Synthesis of Well-Defined Amphiphilic Block Copolymers with 2-(Dimethylamino)ethyl Methacrylate by Controlled Radical Polymerization

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ABSTRACT: Amphiphilic AB block copolymers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) with methyl methacrylate, methyl acrylate, or styrene have been synthesized by atom transfer radical polymerization using well-defined poly(methyl methacrylate), poly(methyl acrylate), and polystyrene as macroinitiators. The molecular weight distributions of the block copolymers are very narrow ($M_w/M_n \sim 1.2$). Kinetic studies indicate the block copolymer formation is a controlled process with molecular weight increase linearly with the conversion. Block copolymers containing different lengths of PDMAEMA segment can be easily prepared by varying the ratio of DMAEMA and macroinitiator. ABA triblock copolymers of PDMAEMA–PDMAEMA have also been prepared using diffunctional PMMA macroinitiator. Clean chain extension to form block copolymer has been achieved when PMMA and PMA were used as the macroinitiators. The molecular weight distributions of the resulting block copolymers are fairly narrow. However, a less complete chain extension from PSt to PDMAEMA was observed due to the relatively slow initiation compared to propagation and/or the presence of the side reactions.

Introduction

Amphiphilic block copolymers have attracted increasing research interest in recent years due to their applications as stabilizers, emulsifiers, or dispersants.¹⁻³ PDMAEMA-PMMA block copolymers have been shown to form micelles in deionized water.² The size and the association number of the micelles can be easily varied in a predictable fashion by adjusting the temperature, pH, and ionic strength of the solution or the block copolymer composition. Amphiphilic block copolymers of PDMAEMA have been synthesized recently via living anionic polymerization⁴ and group transfer polymerization (GTP).^{2,5} However, both have drawbacks, as living anionic polymerization requires rigorous reagent purification which often makes industrial application difficult, and GTP does not allow the preparation of block copolymers with monomers other than (meth)acrylates. Very recently, polystyrene-PDMAEMA block copolymers have also been prepared by nitroxidemediated "living" radical polymerization.⁶ However, the molecular weight of the PDMAEMA segment could not be varied or controlled.

Traditionally well-defined polymer architectures such as block copolymers are prepared via living polymerization techniques. Recent advances in controlled/"living" radical polymerization have made it viable for the synthesis of controlled polymer architectures usually only accessible by living ionic polymerization. Much progress in controlled radical polymerization has been made toward a better control of polymerization in nitroxide-mediated,⁷ metal-mediated,⁸ and atom transfer radical polymerization (ATRP).⁹ ATRP is based on reversible halogen transfer between alkyl halides and transition metals in the low oxidation state to form radicals and transition metals in a higher oxidation state. The dynamic equilibrium between the active radicals and dormant alkyl halides leads to control over the polymerization by maintaining a low concentration

of active radicals and a predetermined concentration of total propagating species (active radicals plus dormant species). ATRP has great tolerance to functional groups on monomers¹⁰ and has been applied successfully toward the preparation of polymers with different architectures.¹¹ Recent advances have been directed toward the polymerization of new monomers^{12,13} and the development of new systems by employing new ligands¹⁴ and new metals.^{15,16}

Despite their potential applications in industry, the synthesis of amphiphilic block copolymers by ATRP has not been extensively reported. This paper reports the synthesis of amphiphilic AB diblock and ABA triblock copolymers of poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) with narrow polydispersities by ATRP using well-defined poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), or polystyrene (PSt) as macroinitiators. Amphiphilic block copolymers of various lengths of PDMAEMA segment have been prepared simply by varying the ratio of the macroinitiator to DMAEMA.

Experimental Section

Materials. Styrene (St), methyl acrylate (MA), and methyl methacrylate (MMA) were distilled over CaH_2 and stored at -30 °C under argon prior to use. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) was freshly distilled before polymerization. CuBr and CuCl were purified according to the published procedure.¹⁷ Other reagents were all commercial products and used without further purification.

