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Ultra high molar mass poly[2-(dimethylamino)ethyl methacrylate] via atom transfer radical polymerization

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Abstract

Well-defined high molecular weight poly[2-(dimethylamino)ethyl methacrylates] [poly(DMAEMA)s] with molar masses up to $\sim 1 \times 10^6$ g/mol were successfully synthesized via atom transfer radical polymerization (ATRP). This was achieved by using *p*-toluenesulfonyl chloride(*p*-TsCl)/CuCl/1,1,4,7,10,10-hexamethyl-triethylenetetramine(HMTETA) initiator/catalyst complex in methanol/water mixture. Well-controlled/'living' behavior was demonstrated throughout the reaction, up to high monomer conversion. The PDI value remained low at 1.26 even for a polymer with very high molecular weight at 1.1×10^6 g/mol. We believe this is the first successful case where controlled ATRP produces a polymer with molar mass exceeding a million!

Keywords: ATRP; Poly(DMAEMA); *p*-Toluenesulfonyl chloride

1. Introduction

Atom transfer radical polymerization (ATRP) is currently one of the most used techniques for synthesizing polymers with well-defined structures due to its high level of control over chain length and distributions [1,2]. In contrast to conventional radical polymerization, the synthesis of high molecular weight polymer is still a challenge for ATRP. This is mainly due to termination and other side reactions during polymerization process resulting in poor control at higher molecular weight, which would require high initiator efficiency, narrow polydispersity index (PDI), and a moderate reaction rate during the polymerization at high monomer-to-initiator ratio. Although some polymers with molecular weight up to 150,000 have been synthesized via this technique [3,4], the successful cases are still limited. Matyjaszewski et al. [3] reported the ATRP of methyl methacrylate (MMA) with *p*-toluenesulfonyl chloride (*p*-TsCl) initiator in conjunction with CuBr/4,4′-di-(5-nonyl)-2,2′-bipyridyl (dNbpy) in diphenyl ether at 90 °C in sealed tubes, yielding polymer of number-average molecular weight (M_n) = 83,000 with polydispersity index (PDI) = 1.18. However, the PDI increased to 1.4 when the M_n increased to 169,000. Matyjaszewski et al. [4] also reported that ATRP of styrene could be well-controlled up to a molecular weight of 30,000 with low PDI (~1.05) using 1-phenylethyl bromide/CuBr/dNbpy initiator catalyst complex, but at higher molecular weight the PDI increased to 1.5 even in dilute solutions. Recently, Xue et al. [5] reported a better result for the ATRP of MMA with phenyl 2-bromomethylpropionate (BMPE)/CuCl/4,4′-*n*-nonyl-2,2′-bipyridine (dnNbpy) initiator catalyst complex system in xylene at 90 °C. However, monomer conversion remained low at less than 60%. ATRP of 2-(dimethylamino)ethyl methacrylate (DMAEMA) was first reported by Zhang et al. [6]. The polymerizations were carried out in non-polar solvents and reasonable control was observed. However, the polydispersity indexes were relatively high, ranging from 1.43–1.61. In contrast, we have recently reported very well-controlled/'living' ATRP of DMAEMA and 2-(diethylamino)ethyl methacrylate (DEAEMA) in protic media [7]. The 'livingness' of poly(DMAEMA) and poly(DEAEMA) have been clearly demonstrated by successful block copolymerizations [7]. Further studies on the ATRP of DMAEMA lead us for the first time to successfully synthesize well-defined very high molecular weight polymers. Poly(DMAEMA) with $M_n \sim 1 \times 10^6$ and low PDI could be achieved. The results are now presented in this paper.

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2. Experimental section

2.1. Materials

DMAEMA (98%, Merck) was purified by passing through an alumina column and distilled prior to use. *p*-Toluenesulfonyl chloride (*p*-TsCl) (99%, Fluka), CuCl (99.99% Aldrich), 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA) (97%, Aldrich) and methanol (99.9%, Aldrich) were used as received.

2.2. Polymerization

A typical polymerization is described. CuCl (0.0119 g, 0.120 mmol) was added to a dry 50 mL Schlenk flask with a magnetic stirring bar, and the Schlenk flask was evacuated and flushed with argon. Distilled DMAEMA (21.0 mL, 125 mmol), HMTETA (0.0326 mL, 0.120 mmol), degassed methanol (13.0 mL) and distilled water (2.0 mL) were added to the Schlenk flask using degassed syringes. The mixture was stirred for 10 min and then degassed by three freeze-pump-thaw cycles. The flask was placed in a water bath maintained at 25±0.2 °C. Finally, *p*-TsCl (0.0076 g, 0.040 mmol) was added. The reaction mixture was stirred for 10 h. The polymerization was terminated by exposing the reaction vessel to air and 10 mL of THF was added. The solution was passed through a basic alumina column and eluted with additional 100 mL of THF. The volume of the solution was reduced using a rotary evaporator and the concentrated solution was poured into hexane for precipitation, yielding a polymer with $M_{n,GPC}=410{,}000$, PDI = 1.18 and 81% monomer conversion. For kinetic studies, at each time interval, 0.5 mL of solution was withdrawn and introduced onto a micro column, fabricated with a glass Pasteur pipette (i.d. 6 mm) packed with 0.7 g of basic alumina (the height of packed alumina was 15 mm). The content was eluted by a total of 5 mL of THF (five successive times of 1 mL each). The filtrate was collected for gravimetric and GPC analysis.

