KEYWORDS:
atom transfer radical polymerization (ATRP);
triblock copolymer;
poly(ethylene oxide);
poly(4-vinylpyridine);
polystyrene.

ABSTRACT

A novel ABC triblock copolymer of poly(ethylene oxide)-b-poly(styrene)-b-poly(4-vinylpyridine) (PEO-b-PS-b-P4VP) was successfully synthesized via atom transfer radical polymerization (ATRP). First, polyethylene glycol monomethyl ether (PEO) terminated with a halogen atom (PEO-Br) was prepared by esterification of PEO with 2-bromoisobutyryl bromide. Next, bromo-terminated poly(ethylene oxide)-b-poly(styrene) (PEO-b-PS) diblock copolymers were obtained by the polymerization of styrene using PEO-Br as the macroinitiator and CuBr/bpy complex as the catalyst. Finally, PEO-b-PS-b-P4VP triblock copolymers were also prepared by ATRP of 4-vinylpyridine (4VP) using PEO-b-PS-Br as the macroinitiator and CuCl/tris[2-(dimethylamino)ethyl]amine (Me6TREN) as the catalyst. The triblock copolymers and precursors were characterized by 1H NMR spectroscopy and gel permeation chromatography (GPC) techniques. The triblock copolymers prepared by this method have a well-defined structure. The results of GPC analysis showed that the as-prepared triblock copolymers had relatively narrow molecular weight distributions. The kinetics of copolymerization was also investigated. The results indicated that the ATRP process of 4VP is "living"/controlled in 2-propanol at conversions below 70%.

INTRODUCTION

ABC triblock copolymers and their synthesis have attracted considerable interest not only for their rich morphological structures but also for their potential applications [1-9]. Generally, a wide range of living/controlled polymerization techniques are available to prepare ABC triblock copolymers of various architectures, solubility, and functionality by the consecutive polymerization of different monomers. These living/controlled polymerization techniques are comprised of living ionic polymerization [10,11] and "living" radical polymerization [12,13]. Moreover, various techniques could also be
combined to prepare ABC triblock copolymer [14,15].

However, the living ionic polymerization is limited because of the need for rigorous conditions, such as strictly low temperature, water- and oxygen-free reaction systems, and a high level of monomer purification. Compared to the living ionic polymerization method, the recent development of "living"/controlled radical polymerizations, especially ATRP has addressed above issues and opened a new route to synthesize polymers with well-defined structures [16-25]. ATRP method can be applied to a large variety of monomers [17-19] and many precise block copolymers have been prepared and reported by ATRP [20-24].

Recently, 4-vinylpyridine (4VP) was employed to prepare the block copolymer via ATRP due to its ability to form self-assembly supramolecular structures [26] and complexes with metal ions [27]. The block copolymer of 4VP has been already prepared via ATRP method by Matyjaszewski et al [28-31]. However, there are some limitations in the polymerization of 4VP by ATRP.

The relatively high final conversion, significant low polydispersity, and good blocking efficiencies were difficult to achieve in 4VP polymerization via ATRP. This was ascribed to its strong coordination effect with the metal catalysts component in the polymerization system. In order to overcome this problem, two approaches have been employed. The first is to adopt a multidentate ligand with strong coordination ability, such as Me₆TREN. The second is to choose protic solvent, such as 2-propanol to further minimize the contamination of the catalyst [31].

In this work, a novel ABC triblock copolymer of PEO-b-PS-b-P4VP was prepared via ATRP. The triblock copolymer consisting of hydrophilic PEO block, hydrophobic PS block and pH-sensitive P4VP block is novel and interesting. Such chain structure of a copolymer shows some excellent properties. For example, it might self-assemble to form various aggregates in aqueous solutions by changing the preparation conditions, such as the solution pH and variation of solution conditions (e.g., solvent mixtures and salt content). During the polymerizations, molecular weight distribution and polymerization kinetics were also investigated.

