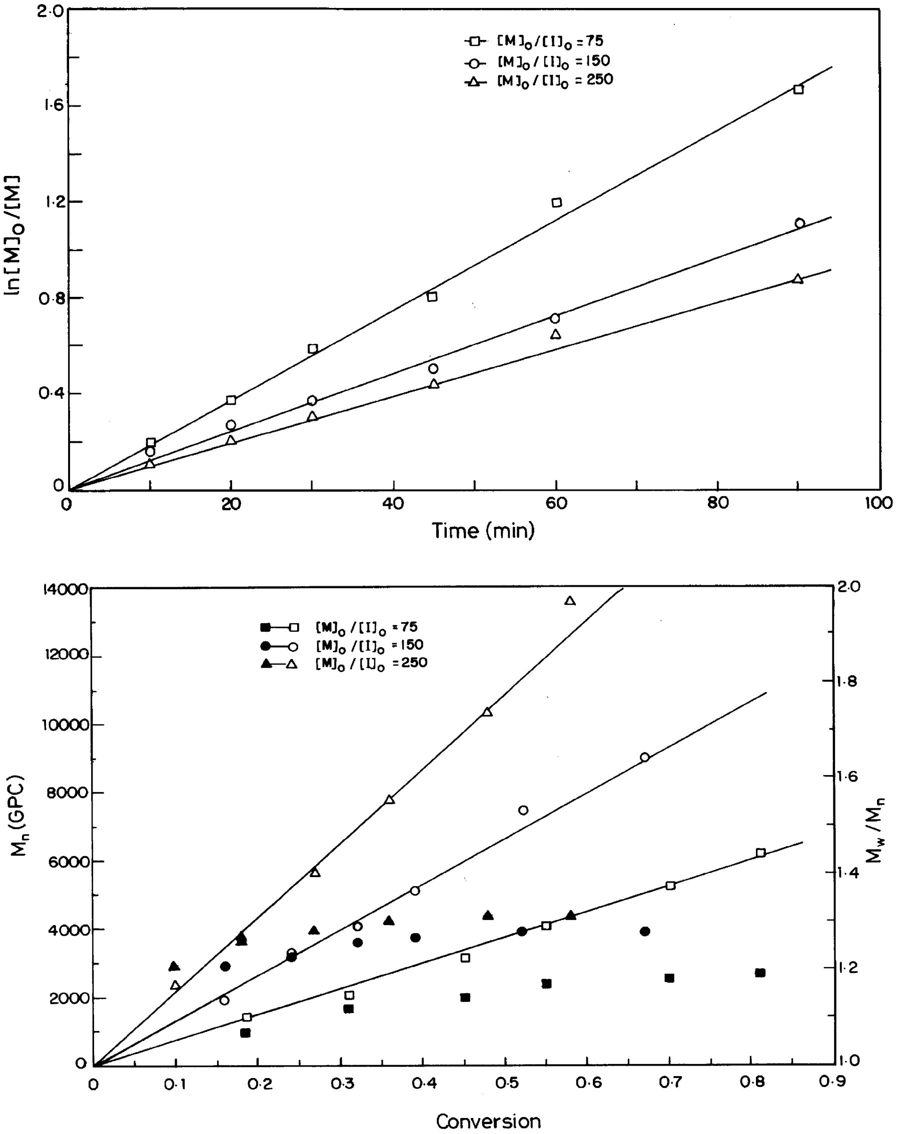

Figure 1. (a) First-order kinetic plots for ATRP of GMA initiated by 2-bromopropionitrile, catalyzed by (*N*-(*n*-propyl)-2-pyridylmethanimine)copper(I) bromide in diphenyl ether as a solvent at an ambient temperature. (b) Number-average molecular weight ($M_{n,GPC}$) (open symbols) and molecular weight distributions (M_w/M_n) (filled symbols) as a function of monomer conversion for the ATRP of GMA with various $[M]_0/[I]_0$ ratios at an ambient temperature in diphenyl ether as a solvent. $[GMA]_0 = 0.0801$ M ($[M]_0/[I]_0$ □ = 75, △ = 150, ○ = 250).

zation media. Less polar solvents, such as toluene and xylene, are not good solvents for ATR polymerization[17d] of GMA, and the polymerization was not observed even after 24 h at ambient temperature. Hence, we observed that the polymerization of GMA could be accomplished in polar solvents at ambient temperature to prepare well-controlled polymers with low polydispersities.

