Synthesis of a Novel Block Copolymer Poly(ethylene oxide)-block-poly(4-vinylpyridine) by Combination of Anionic Ring-Opening and Controllable Free-Radical Polymerization

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ABSTRACT: The block copolymer poly(ethylene oxide)-b-poly(4-vinylpyridine) was synthesized by a combination of living anionic ring-opening polymerization and a controllable radical mechanism. The poly(ethylene oxide) prepolymer with the 2,2,6,6-tetramethylpiperidinyl-1-oxy end group (PEOT) was first obtained by anionic ring-opening polymerization of ethylene oxide with sodium 4-oxy-2,2,6,6-tetramethylpiperidinyl-1-oxy as the initiator in a homogeneous process. In the polymerization UV and electron spin resonance spectroscopy determined the 2,2,6,6-tetramethylpiperidinyl-1-oxy moiety was left intact. The copolymers were then obtained by radical polymerization of 4-vinylpyridine in the presence of PEOT. The polymerization showed a controllable radical mechanism. The desired block copolymers were characterized by gel permeation chromatography, Fourier transform infrared, and NMR spectroscopy in detail. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 4404–4409, 2002

Keywords: ethylene oxide; 4-vinylpyridine; block copolymers; radical polymerization; anionic polymerization; controllability

INTRODUCTION

Polymer scientists have a great interest to prepare polymer materials with precisely controlled molecular weight, narrow polydispersities, and well-defined architectures. Block copolymer attracts special attention for its unique properties and wide applications, which are synthesized by anionic, cationic, or step-growth polymerization traditionally.1–3 However, these polymerization methods are limited strictly with rigid conditions and only a few available monomers. Thus, the combination of several different polymerization mechanisms has become a preferred strategy, which is easier to operate and enlarge the range of monomers by transforming the active species of the block segment’s end group or with the multifunctional initiators.4–7 In this way, many of block copolymers are prepared such as poly[(ethylene oxide)-block-poly(styrene)] (PEO-b-PS),8,9 poly(tetrahydrofuran)-block-poly(styrene) (PTHF-b-PS),10 poly(4-vinylpyridine)-block-poly(N,N-dimethylacrylamide) [P(4-VP)-b-PDMAA],11 and so forth.

In 1993, Georges et al.12 first reported PS with narrow-molecular-weight distribution was prepared by a mixture of benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as an initiating system. The polymerization process showed a “living,” or pseudoliving free-radical mechanism. However, the chemistry had been considered unsuccessful in making copolymers containing non-styrene segments. Recently, 4-VP was investigated, fulfilling the typical TEMPO-mediated radical polymerization.13
In our study, PEO was prepared first with sodium 4-oxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPONa) as an initiator by anionic ring-opening polymerization of ethylene oxide (EO), and then the PEO-b-P4-VP was obtained by polymerization of 4-VP in a controllable radical mechanism. PEO is a good ion-conducting polymer that was found by Wright\textsuperscript{14} in 1975, whereas P4-VP can also be used as this kind of material. Therefore, we wanted to know whether the block copolymer by them may have a better property. Additional study is in process.

**EXPERIMENTAL**

**Materials**

EO was dried by calcium hydride for 1 week and then distilled before use. Diethylene glycol dimethyl ether was distilled under reduced pressure (34 °C/3.6 mmHg) after being dried by calcium hydride for 7 days. BPO was recrystallized from ethanol twice. 4-Hydroxyl-TEMPO was purified by recrystallization with hexane as a solvent. 4-VP was distilled under reduced pressure (58–61 °C/6 mmHg) to remove the stabilizer. All other reagents were purified by common purification procedures.

**Preparation of TEMPONa**

About 5.17 g (0.03 mol) of 4-hydroxy-TEMPO were dissolved in 200 mL of dry diethylene glycol dimethyl ether. Approximately 0.83 g (0.036 mol) of sodium with fresh surface were added in nitrogen atmosphere. The mixture was stirred at room temperature for 3 days and then filtrated. A solution of TEMPONa was obtained, and its concentration was $8.82 \times 10^{-2}$ mol/L titrated with standard HCl.

**Preparation of the Prepolymer of Polyethylene Oxide with TEMPO End (PEO\textsubscript{r})**

To a 20-mL solution of TEMPONa ($8.82 \times 10^{-2}$ mol/L), 10 mL of EO were added under a nitrogen atmosphere in a 150-mL ampule. The mixture was sealed and then heated at 60 °C for 24 h. The polymerization reaction was terminated with 2 mL of methanol. The prepolymer PEO\textsubscript{r} could be purified by a procedure of dissolution/precipitation with chloroform/diethyl ether.