### EXPERIMENTAL

#### Materials

2-Bromoisobutyryl bromide (98%, Alfa) was freshly distilled under vacuum. Triethylamine (TEA) (AR, Beijing Chem. Co.) was refluxed with p-toluene-sulphonyl chloride, stored with CaH₂ over night, and then distilled. 4-(Dimethylamino) pyridine (DMAP) was recrystallized from toluene. Methylene dichloride (CH₂Cl₂) was shaken with concentrated H₂SO₄ until the acid layer remained colourless, then washed with water, aqueous 5 wt% NaHCO₄, and with water again, and finally distilled with CaH₂. PEO (Mₙ=2000 g/mol, Alfa) was dried by azeotropic distillation with toluene before use. Traces of residual toluene were removed under vacuum. Chlorobenzene (99%, Acros) was washed with concentrated H₂SO₄ to remove thiophenes, then washed with water, aqueous 5 wt% Na₂CO₃, and with water again, and finally distilled over anhydrous calcium chloride. CuBr was prepared from CuBr₂ and purified by stirring with glacial acetic acid, followed by filtration and washing the solid three times with ethanol and twice with diethyl ether. The solid was dried under vacuum. CuCl was prepared from CuCl₂ and purified in a manner similar to that used above. Styrene was passed through a column with neutral Al₂O₃ (120-160 mesh) to remove the inhibitor, dried with CaH₂, and distilled under reduced pressure. 4VP was dried with CuH₂ overnight, distilled under vacuum (65°C/18 mmHg), and stored at -18°C prior to use. 2-Propanol was purified in a manner similar to that used for 4VP. All other reagents were purchased from commercial sources and used as received without purification. Me₆TREN was prepared in a one-step synthesis from commercially available tris(2-aminoethyl)amine (TREN) according to the literature [32,33]. All chemicals were purchased from Aldrich unless otherwise stated.

#### Preparation of PEO-Br Macroinitiator

The bromo-capped PEO macroinitiator (PEO-Br) was synthesized according to the literature [34]. In order to avoid cleavage of the polymer chains, as found in case of other derivatizations of PEO, the reaction was carried out at 0°C in CH₂Cl₂ in the presence of TEA and DMAP. In a typical experiment, a 0.92 g (7.50
mmol) DMAP in 20 mL dried methylene dichloride was mixed with 0.51 g (5.00 mmol) TEA. The solution was transferred into a 250 mL three-neck round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer. After cooling to 0ºC, a solution of 2.88 g (12.50 mmol) 2-bromoisobutyryl bromide in 20 mL CH2Cl2 was added under vigorous stirring. Then a solution of 10 g (5 mmol) PEO in 100 mL dried CH2Cl2 was added dropwise into flask slowly in 1 h, and a yellow dispersion was formed. Subsequently, the temperature was allowed to rise to room temperature. The reaction was allowed to continue under stirring for 18 h. After filtration, the solution was concentrated and the crude product was precipitated with cold diethyl ether. PEO-Br macroinitiator was further purified by recrystallization from ethanol. After the given polymer was filtered, washed with cold diethyl ether, and then dried under vacuum at room temperature.

1H NMR (CDCl3), δ: 1.94 ppm (6H, -C(CH3)2Br), 3.38 ppm (3H, -O-CH3), 3.45-3.83 ppm (4H, -CH2-CH2-O-), and 4.33 ppm (2H, -COOCH2-).

Preparation of PEO-b-PS Diblock Copolymer by ATRP
PEO-b-PS diblock copolymers were synthesized via solution polymerization in chlorobenzene. In a typical polymerization, a glass tube was filled with 0.11 g (0.05 mmol) PEO-Br macroinitiator, 2.50 g (25 mmol) styrene, 7.20 mg (0.05 mmol) CuBr, 23.40 mg (0.15 mmol) bpy and 1.13 g chlorobenzene. After degassing with three freeze-pump-thaw cycles, the tube was sealed under vacuum and then immersed in a thermostatic oil bath at 110ºC. After 18 h, the tube was withdrawn and cooled to room temperature. The reaction mixture was then diluted with THF. The solution was filtered through a column with neutral Al2O3 to remove the catalyst, the solution was concentrated and then precipitated with petroleum ether. The PEO-b-PS diblock copolymer was obtained and dried under vacuum overnight at room temperature.

