Grafting of poly(ethylene oxide) with Schiff’s base end group onto chloromethylated polystyrene via Decker-Forster reaction

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SUMMARY: Amphiphilic graft copolymer of polystyrene (PS) as backbone and poly(ethylene oxide) (PEO) as branch chain was prepared by Decker-Forster reaction. PEO with Schiff’s base end group (PEO₁) was obtained by ring-opening polymerization of ethylene oxide (EO) initiated with protected potassium aminoethoxide, and then alkylated with chloromethylated polystyrene (c-PS). A graft copolymer with high grafting efficiency was derived by hydrolysis of the above-mentioned product.

Introduction

Recently much interest has been centered on amphiphilic graft copolymers₁,₂ due to their successful application as surfactants and stabilizers for emulsion or dispersion polymerization, as surface modifiers for plastics and compatibilizer for polymer blends. Among water-soluble polymers, poly(ethylene oxide) is chosen as hydrophilic chain owing to the easy preparation of samples of well-defined molecular weight and of low polydispersity.

Grafting PEO onto PS backbones has been attempted by various methods. Some of them proceed by carbanionic initiation, using a backbone fitted with organometallic sites as polyfunctional initiator for the polymerization of EO monomer³. This type of procedure does not allow a precise characterization of the obtained graft copolymer. The number of carbanionic sites on the backbone, which is not easily accessible in most cases, may be higher than the number of grafts formed because of incomplete initiation.

The graft reaction could also be conducted by anionic deactivation of a “living” monofunctional PEO onto a partly chloromethylated PS backbone⁴. However the strict conditions might be very difficult to be satisfied in practical uses.

In organic chemistry, it is a common procedure to prepare a secondary amine by alkylation of a Schiff’s base produced by condensation of primary amine and aldehyde using halogenated alkane as alkylating agent and then hydrolysis⁵, that is called a Decker-Forster reaction and can be carried out under ordinary conditions. It was reported, however, that the alkylation ability is weakened with increasing carbon chain length of the halogenated alkane.

In order to look for a simple and effective method to prepare the amphiphilic graft copolymer we try to use the Decker-Forster reaction in this system. In our experiments, it was found that the Decker-Forster reaction can be performed successfully in grafting of PEO with Schiff’s base end group onto chloromethylated PS, the graft efficiency of PEO₁, being dependent on the molecular weight of PEO₁, and c-PS, degree of chloromethylation of PS, reaction time and temperature. This new grafting method has a universal significance for other graft copolymerization systems.

Experimental part

Materials
Ethylene oxide (EO) (Shanghai Gaoqiao Chemical Factory, China) and styrene (St) (Shanghai First Reagent Factory, China) were dried with calcium hydride and distilled under N₂ before use. Benzaldehyde and 2-aminoethanol were purified by distillation under reduced pressure, the fractions of 96 °C/5 mmHg for benzaldehyde and 90 °C/10 mmHg for aminoethanol were collected. 1,3,5-Trioxane was obtained from Shanghai Laize Fine Chemicals Institute and used after recrystallization from diethyl ether. Trimethylchlorosilane (Shanghai Qingpu Synthetic Reagent Factory) was distilled at 57 °C before use. Stannic chloride was obtained by dehydration of SnCl₄·5H₂O (Rugao Chemical Reagent Factory, Jiangsu Province, China) and distillation at 114 °C. 2,2’-Azoisobutyronitrile (AIBN) (Shanghai Feida Limited Company) was purified by recrystallization with absolute ethanol, m.p.: 102 °C. All other solvents were purified by common drying and distillation procedures.

Preparation of PS backbone
PS was prepared by ordinary anionic polymerization using butyllithium as initiator. The polymerization was carried out at 40 °C for one hour in benzene, the total solid content of the system was about 20%. The product was precipitated in methanol and dried at 50 °C in vacuum.
Chloromethylation of PS

This reaction was carried out mainly according to the report by Itsuno, but some changes were done by us. The dried PS (1.0 g) was dissolved in 25 mL chloroform containing 3.8 mL of chlorotrimethylsilane and 0.9 g of 1,3,5-trioxane, then 0.5 mL of stannic chloride was added dropwise at 0°C, the mixture was stirred for 30 min at 0°C and then for 2 h at room temperature. The c-PS was precipitated in methanol and washed with cold water twice, then purified by dissolution and precipitation procedure with chloroform/methanol. The chloromethylation degree of PS was calculated from 1H NMR spectra.