2.3. Characterizations

M_n and M_w/M_n (PDI) of the polymers were determined by gel permeation chromatography (GPC). An Agilent 1100 series GPC system equipped with a LC pump, PLgel MIXED-C column, packed with 5 μm particles of different pore sizes for the separation of polymers over a wide range of molecular weight from about 200 to 3 millions, and refractive index (RI) detector were used. The column was calibrated with narrow molecular weight polystyrene standards. HPLC grade THF stabilized with 2,6-*tert*-butyl-4-methylphenol (BHT) containing 1% triethylamine was used as a mobile phase, at a flow rate of 1.0 mL/min at 25 °C. ^{1}H NMR spectra were recorded using a Bruker DRX400 spectrometer in $CDCl_3$. The monomer conversion is calculated from the mass of polymer obtained by gravimetric method.

For poly(DMAEMA) prepared via ATRP using *p*-TsCl initiator, when the M_n is below 50,000 g/mol, the ^{1}H NMR spectra show distinctive peaks for the groups [phenyl: $\delta=7.3$–7.4 (2H); 7.7–7.8 (2H)] and the repeat units. The absolute M_n values can be obtained from the integral ratios of the relevant peaks. We found that the M_n values from the NMR agree reasonably well with those obtained from the GPC, albeit ~10% higher [7]. For very high molar mass poly(DMAEMA), consistent GPC results were obtained from several measurements when the polymer concentrations were <1 mg/mL. However, at higher concentration, it was found that the GPC elution time could vary, possibly caused by aggregation, leading to lower molar mass value. Hence, extra care was taken to ensure appropriate concentrations were used and consistent GPC results were obtained with each sample.

3. Results and discussion

McDonald and Rannard first reported the rate enhancement by small quantity of water in alcoholic media for the ATRP of *n*-butyl methacrylate [8]. Whereas Robinson et al. first reported well-controlled ATRP of 2-hydroxyethyl methacrylate in methanol and methol/H_2O mixture [9].

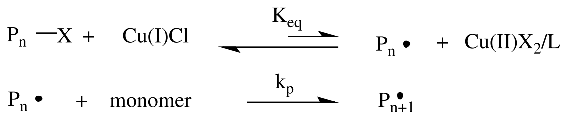
In the attempt to synthesize high molar mass poly(DMAEMA), various experimental reaction conditions with different molar ratio of DMAEMA:*p*-TsCl:CuCl:HMTETA and methanol/H_2O composition were explored. The results of a particular set of experiments with targeted $M_n=300{,}000$ are summarized in Table 1.

The quantity and composition of the solvent mixture (i.e. methanol:H_2O) greatly affected the polymerization. But the effect on the polymerization behavior was different from those for a lower molar mass ATRP of DMAEMA [6]. For runs 1–3, with [DMAEMA]:[*p*-TsCl]:[CuCl]:[HMTETA] ratio kept at 1908:1:1:1, the reactions proceeded well initially. The polymerizations then slowed down and eventually stopped. For example, run 1 stopped at a molar mass of 112,000 with PDI ~1.31, after 6 h of reaction. Increasing the reaction time did not increase molar mass further but PDI varied slightly.

Table 1
Results of atom transfer radical polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) under different conditions at 25 °C

No.	Methanol (mL)	H_2O (mL)	Reaction time (h)	Conversion (%)	$M_{n,theo}$	$M_{n,GPC}$	Polydispersity index
1	7	3	6	42	300,000	112,000	1.31
2	7	2	9.5	45	300,000	130,000	1.23
3	13	2	14	60	300,000	190,000	1.18
4	13	2	7	86	300,000	280,000	1.15

DMAEMA 20 mL (117 mmol); $[DMAEMA]_0:[p\text{-TsCl}]_0:[CuCl]_0:[HMTETA]_0=1908:1:1:1$ (runs 1,2 and 3); 1908:1:3:3 (run 4).



Scheme 1. Propagation step for atom transfer radical polymerization.