1H NMR (CDCl3), δ: 3.38 ppm (3H, -O-CH3), 3.61-3.83 ppm (4H, -CH2-CH2-O-). 1.24-1.63 ppm (4H, -CH2- (styrene units)), 1.71-1.95 ppm (2H, -CH-(styrene units)), 6.2-6.6 ppm (4H, σ-protons of benzene ring and ortho-protons of pyridine ring), 8.2-8.5 ppm (2H, meta-protons of pyridine ring), and 7.04-7.08 ppm (3H, p- and m-protons of benzene ring).

Characterization
The number average molecular weight (Mn) and molecular weight distribution (Mw/Mn) were determined by GPC on a WATER1515 (Waters, USA) gel permeation chromatography (GPC) instrument with a set of HT3, HT4, and HT5, μ-styragel columns with DMF as an eluent (1.0 mL/min) at 35ºC. Polystyrene (PS) standard was utilized for calibration.

1H NMR spectra were recorded at 25ºC on an INOVA-400 NMR spectrometer (Varian, USA) with chloroform-d as a solvent and with tetramethylsilane (TMS) as an internal standard.

RESULTS AND DISCUSSION
Preparation of the PEO-Br and PEO-b-PS Diblock Copolymers
The PEO-Br macroinitiator, PEO-b-PS diblock copolymer, and PEO-b-PS-b-P4VP triblock copolymer were synthesized via ATRP in 2-propanol. In a typical polymerization, a glass tube was filled with 0.42 g (0.02 mmol) of PEO-b-PS, 0.93 g (8 mmol) of 4VP, 0.002 g (0.02 mmol) of CuCl, 9.40 mg (0.04 mmol) of Me6TREN, and 0.30 g of 2-propanol. After degassing with three freeze-pump-thaw cycles, the tube was sealed under vacuum and then immersed in a thermostatic oil bath at 40ºC. At a certain time, the tube was withdrawn and cooled to room temperature. The reaction mixture was then diluted with THF. The solution was filtered through neutral Al2O3 column to remove the catalyst, the solution was concentrated and then precipitated with ether, and a clear, colourless polymer was obtained. The polymer was dried in a vacuum oven overnight at room temperature.

1H NMR (CDCl3), δ: 3.38 ppm (3H, -O-CH3), 3.61-3.83 ppm (4H, -CH2-CH2-O-). 1.24-1.63 ppm (4H, -CH2- (styrene units)), 1.71-1.95 ppm (1H, -CH-(styrene units)), 6.4-6.6 ppm (2H, σ-protons of benzene ring and ortho-protons of pyridine ring), 8.2-8.5 ppm (2H, meta-protons of pyridine ring), and 7.04-7.08 ppm (3H, p- and m-protons of benzene ring).
mer were synthesized in a stepwise process. The overall synthetic protocol was presented in Scheme I. The 1H NMR spectroscopy was employed to characterize the obtained product. Figure 1 is the 1H NMR spectrum of the PEO-Br macroinitiator. It is observed that the peak of the hydroxyl group of PEO in CDCl3 at around 2.45 ppm disappears completely and two new peaks appear at 4.33 and 1.94 ppm. Moreover, the peak integral area ratio of proton signals a, b, and d is 6:2:3. All this suggests that the esterification reaction was completed. The molecular weight of PEO-Br is calculated to be $2.2 \times 10^3$ g/mol, based on the peak integral area ratio of d to c.