**Table 1. Data of PEO\textsubscript{r} with Different Molecular Weights**

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>$M_n$ ($\times 10^3$)</th>
<th>$M_w/M_n$</th>
<th>Conversion of EO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO\textsubscript{r-1}</td>
<td>4.2</td>
<td>1.09</td>
<td>91</td>
</tr>
<tr>
<td>PEO\textsubscript{r-2}</td>
<td>5.8</td>
<td>1.07</td>
<td>87</td>
</tr>
</tbody>
</table>

**Figure 1.** ESR spectrum of PEO\textsubscript{r-1} in benzene solution (10 mg/mL) at room temperature.

**Figure 2.** UV spectrum of PEO\textsubscript{r} in H$_2$O solution at room temperature.
Preparation of the Block Copolymer

Typically, a 100-mL ampule was charged with 0.02 mmol PEOT, 1 mL of 4-VP, and 0.015 mmol of BPO in dimethylformamide (DMF) solution. The mixture was sealed and degassed by three freeze-pump-thaw cycles. The vessel was immersed in a preheated oil bath at 90 °C for 3 h and then heated to 130 °C, which was kept throughout the reaction. The resulting polymer was obtained by precipitation with diethyl ether and then extracted for 40 h by ethyl acetate to remove the unreacted PEOT.

Measurements

The molecular weight and molecular weight distribution were determined by a polyethylene series 200 gel permeation chromatograph (GPC) equipped with a refractive-index detector, DMF as both the solvent and eluent, and standard PS as the calibration. Measurement was performed at 70 °C. Electron spin resonance (ESR) spectra were recorded on a Bruker ER200D-SRC spectrometer. IR spectra were obtained on a Magna-550 Fourier transform infrared (FTIR) spectrometer. 1H NMR spectra were recorded on a DMX 500-MHz spectrometer with tetramethylsilane as the internal standard and chloroform-d (CDCl₃) as the solvent. UV spectra were taken on a 756 MC UV–visible spectrophotometer (Shanghai Third Analytical Instrument Factory, China).

RESULTS AND DISCUSSION

Characterization of the PEO₇ Prepolymer

It has been reported that EO can be polymerized by TEMPONa in tetrahydrofuran (THF) solution. However, the initiator was not well dissolved; therefore, the polymerization was a heterogeneous process that was not easy to control. We found that if diethylene glycol dimethyl ether was used as the solvent instead of THF, this process could be carried out in a homogeneous phase. All the data of the resulting polymers, as Table 1 indicates, show a unimodal GPC trace with a narrow-molecular-weight distribution (less than 1.1). To demonstrate the nitroxyl radical was not destroyed during the anionic polymerization, the ESR spectra (Fig. 1) were measured in which all the prepolymers exhibited three sharp signals, and the $g$ values ($g = 2.0063$) and hyperfine coupling constant $A$ ($A = 15.4$ G) were quite consistent with the standard 4-hydroxy-TEMPO ($g = 2.0070, A = 15.88$ G). In the UV spectrum of prepolymers (Fig. 2), an absorption at 430 nm attributed to the nitroxyl radical was observed.
Characterization of the Block Copolymer PEO-\textit{b}-P(4-VP)

The radical polymerization of 4-VP was carried out at 130 °C with BPO as the initiator in the presence of PEO\textsubscript{T} with a TEMPO moiety at the chain end (see Scheme 1). As it is well known for the polymerization of monomers in the presence of TEMPO, it is better to conduct the polymerization in the bulk conditions to obtain the product with high molecular weight. However, in our experiment in the bulk conditions the homopolymerization of 4-VP were unavoidable. In this case the PEO\textsubscript{T} chain diffused rather low because of the high viscosity, which worsened with the increasing monomer conversion. To decrease the homopolymer of 4-VP, the solution polymerization of 4-VP in the presence of PEO\textsubscript{T} with DMF as a solvent was conducted. Figure 3 illustrates the GPC trace of the prepolymer PEO\textsubscript{T} and the resulting block copolymer in which no homopolymer of 4-VP was discovered. Thus, it clearly indicates that in solution polymerization the block copolymer of PEO-\textit{b}-P(4-VP) in the presence of PEO\textsubscript{T} could be prepared without any homopolymer of 4-VP.

The \textsuperscript{1}H NMR spectrum of the final copolymer is depicted in Figure 4. The sharp signal at 3.6 ppm is due to the methylene protons in the —CH\textsubscript{2}CH\textsubscript{2}O unit of the PEO block. The signals of —CH\textsubscript{2} and —CH in the P(4-VP) block overlap at 1.5, 1.8, and 2.3 ppm, which is corresponds to the rr, mr, and mm of triads\textsuperscript{16,17}. Those at 6.5 and 8.3 ppm could be assigned to the protons at the pyridine ring. The signal at 0.9 ppm was assigned to the methyl protons in the 4-VP unit.