Synthesis of Macroinitiators. PMMA and difunctional PMMA macroinitiators were prepared in 50 vol % anisole solution at 90 °C using CuCl complexed by 4,4'-di(5-nonyl)-2,2'-bipyridyl (dNbpy) as the catalyst and *p*-toluenesulfonyl chloride or 1,2-bis(2-bromopropionyloxy)ethane as the initiators, respectively. PMA was prepared in bulk at 90 °C using CuBr/dNbpy as the catalyst and methyl 2-bromopropionate as the initiator. PSt was prepared in bulk at 110 °C using CuBr complexed by 2,2'-bipyridyl (bpy) as the catalyst and 1-phenylethyl bromide as the initiator. The macroinitiators were

dissolved in THF after the polymerization and were precipitated into methanol after passing through an alumina column.

Synthesis of Block Copolymers. DMAEMA was polymerized in the presence of PMMA, PMA, and PSt macroinitiators in 50 vol % 1,2-dichlorobenzene in sealed tubes at 90 °C using CuCl complexed by 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the catalyst. After the reaction, the tubes were broken, and the samples were dissolved in DMF for further characterization by gas chromatography (GC) and gel permeation chromatography (GPC) using a 0.1% tetrabutylammonium bromide solution in DMF as the eluent. For NMR studies, the reaction mixture was dissolved in THF and precipitated into hexanes after passing through an alumina column.

Characterization. Monomer conversion was determined from the concentration of residual monomers on a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column and a flame ionization detector with helium as the carrier gas. Molecular weights and molecular weight distributions were measured on Phenomenex GPC columns (Guard, 5×10^4 , 10^3 , and 10^2) coupled with a Waters 410 differential refractometer using 0.1% tetrabutylammonium bromide solution in DMF as the eluent. ¹H NMR was performed on a Bruker WP300 instrument using CDCl₃ as the solvent.

Results and Discussion

PMMA with bromine as the radical transferable group was synthesized by ATRP using ethyl 2-bromoisobutyrate as the initiator and CuBr complexed by 4,4'di(tert-butyl)-2,2'-bipyridyl (dTbpy) as the catalyst at 90 °C in 50 vol % diphenyl ether. The resulting PMMA of $M_{\rm n,sec} = 13500$ and $M_{\rm w}/M_{\rm n} = 1.09$ was used as the macroinitiator to form block copolymers with DMAEMA under ATRP conditions. The block copolymerization was carried out using CuBr complexed by 1,1,4,7,10,10hexylmethyltriethylenetetramine (HMTETA) or N,N,-N, N', N'-pentamethyldiethylenetriamine (PMDETA) as the catalyst. The gel permeation chromatograph (GPC) traces of the resulting PMMA-PDMAEMA block copolymers showed a bimodal distribution. The shoulder on the low molecular weight end exhibited the same molecular weight as the macroinitiator. The incomplete chain extension was attributed to the loss of bromine end functional groups during the macroinitiator synthesis. This was likely due to the elimination of HBr from the terminal tertiary carbon. The results are consistent with the deviation of the experimental molecular weights from the theoretical values at medium to high conversion in ATRP of MMA when bromine is used as the exchange halogen.¹⁸

To avoid this problem, a PMMA macroinitiator with chlorine as the end group was prepared using ptoluenesulfonyl chloride (TsĈl) as the initiator and ČuĈl complexed by 4,4'-di(5-nonyl)-2,2'-bipyridyl (dNbpy) as the catalyst in 50% anisole at 90 °C. The resulting PMMA ($\dot{M}_{n,sec} = 17480$, $M_w/M_n = 1.07$) was used as the macroinitiator to prepare block copolymers with DMAE-MA. To match the reactivity of initiation and propagation, polymerization of DMAEMA was carried out using CuCl/HMTETA as the catalyst in 50 vol % 1,2-dichlorobenzene at 90 °C. The GPC traces of the resulting PMMA-PDMEMA block copolymer and the PMMA-Cl macroinitiator are shown as a stacked plot in Figure 1. The absence of the PMMA macroinitiator peak on the GPC trace of PMMA-PDMAEMA block copolymer indicates the complete conversion of the macroinitiator to the block copolymer. This suggests that the chain ends of the macroinitiator are fully functionalized. As shown in Figure 2, the molecular weights of the block



