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

Xuan Zhang and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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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 ($M_w/M_n<1.2$). 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—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 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. PDMAEMA—PMMA block copolymers have been shown to form micelles in deionized water. 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 polymerization and group transfer polymerization (GTP). 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 nitroxide-mediated “living” radical polymerization. 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, metal-mediated, and atom transfer radical polymerization (ATRP). 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 monomers and has been applied successfully toward the preparation of polymers with different architectures. Recent advances have been directed toward the polymerization of new monomers and the development of new systems by employing new ligands and new metals.

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 $-30^\circ$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. 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 touluenesulfonfyl chloride or 1,2-bis(2-bromopropiolato)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-hexamethyltriphenylenetetramine (HMTETA) as the catalyst. After the reaction, the tubes were broken, and the samples were dissolved in DMF for further characterization by gel permeation chromatography (GPC) and gel permeation chromatography (GPC) using a 0.1% tetraethylammonium bromide solution in DMF as the eluent. For NMR studies, the reaction mixture was dissolved in DMSO-δ as the solvent.

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 × 10³, 10³, and 10²) coupled with a Waters 410 differential refractometer using 0.1% tetraethylammonium bromide solution in DMF as the eluent. 1H NMR was performed on a Bruker WP300 instrument using CDCl 3 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 Mₙ,sec = 13 500 and Mₙ/Mₚ = 1.09 was used as the macroinitiator to form block copolymers with DMEAEMA under ATRP conditions. The block copolymerization was carried out using CuBr complexed by 1,1,4,7,10,10-hexamethyltriphenylenetetramine (HMTETA) or 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.

To avoid this problem, a PMMA macroinitiator with chlorine as the end group was prepared using p-toluenesulfonfyl chloride (TsCl) as the initiator and CuCl complexed by 4,4′-di(5-nonyl)-2,2′-bipyridyl (dNbpy) as the catalyst at 50% anisole at 90 °C. The resulting PMMA (Mₙ,sec = 17 480, Mₚ/Mₙ = 1.07) was used as the macroinitiator to prepare block copolymers with DMEAEMA. 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–PDMAEMA 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 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 (Mₚ/Mₙ < 1.2). Addition of CuCl₂ do not improve the formation of the block copolymer significantly as shown in the table.
DMAEMA to macroinitiator. The results for the ABA triblock copolymers are summarized in Table 2.

The PMMA macroinitiator (M<sub>n,sec</sub> = 24 100 and M<sub>n</sub>/M<sub>n</sub> = 1.15) was prepared using methyl 2-bromopropionate as the initiator and CuBr/dNbpy as the catalyst in bulk. The initiation from PMMA 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 PMMA–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–DMAEMA 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<sub>n,sec</sub> = 2110 and M<sub>n</sub>/M<sub>n</sub> = 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 copolymer 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 SN2 type nucleophilic attack of the amino group on the terminal Br groups.

### Table 1. Synthesis of PDMAEMA Block Copolymers Using PMMA Macroinitiators<sup>a</sup> in 50 vol.% 1,2-Dichlorobenzene at 90 °C

<table>
<thead>
<tr>
<th>Macroinitiator</th>
<th>Conv (%)</th>
<th>Target MW of 2nd block</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; of diblock</th>
<th>M&lt;sub&gt;n,sec&lt;/sub&gt; of diblock</th>
<th>M&lt;sub&gt;w&lt;/sub&gt; of diblock</th>
<th>Theoretical ratio</th>
<th>Ratio by GPC</th>
<th>Ratio by NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>52.5</td>
<td>20 000</td>
<td>27 980</td>
<td>24 630</td>
<td>1.12</td>
<td>0.636</td>
<td>0.409</td>
<td>0.565</td>
</tr>
<tr>
<td>PMMA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>46.6</td>
<td>20 000</td>
<td>26 800</td>
<td>23 180</td>
<td>1.10</td>
<td>0.565</td>
<td>0.326</td>
<td>0.525</td>
</tr>
<tr>
<td>PMMA&lt;sup&gt;d&lt;/sup&gt;</td>
<td>57.0</td>
<td>20 000</td>
<td>40 280</td>
<td>32 070</td>
<td>1.14</td>
<td>1.38</td>
<td>0.835</td>
<td>1.23</td>
</tr>
<tr>
<td>PMMA&lt;sup&gt;e&lt;/sup&gt;</td>
<td>72.0</td>
<td>80 000</td>
<td>75 080</td>
<td>46 050</td>
<td>1.18</td>
<td>3.49</td>
<td>1.63</td>
<td>2.48</td>
</tr>
</tbody>
</table>

<sup>a</sup>M<sub>n,sec</sub> = 17 480 and M<sub>n</sub>/M<sub>n</sub> = 1.07 for PMMA–Cl. <sup>b</sup>[CuCl]<sub>2</sub> = [HMTETA]<sub>b</sub> = [macroinitiator]<sub>b</sub> = 0.0233 M, [DMAEMA]<sub>b</sub> = 2.96 M. <sup>c</sup>[CuCl]<sub>2</sub> = 0.0186 M, [CuCl]<sub>2</sub> = 0.0046 M, [HMTETA]<sub>b</sub> = [macroinitiator]<sub>b</sub> = 0.0233 M, [DMAEMA]<sub>b</sub> = 2.96 M. <sup>d</sup>[CuCl]<sub>2</sub> = [HMTETA]<sub>b</sub> = [macroinitiator]<sub>b</sub> = 0.00606 M, [DMAEMA]<sub>b</sub> = 2.96 M.