The obtained PEO-Br was functionalized with 2-bromoisobutyryl group, which could be used as macroinitiator for ATRP due to the electron drawing effect of ester group. Figure 2 shows the 1H NMR spectrum of PEO-b-PS (A) diblock copolymer.
spectrum of the PEO-b-PS (A) diblock copolymer. In the $^1$H NMR spectrum of PEO-b-PS a new set of peaks is observed compared to the spectrum of PEO-Br. The proton signals at 1.24-1.63 ppm, 1.71-1.95 ppm, and 6.4-7.08 ppm are assigned to -CH$_2$-, -CH- and benzene ring of the repeated styrene unit in the backbone of the PEO-b-PS diblock copolymer. These data illustrate the presence of the PS block in the polymer chain. According to 1H NMR spectroscopy, the molecular weight of PEO-b-PS (A) diblock copolymer is $2.11 \times 10^4$ g/mol based on the peak integral area ratio of b to f.

The number average molecular weight and molecular weight distribution of PEO-Br macroinitiator and the obtained PEO-b-PS diblock copolymers prepared with ATRP route were further determined by GPC. The results are summarized in Table 1. For example, the $M_n$ value of sample PEO-Br, based on GPC analysis, is $1.29 \times 10^4$ g/mol and the value of $M_n/M_n$ is 1.04. After chain extension reaction, the $M_n$ value of sample PEO-b-PS (A) is $2.28 \times 10^4$ g/mol and the value of $M_n/M_n$ is 1.08. All this indicates that the ATRP of styrene was well controlled.

Table 1. GPC and $^1$H NMR data of the PEO-b-PS-b-P4VP (PESV) triblock copolymers and their precursors.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Macro-initiator</th>
<th>$M_n$,$^a$ (×10$^4$ g/mol)</th>
<th>$M_w/M_n$</th>
<th>$M_n$,$^b$ (×10$^4$ g/mol)</th>
<th>PEO$^c$ (wt%)</th>
<th>PS$^c$ (wt%)</th>
<th>P4VP$^c$ (wt%)</th>
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</thead>
<tbody>
<tr>
<td>PEO-Br</td>
<td>-</td>
<td>1.29</td>
<td>1.03</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PEO-b-PS (A)</td>
<td>-</td>
<td>2.28</td>
<td>1.08</td>
<td>2.11</td>
<td>9</td>
<td>91</td>
<td>-</td>
</tr>
<tr>
<td>PESV-1</td>
<td>A</td>
<td>4.06</td>
<td>1.19</td>
<td>2.79</td>
<td>7</td>
<td>69</td>
<td>24</td>
</tr>
<tr>
<td>PESV-2</td>
<td>A</td>
<td>5.02</td>
<td>1.26</td>
<td>3.29</td>
<td>6</td>
<td>59</td>
<td>35</td>
</tr>
<tr>
<td>PESV-3</td>
<td>A</td>
<td>6.38</td>
<td>1.35</td>
<td>3.73</td>
<td>5</td>
<td>52</td>
<td>43</td>
</tr>
<tr>
<td>PESV-4</td>
<td>A</td>
<td>7.83</td>
<td>1.45</td>
<td>4.44</td>
<td>4</td>
<td>44</td>
<td>52</td>
</tr>
<tr>
<td>PEO-b-PS (B)</td>
<td>-</td>
<td>2.09</td>
<td>1.08</td>
<td>1.10</td>
<td>20</td>
<td>80</td>
<td>-</td>
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<td>B</td>
<td>2.95</td>
<td>1.12</td>
<td>1.42</td>
<td>15</td>
<td>63</td>
<td>22</td>
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<tr>
<td>PESV-6</td>
<td>B</td>
<td>4.40</td>
<td>1.12</td>
<td>2.29</td>
<td>10</td>
<td>39</td>
<td>51</td>
</tr>
<tr>
<td>PESV-7</td>
<td>B</td>
<td>4.78</td>
<td>1.18</td>
<td>2.67</td>
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<td>34</td>
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<td>5.00</td>
<td>1.23</td>
<td>3.36</td>
<td>7</td>
<td>26</td>
<td>67</td>
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<tr>
<td>PESV-9</td>
<td>B</td>
<td>5.98</td>
<td>1.25</td>
<td>3.70</td>
<td>6</td>
<td>24</td>
<td>70</td>
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<tr>
<td>PEO-b-PS (C)</td>
<td>-</td>
<td>2.69</td>
<td>1.08</td>
<td>2.53</td>
<td>8</td>
<td>82</td>
<td>-</td>
</tr>
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</table>

Bimodal elution peak in GPC curve

(a) Determined by $^1$H NMR. (b) Determined by GPC. (c) Weight fraction of PEO, PS, and P4VP in the copolymer determined by $^1$H NMR spectroscopy technique, respectively.