Figure 1. Stack plot of GPC traces of PMMA–PDMAEMA block copolymer and PMMA macroinitiator. Reaction conditions: $[CuCl]_0 = [HMTETA]_0 = [PMMA–Cl]_0 = 0.0116 \text{ M}$, $[DMAEMA]_0 = 2.96 \text{ M}$ in 50 vol % 1,2-dichlorobenzene at 90 °C.



Figure 2. Evolution of experimental molecular weight and polydispersity with conversion for the synthesis of PMMA–PDMAEMA block copolymer using PMMA as the macroinitiator. Reaction conditions: $[CuCl]_0 = [HMTETA]_0 = [PMMA-Cl]_0 = 0.0233$ M, $[DMAEMA]_0 = 2.96$ M in 50 vol % 1,2-dichlorobenzene at 90 °C.

copolymers increase linearly with the conversion of DMAEMA, indicating the "living" nature of the block copolymer formation. Block copolymers with different target molecular weights of PDMAEMA segment can be prepared by varying monomer-to-macroinitiator ratio (Table 1). The molecular weight distribution of the block copolymers are very narrow ($M_w/M_n < 1.2$). Addition of CuCl₂ do not improve the formation of the block copolymer significantly as shown in the table.

The difunctional macroinitiator Cl-PMMA-Cl was prepared using CuCl/dNbpy as the catalyst and 1,2-bis-(2-bromopropionyloxy)ethane as the difunctional initiator. It is known that Cl atoms on the copper catalyst will gradually exchange onto the polymer chain ends under these reaction conditions.¹⁹ The difunctional PMMA macroinitiator ($M_{n.sec} = 33\ 010$ and $M_w/M_n =$ 1.17) is likely to have active chlorines at both chain ends which can potentially chain extend under ATRP conditions. The triblock copolymer synthesis was carried out under similar conditions as those of the diblock copolymer (Table 2). The chain extension from the PMMA macroinitiator was complete as indicated by the absence of the original macroinitiator peak in the GPC trace of PDMAEMA-PMMA-PDMAEMA block copolymer. Block copolymers containing PDMAEMA segment of various lengths were prepared by varying the ratio of

Table 1. Synthesis of PDMAEMA Block Copolymers Using PMMA Macroinitiators^a in 50 vol % 1,2-Dichlorobenezene at 90 °C

macroinitiator	conv (%)	target MW of 2nd block	M _{n,th} of diblock	$M_{ m n,sec}$ of diblock	M _w /M _n of diblock	theoretical ratio	ratio by GPC	ratio by NMR
PMMA ^b	52.5	20 000	27 980	24 630	1.12	0.636	0.409	0.565
PMMA ^c	46.6	20 000	26 800	23 180	1.10	0.565	0.326	0.525
PMMA ^d	57.0	40 000	40 280	32 070	1.14	1.38	0.835	1.23

^{*a*} $M_{n,sec} = 17\,480$ and $M_w/M_n = 1.07$ for PMMA-Cl. ^{*b*} $[CuCl]_0 = [HMTETA]_0 = [macroinitiator]_0 = 0.0233$ M, $[DMAEMA]_0 = 2.96$ M. ^{*c*} $[CuCl]_0 = 0.0186$ M, $[CuCl_2]_0 = 0.00466$ M, $[HMTETA]_0 = [macroinitiator]_0 = 0.0233$ M, $[DMAEMA]_0 = 2.96$ M. ^{*d*} $[CuCl]_0 = [HMTETA]_0 = [macroinitiator]_0 = 0.0066$ M, $[DMAEMA]_0 = 2.96$ M.