Bulk polymerization of GMA carried out using various initiators at ambient temperature is summarized in Table 2. Other than bromopropionitrile and *p*-dibromoxylene initiators, we have observed slightly higher polydispersities ($M_w/M_n > 1.5$), and the number-average molecular weight $M_{n(GPC)}$ also deviated from the theoretical M_n values.

Figure 2 shows the ^{1}H NMR spectrum (Bruker 300 MHz) of the polymer, and it revealed that the epoxy ring remained intact during the reaction. The proton resonances for the oxirane ring were assigned to the peaks at 3.23 ppm (d) and (e) at 2.66 and 2.88 ppm. The two protons labeled (e) in Figure 2 are in different chemical environments and consequently give two different resonances. The signals at 4.32 and 3.81 ppm were assigned to the methylene protons of the side groups at position c. The resonances at 1.73, 1.69, and 1.95 ppm are assigned as methylene protons of glycidyl methacrylate and methine protons of the initiator. The methyl protons of PGMA and the initiator are assigned at 0.92 (a) and 1.08 (a^1) ppm, respectively.

In summary, we have demonstrated that a well-defined functionalized polymer poly(glycidyl methacrylate) could be prepared by atom transfer radical polym-

Table 2. Bulk Polymerization of GMA in Different Initiators at Ambient Temperature[a]

initiator	time (min)	conv (%)	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n
2-bromopropionitrile	60	78.0	16 630	9 150	1.23
1-phenylethyl bromide	65	82.2	17 530	63 500	1.71
p-dibromoxylene	120	86.6	18 470	87 900	1.40
benzyl bromide	150	73.0	15 560	70 350	1.59
methyl 2-bromopropionate	180	71.4	15 200	49 600	1.83

[a] ATRP conditions: [GMA]/[BPN]/[CuBr]/[PPMI] = 150/1/0.5/1.

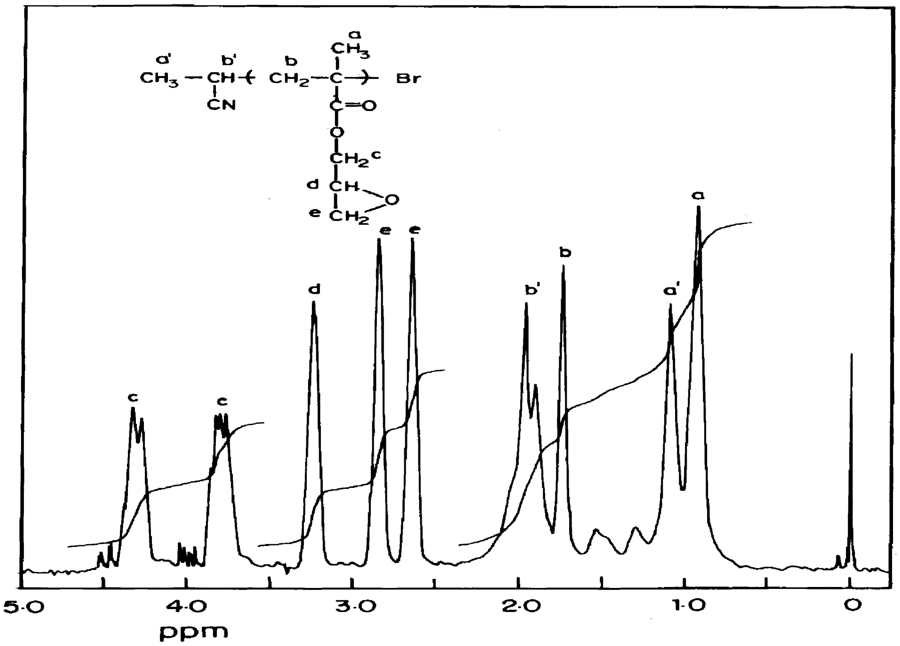

Figure 2. ^{1}H NMR spectrum of poly(glycidyl methacrylate) recorded at 25 °C (solvent: $CDCl_3$).

erization at ambient temperature using various solvents and the initiators. Linear increase of molecular weights with conversion and low polydispersity indices (M_w/M_n < 1.3) were obtained in the ATRP of GMA. The $M_{n(th)}$ of the final polymers was controlled by the ratio of $[M]_0/[I]_0$, and the polymerization carried out in an aqueous media showed faster rates, reduced control, and higher polydispersities, and this could possibly due to the low solubility of monomer in the aqueous media. The oxirane ring of the polymers remained intact under the conditions of atom transfer radical polymerization as indicated by the ^{1}H NMR spectrum. Further work on detailed kinetic studies and preparations of block copolymers by ATRP are under investigation in our group.