**Synthesis of PEO-b-PS-b-P4VP Triblock Copolymer**

P4VP is a pH-sensitive polymer which is soluble in water when the pH value is below 4.7 and becomes insoluble when the pH is high (>4.7). Therefore, block copolymer of P4VP could respond to pH values in water solution and self-assemble to form different supramolecular structures [26]. Additionally, the complexing properties of the P4VP, e.g., toward metallic salts, make it act as an interesting multidentate ligand for the preparation of block copolymer/nanoparticle mixtures [35]. Thus, we choose P4VP as the third block. The ATRP of 4VP was accomplished in 2-propanol at 40ºC using PEO-b-PS-Br as the macroinitiator and Me$_6$TREN/CuCl as the catalyst (Scheme I). The polymerization was also carried out at 50ºC. However, it was found that high conversion was reached in a short period of time. In Figure 3, the GPC curve 'a' showed the presence of a shoulder. These might be because at higher temperature the rate of propagation was much higher compared to the rate of equilibrium between dormant and active species. Thus, it was not sufficient to investigate the kinetics...
of polymerization of 4VP at 50°C. While the polymerization rate was moderate and a triblock copolymers PEO-b-PS-b-P4VP with controlled molecular weights and a very narrow distribution was obtained at 40°C (Figure 3, curve c).

Moreover, a mixed halogen system of PEO-b-PS-Br/CuCl had also been used to prepare the triblock copolymers, as halide exchange could control ATRP more efficiently [36]. In our work, the PEO-b-PS-Br/CuBr initiation/catalyst system was also employed to prepare the triblock copolymers with ATRP technology. Curve b in Figure 3 shows a typical GPC curve of the PEO-b-PS-b-P4VP triblock copolymer synthesized by using PEO-b-PS (A) as the macrominitiator and CuBr/Me6TREN complex as the catalyst. As it was observed, the results of triblock copolymer show bimodal elution peak. It implies that the PEO-b-PS-Br/CuBr initiator/catalyst system gave essentially uncontrolled polymerization. Whereas, the GPC curve of triblock copolymer synthesized using PEO-b-PS-Br/CuCl as initiator/catalyst system displayed narrow and unimodal elution peak as shown as curve c in Figure 3. This might be ascribed to the mixed R-Br/CuCl halogen system, which provided faster initiation and slower propagation process to control ATRP more effectively [36].

The influence of the molecular weight of PEO-b-PS macroinitiators, especially the units of PS segments, on the control of ATRP was also investigated. Several PEO-b-PS block copolymers with different molecular weights were prepared (Table 1). It was observed that a better controlled copolymerization was obtained using PEO-b-PS with 1.10×10⁴ g/mol molecular weight as the macronitiator under the ATRP condition, because the molecular weight distribution of the triblock copolymer was very narrow within 1.12-1.25 range. The polymerization can be weakly controlled with the increase in PEO-b-PS molecular weight, namely the increase of the units of PS segments. As shown in Table 1, the values of M_w/M_n range between 1.19 and 1.45 when initiated by PEO-b-PS with 2.11×10⁴ g/mol molecular weight. An uncontrolled ATRP process with bimodal elution peak in GPC curve is obtained when the molecular weight of PEO-b-PS was further increased to 2.53×10⁴ g/mol. This might be ascribed to a poor solubility of PEO-b-PS in the 2-propanol with the increase of PS segment.

