

## Controlled/"Living" Radical Polymerization of 2-(Dimethylamino)ethyl Methacrylate

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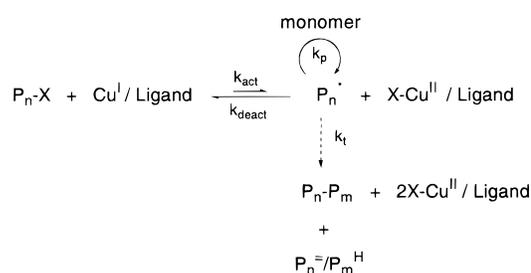
Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) and quaternized PDMAEMA have attracted much attention in recent years as water-soluble polymers due to the variety of applications related to environmental protection. The temperature-sensitive solubility of PDMAEMA in water also renders it potentially applicable in fields such as drug delivery systems, sensors, etc.<sup>1,2</sup> Amphiphilic block copolymers of DMAEMA form micelles and act as stabilizers in dispersion polymerizations.<sup>3–5</sup> Recently, DMAEMA has been polymerized in a controlled fashion via living anionic polymerization<sup>6,7</sup> and group transfer polymerization (GTP).<sup>8,9</sup> However, both have drawbacks, as living anionic polymerization requires stringent experimental conditions that often make industrial application difficult, and GTP only allows the preparation of block copolymers with other (meth)acrylates. Recently, polystyrene–PDMAEMA block copolymers have been prepared by stable free-radical polymerization.<sup>10</sup> However, the molecular weight of the PDMAEMA segment was not controlled, and furthermore, homopolymerization of DMAEMA was not successful.

Research on controlled/"living" radical polymerization has grown rapidly in recent years. Several new methods have been developed to gain control over the molecular weight and polydispersity of the polymer chains.<sup>11–16</sup> One of the most successful systems is atom transfer radical polymerization (ATRP). Typically a Cu(I)/bpy system is used as the catalyst,<sup>12–14</sup> but systems employing other metals<sup>15–17</sup> and ligands<sup>18–20</sup> have also been reported. ATRP has tolerance to a variety of functional groups on the monomers and has been applied toward the preparation of well-defined polymers such as substituted styrenes, (meth)acrylic esters, and acrylonitrile.<sup>21–24</sup> Controlled polymerization in ATRP is achieved by establishing a dynamic equilibrium between the propagating and dormant species with copper complexes acting as a reversible halogen atom transfer reagent (Scheme 1). As a result, the concentration of the propagating species is greatly lowered, and the contribution of termination to the overall reaction is suppressed.

This paper reports the controlled/"living" radical polymerization of DMAEMA via ATRP. Well-defined PDMAEMA has been synthesized using copper bromide complexed by different amine ligands as the catalyst, and ethyl 2-bromoisobutyrate (EBiB) or 2-bromopropionitrile (BPN) as the initiator in a variety of solvents.

When DMAEMA was polymerized using CuBr with 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the ligand and BPN as the initiator, a linear increase of measured number average molecular weight,  $M_{n,sec}$ , vs monomer conversion up to 80% was observed

Scheme 1



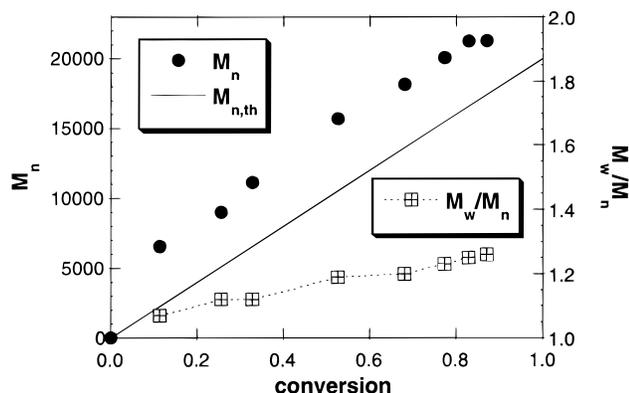
indicating a controlled/"living" process with a negligible amount of transfer (Figure 1).<sup>25</sup> Relatively straight kinetic lines in the semilogarithmic plot were obtained suggesting fast initiation and negligible termination (Figure 2). This was further supported by the low polydispersities of the obtained polymers. The  $M_{n,sec}$  was close to the theoretical molecular weight,  $M_{n,th}$ , defined by eq 1 where  $\Delta[M]$  is the change in monomer concentration,  $[I]_0$  is the initial concentration of the initiator, and MW is the molecular weight of the monomer.