Acknowledgment. R. Krishnan thanks the Council of Scientific and Industrial Research (CSIR, New Delhi), India, for an award of Senior Research Fellowship.

References and Notes

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(2) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 1185.
(3) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66.
(4) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(5) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.
(6) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(7) Qiu, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 5643.
(8) Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 2216.
(9) Matyjaszewski, K.; Jo, S. M.; Paik, H.-J.; Gaynor, S. G. *Macromolecules* **1997**, *30*, 6398.
(10) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.
(11) Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576.
(12) Lecomte, P.; Drapier, I.; Dubois, P.; Teyssie, P.; Jerome, R. *Macromolecules* **1997**, *30*, 7631.
(13) (a) Louie, J.; Grubbs, R. H. *Chem. Commun.* **2000**, 1479. (b) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.
(14) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921 and references therein.
(15) (a) Kim, J.-B.; Bruening, M. L.; Baker, G. L. *J. Am. Chem. Soc.* **2000**, *123*, 7616. (b) Huang, W.; Baker, G. L.; Bruening, M. L. *Angew, Chem., Int. Ed.* **2001**, *40*, 1570.
(16) (a) Wang, X.-S.; Luo, N.; Ying, S. K. *Polymer* **1999**, *40*, 4157. (b) Zhang, X.; Wang, P.; Zhu, P.; Ye, C.; Xi, F. *Macromol. Chem. Phys.* **2000**, *201*, 1853. (c) Wang, X.-S.; Armes, S. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41* (1), 413.
(17) (a) Teodorescu, M.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4826. (b) Teodorescu, M.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2000**, *21*, 190. (c) Redemacher, J. T.; Baum, M.; Pallack, M. E.; Brittain, W. J.; Simonsick, W. J. *Macromolecules* **2000**, *33*, 284. (d) Zhang, H.; Xia, J.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5167.
(18) Wang, X. S.; Jackson, R. A.; Armes, S. P. *Macromolecules* **2000**, *33*, 255.
(19) Wang, X. S.; Malet, F. L. G.; Armes, S. P.; Haddleton, D. M.; Perrier, S. *Macromolecules* **2001**, *34*, 162.
(20) (a) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190. (b) Haddleton, D. M.; Kukulj, D.; Duncalf, D. J.; Heming, A. M.; Shooter, A. J. *Macromolecules* **1998**, *31*, 5201.
(21) Matyjaszewski, K.; Coca, S.; Jasieczek, C. B. *Macromol. Chem. Phys.* **1997,** *198*, 4011.
(22) In a typical solution polymerization, a dry glass tube was charged with CuBr (8.76 mg, 0.061 mmol) and *N*-(*n*-propyl)-2-pyridylmethanimine (36 mg, 0.122 mmol), GMA (2.5 mL, 0.0183 mol), diphenyl ether (2.5 mL), and a magnetic stir bar. The tube was fitted with a rubber septum and degassed by three freeze−pump−thaw cycles. The solution turned dark brown and homogeneous. The initiator 2-bromopropionitrile (10.5 μL, 0.121 mmol) was added via a degassed syringe, and the solution became progressively more viscous, indicating the onset of polymerization. After various time intervals, the polymers were dissolved in tetrahydrofuran and then filtered through the silica gel column. Conversion was measured by gravimetry and molecular weights determined by GPC (Waters 515 liquid chromatograph connected with four Ultrastyragel GPC columns (guard, 10^3 Å, 10^4 Å, and 10^5 Å); eluent: THF; flow rate: 1 mL/min).
(23) It could be noted here that we have observed low polydispersity of polymers in diphenyl ether as a solvent when compared to other solvents. Hence, we have chosen diphenyl ether for polymerization.
(24) Kuchta, F. D.; Van Herk, A. M.; German, A. L. *Macromolecules* **2000**, *33*, 3641.

MA025637C