Figure 4. \textsuperscript{1}HNMR spectrum of the diblock copolymer obtained in CDCl\textsubscript{3}. Polymerization conditions: [PEO\textsubscript{T-1}] = 2.0 \times 10^{-2} \text{ mol/L}, [PEO\textsubscript{T-1}]/[BPO] = 1.3, and \textit{T} = 130 °C in DMF.

Figure 5. Dependence of \textit{M}_n and \textit{M}_w/\textit{M}_n on the conversion of 4-VP in DMF in the presence of PEO\textsubscript{T-1}, [PEO\textsubscript{T}] = 2.0 \times 10^{-2} \text{ mol/L}, [PEO\textsubscript{T}]/[BPO] = 1.3, and \textit{T} = 130 °C.
the methyl protons in the TEMPO moiety. The formation of the copolymer could also be confirmed by the IR spectrum. The sample exhibited absorption at 2929, 1597, and 1415 cm$^{-1}$, which could be assigned to the 4-VP block. Also, the absorption at 2853 and 1105 cm$^{-1}$ was due to the PEO block. The relationship of monomer conversion with molecular weight and molecular weight distribution is portrayed in Figure 5 in which the molecular weight is in proportion to the conversion, and in all cases the molecular weight distribution of block copolymer was less than 1.3. Figure 6 displays the first-order relationship of ln([M$_0$]/[M]) with polymerization time ([M$_0$] and [M] stand for the original and monomer concentration now, respectively). Therefore, in our system the block copolymerization of 4-VP in the presence of PEO$_T$ was conducted under a controllable radical polymerization mechanism.

**Table 2.** Effect of PEO$_T$ Molecular Weight on the Polymerization in DMF$^a$

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>$M_n$ $\times 10^4$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO$_{T,1}$</td>
<td>12</td>
<td>7.8</td>
<td>2.5</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>23.9</td>
<td>3.8</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>39.8</td>
<td>6.2</td>
<td>1.25</td>
</tr>
<tr>
<td>PEO$_{T,2}$</td>
<td>12</td>
<td>8.4</td>
<td>3.2</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>25.5</td>
<td>4.4</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>47.5</td>
<td>6.5</td>
<td>1.51</td>
</tr>
</tbody>
</table>

$^a$ [PEOT] = 2.0 $\times$ 10$^{-2}$ mol/L, 1 mL 4-VP, [PEOT]/[BPO] = 1.3, and $T$ = 130 °C.

**Table 3.** Effect of Concentration of PEO$_{T,1}$ on the Copolymerization; Polymerization of 4-VP in DMF$^a$

<table>
<thead>
<tr>
<th>Concentration of PEO$_{T,1}$ ($\times 10^{-2}$ mol/L)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>$M_n$ $\times 10^4$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>12</td>
<td>18.1</td>
<td>3.9</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>33.7</td>
<td>4.5</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>51.0</td>
<td>7.1</td>
<td>1.47</td>
</tr>
<tr>
<td>2.0</td>
<td>12</td>
<td>7.8</td>
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<td>1.21</td>
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<td>23.9</td>
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<tr>
<td></td>
<td>48</td>
<td>39.8</td>
<td>6.2</td>
<td>1.25</td>
</tr>
</tbody>
</table>

$^a$ 1 mL 4-VP, [PEOT]/[BPO] = 1.3, $T$ = 130 °C.

**Effect of Molecular Weight and Concentration of PEO$_T$ on Copolymerization**

Table 2 shows the effect of the PEO$_T$ molecular weight on the copolymerization. When the PEO$_T$ with lower molecular weight was used, the molecular weight distribution of the copolymers was rather narrow and conversion was lower. It was suggested that in the conditions of the same molar concentration, PEO$_T$ with lower molecular weight showed the relatively higher diffusion ability as well as lower system viscosity, and the dormants were easy to form by coupling of propagating species with TEMPO; therefore, the left concentration of propagating species was low leading to the low polymerization rate, low molecular weight, and low conversion.

Table 3 lists the results of the polymerization of 4-VP in the presence of PEO$_{T,1}$ with different concentrations. For the same kind of PEO$_T$, the higher the PEO$_T$ concentration, the higher the TEMPO concentration attached in the end of PEO. Thus the PEO$_T$ with higher concentration can exert better control on the polymerization of 4-VP by reversible termination of TEMPO with propagating radical species.$^8$ In this case the dormant amount is high; therefore, the left concentration of propagating species is also low leading to the low polymerization rate, low molecular weight, and low conversion.

**REFERENCES AND NOTES**