Figure 4 is the ¹H NMR spectrum of PEO-b-PS-b-P4VP triblock copolymer. In the ¹H NMR spectrum, the two new peaks, at 6.2-6.6 ppm and 8.2-8.5 ppm appear besides the peaks of PEO and PS segments in the polymer chain. These peaks at 6.2-6.6 and 8.2-8.5 ppm are assigned to the ortho- and meta-protons of pyridine ring of the P4VP block, respectively. These data illustrate the presence of the P4VP block in the
polymer chain. Moreover, the length of the each segment and the composition of the copolymer were also analyzed by \(^1\)H NMR spectroscopy technique.

The molecular weights and molecular weight distributions of triblock copolymers were further investigated by GPC. Figure 5 presents the typical GPC curves of the triblock copolymers PEO-b-PS-b-P4VP (PESV-1, PESV-2, PESV-3, PESV-4) by using PEO-b-PS (A) as a macoinitiator. An increase in molecular weight was observed after the chain extension reaction. For example, the molecular weight of the copolymer increased from 2.28×10\(^4\) g/mol to 7.83×10\(^4\) g/mol. The polydispersity index was low, ranging from 1.08 to 1.45. The polydispersity index of the copolymer was a little higher than that of the macoinitiator, but it was still lower than the theoretical value of 1.5 for the controlled/"living" free radical polymerization. Furthermore, the variation of GPC traces with the evolution of the polymerization in Figure 5 shows clearly the growth of the block copolymers. A small shoulder is observed in the curves of the triblock copolymer at low retention times.

Table 1 presents the molecular weights, molecular weight distributions, and compositions (block lengths and P4VP contents in weight) of all the triblock copolymers and their precursor synthesized in this work. The P4VP block length ranges from 3.20×10\(^3\) g/mol to 2.59×10\(^4\) g/mol, corresponding to 22 to 70 wt% in the triblock copolymers. It must be mentioned that the \(\overline{M}_n\) values determined by GPC of the triblock copolymers are a little higher than those obtained by \(^1\)H NMR which are ascribed to the difference in hydrodynamic properties of the triblock copolymers and the polystyrene standards used in GPC measurements.

In order to investigate "living" characteristics during the polymerization of 4VP initiated by PEO-b-PS (A), a systemic study was performed. Figure 6 represents the linear dependence of ln([M]_0/[M]) on reaction time. It is found that the semi-logarithmic plot of ln([M]_0/[M]) versus reaction time is nearly linear

Figure 5. GPC traces of PEO-Br, PEO-b-PS (A) and its related triblock copolymers PEO-b-PS-b-P4VP (PESV) with various \(\overline{M}_n\) (PESV-1, PESV-2, PESV-3, PESV-4).

Figure 6. First-order kinetic plots for the ATRP of 4VP initiated by PEO-b-PS (A).

Figure 7. Evolution of molecular weight distribution and average molecular weight vs conversion.
which suggests that there is a constant concentration of active species during polymerization and the polymerization reaction is first order with respect to monomer concentration. Figure 7 shows the dependence of the average number molecular weight and polydispersity index versus conversion for the 4VP monomer in 40ºC, respectively. The average molecular weight increases linearly with the increase of monomer conversion, and producing a narrow molecular weight distribution. However, there is a continuous increase in the molecular weight distribution throughout the reaction in agreement with the work of Prez [37] which might be ascribed to the nucleophilic substitution reactions of the halogen end groups by vinylpyridine units [31].

CONCLUSION

The ABC triblock copolymers PEO-b-PS-b-P4VP with different molecular weights were successfully synthesized in a two-step ATRP process. Their well-defined block architectures were confirmed by 1H NMR and GPC studies. The molecular weights of P4VP block ranged from 3.2×10^3 g/mol to more than 2.0×10^4 g/mol in the triblock copolymers, corresponding to 22-70 wt%. All the triblock copolymers synthesized in this work possessed narrow molecular weight distribution ranging from 1.08 to 1.45. The kinetics experiment indicated that the ATRP of 4VP was "living"/controlled.

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