Similar results were observed for runs 2 and 3 with different amount and compositions of the solvent mixture. The rate of reaction was slower for solvent mixture with lower H_2O contents (run 2), and with higher solvent/monomer ratio (run 3). Both reactions 2 and 3 stopped at molar masses well below the targeted value of 300,000. This is in contrast with the results obtained under almost identical conditions for lower molar mass ATRP of DMAEMA (target $M_n = 13{,}800$) which was well-controlled with high monomer conversion [7]. It is believed that one of the main factors for the different behavior of high-molar mass polymerization was caused by the increased viscosity of the polymerization solution. Increased solution viscosity perturbs the equilibria and the rate of propagation involved in the propagation step (Scheme 1) [10] causing the overall rate of polymerization to slow down and eventually stop (runs 1–3). The mobility of the long polymer chain could be substantially retarded by increased viscosity, thus reducing the frequency of its growing chain ends to 'surface' from the 'interior' of the polymer coil for the deactivation and propagation processes.

The problem of low conversion however could be overcome by increasing the concentration of the catalyst system. Increasing the molar contents of CuCl and the ligand HMTETA increased the reaction rate and the polymerization improved tremendously. Using the molar ratio of [DMAEMA]:[p-TsCl]:[CuCl]:[HMTETA] at 1908:1:3:3, very well-controlled poly(DMAEMA) with high molar mass of 280,000 and PDI of 1.15 was achieved (run 4).

Employing the same experimental conditions with high catalyst/initiator molar ratio of 3:1, poly(DMAEMA)s of very high molar masses (up to $\sim 1\times10^6$) with low PDI values were successfully synthesized.

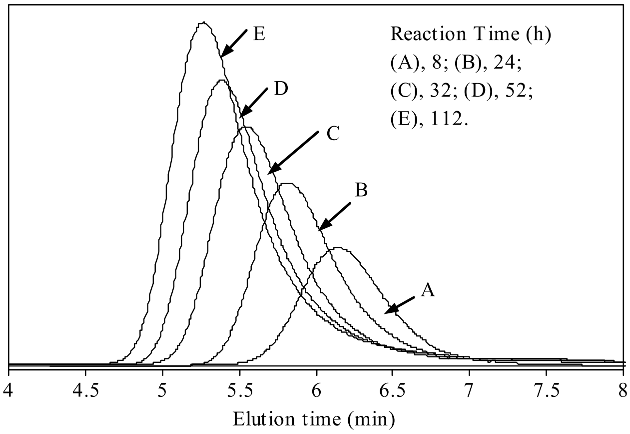


Fig. 1. GPC traces for homopolymerization of DMAEMA under the following conditions: 5:3 v/v monomer/solvent (methanol:$H_2O = 13{:}2$ v/v); $[CuCl]_0$:$[HMTETA]_0$:$[p\text{-TsCl}]_0 = 3{:}3{:}1$, $[p\text{-TsCl}]_0 = 0.023$ mmol; $[DMAEMA]_0 = 148$ mmol, and at 25 °C; final $M_{n,GPC} = 766{,}000$, PDI = 1.18.

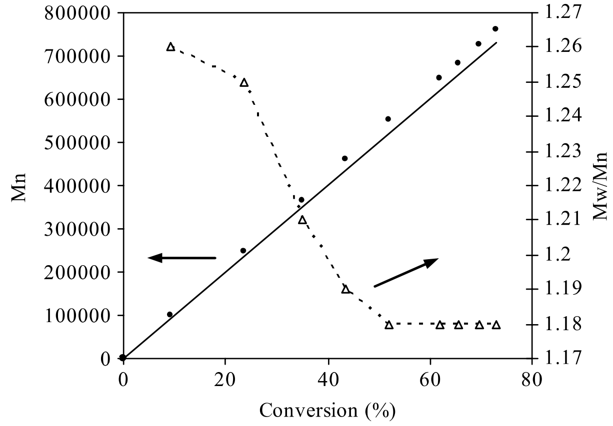


Fig. 2. Plot of M_n as a function of DMAEMA %conversion (linear line is $M_{n,theo}$). Also shown is the variation in the PDI as a function of DMAEMA %conversion. $[CuCl]_0$:$[HMTETA]_0$:$[p\text{-TsCl}]_0 = 3{:}3{:}1$, $[p\text{-TsCl}]_0 = 0.023$ mmol; $[DMAEMA]_0 = 148$ mmol, in 5:3 v/v monomer/solvent (methanol:$H_2O = 13{:}2$ v/v) and at 25 °C.