$$M_{n,th} = (\Delta[M]/[I]_0) \times MW \quad (1)$$

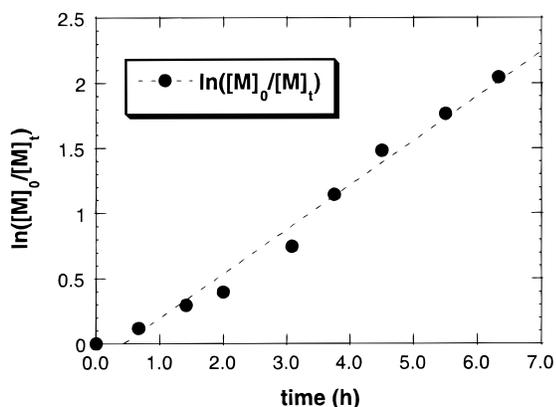
The close correlation of  $M_{n,th}$  with  $M_{n,sec}$  indicated that BPN was an efficient initiator for the system, and that the number of active chains remained constant during the polymerization. The deviation of  $M_{n,sec}$  from  $M_{n,th}$  may be partially due to differences in the hydrodynamic volume of PDMAEMA and polystyrene standards in DMF. The polydispersities remained quite low ( $M_w/M_n < 1.25$ ) throughout the reaction, indicating a fast and dynamic exchange between the active and the dormant chain ends. EBiB could also be used as the initiator for the polymerization of DMAEMA but polymers with slightly higher polydispersities ( $M_w/M_n \sim 1.5$ ) were obtained. When *p*-toluenesulfonyl chloride (TsCl) was used as the initiator, the polymerization was slower and had a lower initiator efficiency, possibly due to the presence of side reactions such as nucleophilic attack of monomer on the initiator.

The gel permeation chromatographs (GPC) of some polymers synthesized by ATRP are shown in Figure 3. All of the GPC traces show a small tailing toward the low molecular weights. This may be contributed to the adsorption of PDMAEMA on the GPC column, a phenomenon previously reported.<sup>3,7</sup> Addition of 1 vol % triethylamine to the GPC eluent (DMF) in our studies did not minimize these effects.

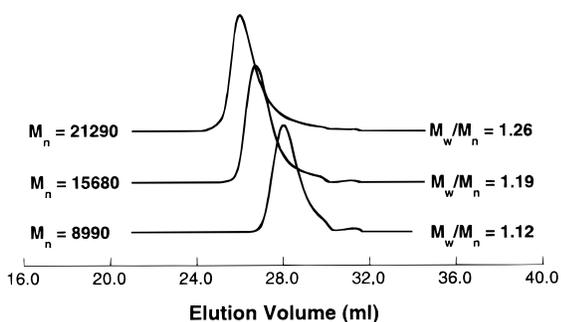
Additional experiments of varying conditions were carried out in sealed tubes using ethyl 2-bromoisobutyrate as the initiator to assess the effects of ligand, solvent, and temperature.<sup>26</sup> Different amine ligands, such as *N,N,N,N*-tetramethylethylenediamine (TME-DA), *N,N,N,N'*-pentamethyldiethylenetriamine (PM-DETA), 2,2'-bipyridine (bpy), and bipyridine derivatives, can be used as the ligands for copper to promote ATRP of DMAEMA. The polymers obtained using above-mentioned ligands have slightly broader molecular weight distributions than in the case of HMTETA. Polymerization of DMAEMA can also be carried out using a lower catalyst-to-initiator ratio without sacrificing the control of the polymerization (Table 1). Well-



**Figure 1.** Evolution of experimental molecular weight and polydispersity with conversion in the solution polymerization of DMAEMA in 50 vol. % of dichlorobenzene initiated by 2-bromopropionitrile (BPN).  $[\text{CuBr}]_0 = [\text{BPN}]_0 = [\text{HMTETA}]_0 = 0.0233 \text{ M}$ ,  $[\text{DMAEMA}]_0 = 2.96 \text{ M}$ , and  $T = 50 \text{ }^\circ\text{C}$ .



**Figure 2.** Semilogarithmic kinetic plot for ATRP of DMAEMA in 50 vol. % dichlorobenzene with  $[\text{CuBr}]_0 = [\text{BPN}]_0 = [\text{HMTETA}]_0 = 0.0233 \text{ M}$ ,  $[\text{DMAEMA}]_0 = 2.96 \text{ M}$ , and  $T = 50 \text{ }^\circ\text{C}$ .



**Figure 3.** GPC traces of PDMAEMA prepared in the solution polymerization in 50 vol. % dichlorobenzene.  $[\text{CuBr}]_0 = [\text{BPN}]_0 = [\text{HMTETA}]_0 = 0.0233 \text{ M}$ ,  $[\text{DMAEMA}]_0 = 2.96 \text{ M}$ , and  $T = 50 \text{ }^\circ\text{C}$ .

defined DMAEMA can be prepared in various polar solvents, such as anisole, butyl acetate (BuOAc), dichlorobenzene, etc. (Table 2). The reaction media are slightly green and homogeneous. Nonpolar solvents, such as toluene, are not good solvents for ATRP of DMAEMA. The low solubility of the copper catalyst in nonpolar solvents results in a slow and poorly controlled polymerization. Unlike ATRP of styrene or acrylates which is usually carried out at 90 to 110  $^\circ\text{C}$ ,<sup>13,27</sup> polymerization of DMAEMA can be accomplished at much lower temperatures. In particular, well-controlled polymers with low polydispersity can be prepared at room temperature (Table 3).