### Table 2. Synthesis of PDMAEMA ABA Triblock Copolymers Using PMMA Macroinitiators<sup>a</sup> in 50 vol.% 1,2-Dichlorobenzene at 90 °C

<table>
<thead>
<tr>
<th>Macroinitiator</th>
<th>Conv (%)</th>
<th>Target MW of PDMAEMA</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; of triblock</th>
<th>M&lt;sub&gt;n,sec&lt;/sub&gt; of triblock</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt; of triblock</th>
<th>Theoretical ratio</th>
<th>Ratio by GPC</th>
<th>Ratio by NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>52.5</td>
<td>20 000</td>
<td>27 980</td>
<td>24 630</td>
<td>1.12</td>
<td>0.636</td>
<td>0.409</td>
<td>0.565</td>
</tr>
<tr>
<td>PMMA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>46.6</td>
<td>20 000</td>
<td>26 800</td>
<td>23 180</td>
<td>1.10</td>
<td>0.565</td>
<td>0.326</td>
<td>0.525</td>
</tr>
<tr>
<td>PMMA&lt;sup&gt;d&lt;/sup&gt;</td>
<td>57.0</td>
<td>20 000</td>
<td>40 280</td>
<td>32 070</td>
<td>1.14</td>
<td>1.38</td>
<td>0.835</td>
<td>1.23</td>
</tr>
<tr>
<td>PMMA&lt;sup&gt;e&lt;/sup&gt;</td>
<td>72.0</td>
<td>80 000</td>
<td>75 080</td>
<td>46 050</td>
<td>1.18</td>
<td>3.49</td>
<td>1.63</td>
<td>2.48</td>
</tr>
</tbody>
</table>

<sup>a</sup>M<sub>n,sec</sub> = 33 010 and M<sub>n</sub>/M<sub>n</sub> = 1.17 for Cl–PMA–Cl. <sup>b</sup>[CuCl]<sub>2</sub> = [HMTETA]<sub>b</sub> = [Cl–PMA–Cl]<sub>b</sub> = 0.0233 M, [DMAEMA]<sub>b</sub> = 2.96 M. <sup>c</sup>[CuCl]<sub>2</sub> = [HMTETA]<sub>b</sub> = [Cl–PMA–Cl]<sub>b</sub> = 0.0116 M, [DMAEMA]<sub>b</sub> = 2.96 M.

### Table 3. Synthesis of PDMAEMA Block Copolymers Using PMA and PST Macroinitiators<sup>a</sup> in 50 vol.% 1,2-Dichlorobenzene

<table>
<thead>
<tr>
<th>Macroinitiator</th>
<th>Conv (%)</th>
<th>Target MW of 2nd block</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; of diblock</th>
<th>M&lt;sub&gt;n,sec&lt;/sub&gt; of diblock</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt; of diblock</th>
<th>Theoretical ratio</th>
<th>Ratio by GPC</th>
<th>Ratio by NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>47.4</td>
<td>25 000</td>
<td>35 950</td>
<td>39 230</td>
<td>1.15</td>
<td>0.853</td>
<td>0.628</td>
<td>0.895</td>
</tr>
<tr>
<td>PMA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>38.8</td>
<td>25 000</td>
<td>33 800</td>
<td>45 270</td>
<td>1.15</td>
<td>0.694</td>
<td>0.878</td>
<td>0.805</td>
</tr>
<tr>
<td>PST&lt;sup&gt;d&lt;/sup&gt;</td>
<td>86.3</td>
<td>20 000</td>
<td>17 260</td>
<td>10 130</td>
<td>1.93</td>
<td>4.98</td>
<td>3.80</td>
<td>1.75</td>
</tr>
</tbody>
</table>

<sup>a</sup>M<sub>n,sec</sub> = 110 °C. M<sub>n</sub>/M<sub>n</sub> = 1.15 for PMA–Br, M<sub>n,sec</sub> = 2110 and M<sub>n</sub>/M<sub>n</sub> = 1.06 for PST–Br. <sup>b</sup>[CuCl]<sub>2</sub> = [HMTETA]<sub>b</sub> = 0.0233 M, [macroinitiator]<sub>b</sub> = 0.0186 M, [DMAEMA]<sub>b</sub> = 2.96 M. <sup>c</sup>[CuCl]<sub>2</sub> = 0.0186 M, [CuCl]<sub>2</sub> = 0.0046 M, [HMTETA]<sub>b</sub> = [macroinitiator]<sub>b</sub> = 0.0233 M, [DMAEMA]<sub>b</sub> = 2.96 M. <sup>d</sup>[CuCl]<sub>2</sub> = [HMTETA]<sub>b</sub> = [macroinitiator]<sub>b</sub> = 0.0233 M, [DMAEMA]<sub>b</sub> = 2.96 M, T = 90 °C.

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**Figure 3.** Stack plot of GPC traces of PMA–PDMAEMA block copolymer and PMA macroinitiator. Reaction conditions: [CuCl]<sub>2</sub> = [HMTETA]<sub>b</sub> = 0.0233 M, [PMA–Br]<sub>b</sub> = 0.0186 M, [DMAEMA]<sub>b</sub> = 2.96 M in 50 vol.% 1,2-dichlorobenzene at 90 °C.
GPC analyses of the block copolymers were carried out on Phenomenex columns (Guard, 5 × 10^4, 10^3, and 10^2) 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 in- 

dexed. 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. As a result, the relative comono- 

mer composition determined by GPC shows lower ratios 

of PDMAEMA to macroinitiator than the theoretical 

values. 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 aryl 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-(dimethylami- 

no)ethyl methacrylate with methyl methacrylate, meth- 

yl acrylate, and styrene have been synthesized by atom 

transfer radical polymerization using well-defined poly- 

(methyl methacrylate), poly(methyl acrylate), and poly- 

styrene macroinitiators. ABA triblock copolymers of 

PDMAEMA–PMM–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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