The results of a typical high-molar mass polymerization experiment under the conditions of [DMAEMA]:[p-TsCl]:[CuCl]:[HMTETA] = 6370:1:3:3 at 25 °C are given below. The GPC traces at various time intervals are presented in Fig. 1, showing the smooth increment of molar masses with narrow distribution. The corresponding M_n and PDI versus conversion plots are shown in Fig. 2 showing a linear increase of M_n up to 72% conversion with final PDI ~1.18. The plot of $\ln([M]_0/[M])$ versus time was linear, up to ~72% conversion of monomer, showing the controlled/'living' character of the polymerization process (Fig. 3(a)). At a higher temperature of 50 °C under identical conditions, the polymerization remained well-controlled. Fig. 3(b) shows the linear kinetic plot of $\ln([M]_0/[M])$ versus reaction time, in which the last point corresponds to 80% conversion. Higher monomer conversion could be achieved at 50 °C due to the lower solution viscosity at higher temperature, enabling easy sample withdrawal. The PDI, however was slightly higher at ~1.23. The plots of M_n and PDI versus reaction time are shown in Fig. 4.

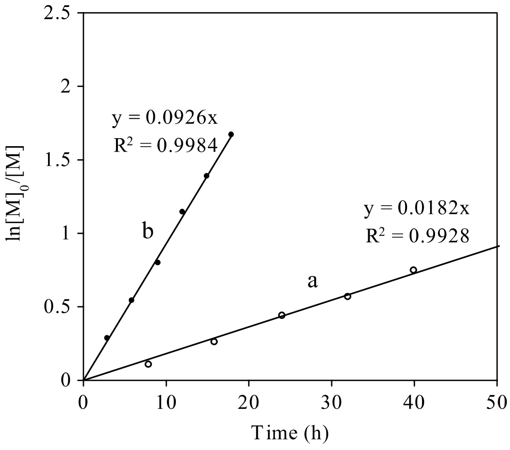


Fig. 3. Semilogarithmic kinetic plots of ATRP of DMAEMA: $[CuCl]_0$:$[HMTETA]_0$:$[p\text{-TsCl}]_0 = 3{:}3{:}1$, $[p\text{-TsCl}]_0 = 0.023$ mmol; $[DMAEMA]_0 = 148$ mmol. (a), at 25 °C; (b), at 50 °C.

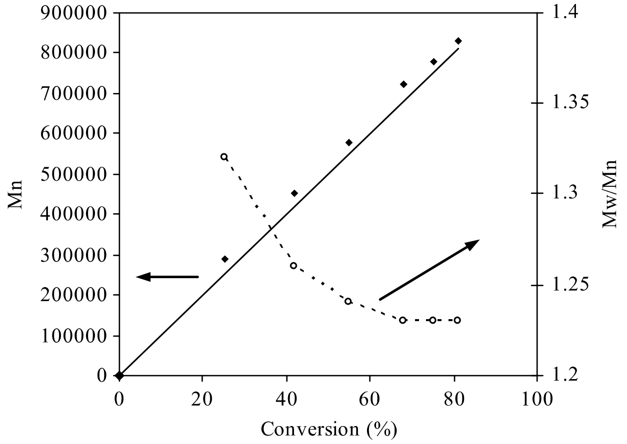


Fig. 4. Plot of M_n and PDI as a function of DMAEMA %conversion at 50 °C (linear line is $M_{n,theo}$). $[CuCl]_0$:$[HMTETA]_0$:$[p\text{-}TsCl]_0=3:3:1$, $[p\text{-}TsCl]_0=0.023$ mmol; $[DMAEMA]_0=148$ mmol, in 5:3 v/v monomer/solvent (methanol:$H_2O=13:2$ v/v); final $M_{n,GPC}=831{,}100$, PDI = 1.23.

Hence, another experiment designed for an even higher $M_n=1{,}200{,}000$ was carried out at 50 °C. The reaction conditions of $[CuCl]_0$:$[HMTETA]_0$:$[p\text{-}TsCl]_0=3:3:1$ in 20:11 v/v monomer/solvent (methanol:$H_2O=10:1$ v/v) were employed. The M_n of the polymer obtained after 24 h of reaction was as high as 1.1×10^6 g/mol! The monomer conversion was ~85% and the PDI was ~1.26.

We believe the good solubility of both the poly(DMAEMA) and HMTETA complexes of CuCl/$CuCl_2$ in the reaction medium are key to the success of the high molar-mass polymerization. In addition, the results from ^1H NMR analysis indicate no or insignificant transesterification reaction occurred under the present polymerization systems. As the transesterification product is methyl methacrylate (MMA), its presence could easily be detected at ~3.5 ppm, corresponding to the protons of $-COOCH_3$ group [7,11].

4. Conclusions

Poly(DMAEMA)s of very high molar masses have been successfully synthesized via ATRP using *p*-TsCl/CuCl/HMTETA initiator catalyst complex in methanol/water mixture. Well-controlled/‘living’ behavior is demonstrated throughout the reaction, up to high monomer conversion. The PDI values remained low even for a polymer with very high molecular weight at $\sim1\times10^6$ g/mol. As far as we are aware of, the molecular weights achieved in the present study are by far the highest ever reported via a controlled ATRP technique.

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