**Table 1. Solution Polymerization of DMAEMA Catalyzed by Copper(I) Bromide Complexed by Different Ligands at 90  $^\circ\text{C}$ <sup>a</sup>**

ligand	time (h)	convn (%)	$M_{n,\text{th}}$	$M_{n,\text{sec}}$	$M_w/M_n$
bpy <sup>b</sup>	1.25	84.7	16 940	20 530	1.55
TMEDA <sup>b</sup>	4.25	75.6	15 120	18 610	1.53
PMDETA <sup>c</sup>	1.00	67.5	13 500	17 550	1.61
HMTETA <sup>c</sup>	1.25	79.1	15 820	17 880	1.45
HMTETA <sup>d</sup>	2.00	75.0	15 000	14 160	1.49

<sup>a</sup> Reaction conditions:  $[\text{CuBr}]_0 = [\text{EBiB}]_0 = 0.0233$ ;  $[\text{DMAEMA}]_0 = 2.96 \text{ M}$  in 50 vol. % anisole in sealed tubes. <sup>b</sup>  $[\text{ligand}]_0 = 0.0466 \text{ M}$ . <sup>c</sup>  $[\text{ligand}]_0 = 0.0233 \text{ M}$ . <sup>d</sup>  $2[\text{CuBr}]_0 = 2[\text{HMTETA}] = [\text{EBiB}]_0 = 0.0233 \text{ M}$ ;  $[\text{DMAEMA}]_0 = 2.96 \text{ M}$  in 50 vol. % dichlorobenzene.

**Table 2. Solution Polymerization of DMAEMA in Different Solvents at 90  $^\circ\text{C}$ <sup>a</sup>**

solvent	time (h)	convn (%)	$M_{n,\text{th}}$	$M_{n,\text{sec}}$	$M_w/M_n$
anisole	1.25	79.1	15 820	17 880	1.45
dichlorobenzene	1.25	77.6	15 520	15 770	1.43
BuOAc	1.50	85.6	30 820	25 260	1.57
toluene	4.25	32.6	6 520	73 560	2.81
ethylene carbonate	1.00	62.5	12 500	11 490	1.51

<sup>a</sup> Reaction conditions:  $[\text{CuBr}]_0 = [\text{HMTETA}]_0 = [\text{EBiB}]_0 = 0.0233 \text{ M}$ ;  $[\text{DMAEMA}]_0 = 2.96 \text{ M}$  in 50 vol. % solvent in sealed tubes.

**Table 3. Solution Polymerization of DMAEMA in 50 Vol. % Dichlorobenzene at Different Temperatures<sup>a</sup>**

temperature	time (h)	convn (%)	$M_{n,\text{th}}$	$M_{n,\text{sec}}$	$M_w/M_n$
90.0	1.25	77.6	15520	15770	1.43
70.0	1.25	63.7	12740	13100	1.37
50.0	1.80	68.9	13780	14140	1.37
22.8	4.67	67.2	13440	18910	1.25

<sup>a</sup> Reaction conditions:  $[\text{CuBr}]_0 = [\text{HMTETA}]_0 = [\text{EBiB}]_0 = 0.0233 \text{ M}$ ;  $[\text{DMAEMA}]_0 = 2.96 \text{ M}$  in sealed tubes.

In summary, we have demonstrated that well-defined poly(2-(dimethylamino)ethyl methacrylate) can be prepared by atom transfer radical polymerization. Various ligands can be used in the system, and different reaction conditions such as temperature, initiator, and solvent can be varied to optimize polymerization. Further work toward the preparation of amphiphilic AB diblock and ABA triblock copolymers by ATRP are underway in our group.

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- (25) In a typical experiment run in a flask, a dry round-bottom flask was charged with CuBr (13.4 mg, 0.093 mmol), 1,1,4,7,10,10-hexamethyltriethylenetetramine (25.4  $\mu$ L, 0.093 mmol), 2-(dimethylamino)ethyl methacrylate (2 mL, 5.9 mmol), dichlorobenzene (2 mL), and a magnetic stir bar. The flask was fitted with a rubber septum and degassed by three freeze–pump–thaw cycles. The flask was immersed in an oil bath thermostated at 50 °C, and this was followed by dropwise addition of 2-bromopropionitrile (8  $\mu$ L, 0.093 mmol). After various time intervals, samples were taken out via degassed syringes and dissolved in DMF to measure conversion (GC) and molecular weight (GPC).
- (26) In a typical sealed tube experiment, a dry long glass-tube was charged with CuBr (6.7 mg, 0.047 mmol), ligand (0.047 or 0.093 mmol), ethyl 2-bromoisobutyrate (6.8  $\mu$ L, 0.047 mmol), 2-(dimethylamino)ethyl methacrylate (1 mL, 5.9 mmol), solvent (1 mL), and a magnetic stir bar. The glass tube was degassed by three freeze–pump–thaw cycles and sealed by flame. The glass tube was immersed in an oil bath thermostated at 50, 70, or 90 °C. After a certain time, the glass tube was taken out and broken. The sample was dissolved in DMF to measure conversion (GC) and molecular weight (GPC).
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