Table 2. Synthesis of PDMAEMA ABA Triblock Copolymers Using PMMA Macroinitiators^a in 50 vol % 1,2-Dichlorobenezene at 90 $^\circ\mathrm{C}$

macroinitiator	conv (%)	target MW of PDMAEMA	M _{n,th} of triblock	M _{n,sec} of triblock	M _w ∕M _n of triblock	theoretical ratio	ratio by GPC	ratio by NMR
PMMA ^b	47.8	40 000	52 130	44 260	1.17	0.683	0.341	0.622
PMMA ^c	74.3	80 000	92 450	69 270	1.24	2.12	1.10	1.59

^{*a*} $M_{n,sec} = 33\ 010$ and $M_w/M_n = 1.17$ for Cl-PMMA-Cl. ^{*b*} [CuCl]₀ = [HMTETA]₀ = [Cl-PMMA-Cl]₀ = 0.0233 M, [DMAEMA]₀ = 2.96 M. ^{*c*} [CuCl]₀ = [HMTETA]₀ = [Cl-PMMA-Cl]₀ = 0.0116 M, [DMAEMA]₀ = 2.96 M.

 Table 3. Synthesis of PDMAEMA Block Copolymers Using PMA and PSt Macroinitiators^a in 50 vol %

 1,2-Dichlorobenezene

macroinitiator	conv (%)	target MW of 2nd block	M _{n,th} of diblock	M _{n,sec} of diblock	M _w /M _n of diblock	theoretical ratio	ratio by GPC	ratio by NMR
PMA^b	47.4	25 000	35 950	39 230	1.15	0.853	0.628	0.895
PMA^{c}	38.8	25 000	33 800	45 270	1.15	0.694	0.878	0.805
PSt^d	86.3	20 000	17 260	10 130	1.83	4.98	3.80	3.75

^{*a*} $M_{n,sec} = 24\ 100$ and $M_w/M_n = 1.15$ for PMA–Br, $M_{n,sec} = 2110$ and $M_w/M_n = 1.06$ for PSt–Br. ^{*b*} $[CuCl]_0 = [HMTETA]_0 = 0.0233$ M, [macroinitiator]_0 = 0.0186 M, [DMAEMA]_0 = 2.96 M, T = 90 °C. ^{*c*} $[CuCl]_0 = 0.0186$ M, $[CuCl_2]_0 = 0.00466$ M, $[HMTETA]_0 = 0.0233$ M, [macroinitiator]_0 = 0.0186 M, [DMAEMA]_0 = 2.96 M, T = 90 °C. ^{*c*} $[CuCl]_0 = [HMTETA]_0 = [macroinitiator]_0 = 0.0233$ M, $[DMAEMA]_0 = 2.96$ M, T = 90 °C. ^{*d*} $[CuCl]_0 = [HMTETA]_0 = [macroinitiator]_0 = 0.0233$ M, $[DMAEMA]_0 = 2.96$ M, T = 10 °C.

DMAEMA to macroinitiator. The results for the ABA triblock copolymers are summarized in Table 2.

The PMA macroinitiator ($M_{n,sec} = 24 \ 100$ and M_w/M_n = 1.15) was prepared using methyl 2-bromopropionate as the initiator and CuBr/dNbpy as the catalyst in bulk. The initiation from PMA is relatively slow compared to the propagation of DMAEMA since halogen abstraction from secondary C-Br is slower than that from tertiary C-Br. Furthermore, the equilibrium constant for acrylate in ATRP is significantly smaller than that for methacrylate. Therefore, the synthesis of block copolymers with DMAEMA has a potential problem of slow initiation which may lead to the incomplete block copolymer formation. The preparation of the block copolymer was carried using PMA-Br as the macroinitiator and CuCl/HMTETA as the catalyst. Chlorine was employed as the exchange halogen to avoid slow initiation. In the initiation step, C-Br bonds were broken. As the reaction proceeded, chlorine quickly exchanged with bromine, and most chain ends were terminated with chlorine. The rate of initiation was enhanced compared to the rate of propagation since during the propagation stronger C–Cl bonds were broken. Block copolymers of PMA-PDMAEMA were successfully prepared under these conditions. The GPC traces showed the absence of the macroinitiator (Figure 3) and the complete chain extension from PMA to form block copolymers with higher molecular weights and narrow polydispersities (Table 3).

The bromine functionalized PSt macroinitiator ($M_{n,sec}$ = 2110 and M_w/M_n = 1.06) with low polydispersity was prepared using 1-phenylethyl bromide (PEB) as the initiator and CuBr/dTbpy as the catalyst. Successful chain extension to PMA was achieved using the PSt macroinitiator. However, the synthesis of block copoly-



Figure 3. Stack plot of GPC traces of PMA–PDMAEMA block copolymer and PMA macroinitiator. Reaction conditions: $[CuCl]_0 = [HMTETA]_0 = 0.0233 \text{ M}$, $[PMA-Br]_0 = 0.0186 \text{ M}$, $[DMAE-MA]_0 = 2.96 \text{ M}$ in 50 vol % 1,2-dichlorobenzene at 90 °C.

mer with PDMAEMA was less successful. When the polymerization of PDMAEMA was carried out at 90 °C using CuBr/HMTETA as the catalyst, the chain extension was incomplete with a significant amount of PSt macroinitiator remained. When the polymerization of PDMAEMA was carried out at 110 °C using CuCl/ HMTETA as the catalyst, the chain extension from PSt to PDMAEMA was improved. However, the presence of PSt homopolymer in the PSt-PDMAEMA block copolymer was evident as the GPC trace of the block copolymer showed a small shoulder corresponding to the molecular weight of the macroinitiators. The molecular weight distribution of the resulting block copolymer was quite broad (Table 3). This is likely due to the slow initiation from the PSt macroinitiator and/or the presence of the side reactions such as $S_N 2$ type nucleophilic attack of the amino group on the terminal Br groups.

GPC analyses of the block copolymers were carried out on Phenomenex columns (Guard, 5×10^4 , 10^3 , and 10²) using 0.1% tetrabutylammonium bromide solution in DMF as the eluent and PMMA as molecular weight standard. In general, the number-average molecular weight agrees with the theoretical molecular weight when the content of PDMAEMA in the block copolymer is low. Larger deviation toward low molecular weight is observed when the content of PDMAEMA is increased. This is likely due to the adsorption of PD-MAEMA onto the GPC column which would result in an increase in retention time and lead to lower detected molecular weights.^{4,5} As a result, the relative comonomer composition determined by GPC shows lower ratios of PDMAEMA to macroinitiator than the theoretical values. ¹H NMR in a nonselective solvent (CDCl₃) was also carried out to determine the composition of the block copolymers. The signal at δ 4.0–4.2 arisen from methoxy protons of PDMAEMA was integrated over the signal at δ 3.6–3.8 from methoxy protons for block copolymers with PMMA and PMA and over the signal at δ 6.2–6.8 from anyl protons for block copolymers with PSt. Good agreement between the measured copolymer composition by ¹H NMR and the theoretical ones was obtained. Detailed results are summarized in Tables 1 - 3

Conclusion

Amphiphilic AB block copolymers of 2-(dimethylamino)ethyl methacrylate with methyl methacrylate, methyl acrylate, and styrene have been synthesized by atom transfer radical polymerization using well-defined poly-(methyl methacrylate), poly(methyl acrylate), and polystyrene macroinitiators. ABA triblock copolymers of PDMAEMA-PMMA-PDMAEMA have also been prepared using difunctional PMMA macroinitiator. Clean chain extension to form block copolymer has been achieved when PMMA and PMA were used as the macroinitiators. The molecular weight distributions of the resulting block copolymers are fairly narrow. However, a less complete chain extension from PSt to PDMAEMA was observed due to the relatively slow initiation compared to the propagation and/or the presence of the side reactions.

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