Preparation of PEO with Schiff’s base end group (PEO<s><s><sub>e</sub></s><s></s>)

This kind of PEO was obtained according to a procedure described earlier, here we only outline it briefly as follows:

\[
\text{H}_2\text{NCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{K}} \text{CH=NCH}_2\text{CH}_2\text{O}^- \xrightarrow{2\text{CH}_3\text{OH}} \text{CH=NCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_\text{m}\text{OH}
\]

**Grafting of PEO<sub>e</sub> onto c-PS**

To a 250 mL three-neck flask fitted with thermometer, magnetic stirring and condenser, 3.0 g of PEO<sub>e</sub> (1.5 × 10<sup>-3</sup> mol), 0.6 g of c-PS (1.0 × 10<sup>-3</sup> mol) and 90 mL xylene were added sequentially. It was allowed to react about 24 h at 100°C, then hydrolyzed about 1 h by addition of 1 mL water. The chlorine ions were detected as a white precipitate by addition of silver nitrate aqueous solution into the hydrolyzed system. The graft product was precipitated in petroleum ether and then purified by extraction with diethyl ether to remove the unreacted c-PS and with methanol to remove the remained PEO<sub>e</sub>.

**Instruments**

IR spectra were recorded with a Nicolet Magna-550 FTIR spectrometer. 1H NMR was scanned with a Bruker MSL-300 NMR spectrometer with tetramethylsilane as internal standard and CDCl<sub>3</sub> as solvent. The molecular weight and molecular weight distribution were measured using a Shimadzu LC-3A gel permeation chromatograph (GPC) equipped with a microcomputer and a series of columns HSG-30 and HSG-60 from Du Pont. The conditions were as follows: injection volume: 0.1 mL (concentration of sample: 0.1 g/mL), eluent: tetrahydrofuran, flow rate: 1 mL/min, pump pressure: 60 kg/cm<sup>2</sup> (5.98 × 10<sup>6</sup> Pa), detecting wavelength: 254 nm. The GPC was calibrated with standard PS samples.

**Results and discussion**

Effect of molecular weight of c-PS and PEO<sub>e</sub> on the graft ratio

The grafting efficiency of PEO<sub>e</sub> was measured by NMR spectra. Fig. 1 shows the spectra of c-PS before (A) and after grafting of PEO<sub>e</sub> (B). The peak assignments are as follows: δ = 1.0–2.3 (−CH−CH<sub>2</sub>−), 4.5 (−CH<sub>2</sub>Cl), 6.4–6.9 (m-protons of benzene ring) and 6.9–7.4 ppm (o- and p-protons of benzene ring) for PS, and δ = 3.6–3.7 ppm (−CH<sub>2</sub>CH<sub>2</sub>O−) for PEO. We used the proton peak area of −CH<sub>2</sub>Cl at 4.5 ppm as the measurement of PEO graft efficiency, and A<sub>1</sub> and A<sub>2</sub> are the peak areas of −CH<sub>2</sub>Cl before and after grafting, so the graft efficiency could be derived from the following equation:

\[
\text{graft ratio of PEO (in %)} = \frac{A_1 - A_2}{A_1} \times 100\%
\]

Tab. 1 shows the dependence of graft ratio on the reaction conditions. The long carbon chain of c-PS did not inhibit the alkylation of PEO<sub>e</sub>. The graft ratio tends to increase with decreasing molecular weight of c-PS and PEO<sub>e</sub>, and to decrease with increasing content of chloromethylated PS in PS although the average number of grafts in the PS backbone is still rising in the highly chloromethylated PS.

Effect of reaction time and temperature on the graft ratio

The graft ratio is sensitive to temperature; Fig. 2 illustrates that the graft ratio increases with rising temperature. It may be attributed to the drop of the system viscos-
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...ity at higher temperature, which favors the diffusion and reaction between c-PS and PEO, macromolecules.

The effect of reaction time on the graft ratio is complicated. The graft ratio increases with the reaction time at first, and then decreases as shown in Fig. 3. The side-reaction shown in the following reaction scheme might be the direct cause for this decrease:

Fig. 1. NMR spectra of c-PS before (A) and after grafting of PEO, (B)

Fig. 2. Effect of reaction temperature on the graft ratio (reaction time: 24 h; solvent: xylene; $M_n$ of c-PS: $8.6 \times 10^3$; degree of chloromethylation: 20%; $M_n$ of PEO: $8.7 \times 10^3$)

Fig. 3. Effect of reaction time on the graft ratio (reaction temperature: 100 °C; solvent: xylene; $M_n$ of c-PS: $8.6 \times 10^3$; degree of chloromethylation: 20%; $M_n$ of PEO: $8.7 \times 10^3$)
Decker-Forster reaction was performed successfully in the grafting of PEO with Schiff’s base end group onto chloromethylated PS. The grafting efficiency of PEO, is dependent on the molecular weight of PEO, and c-PS, chloromethylation degree of PS, reaction time and temperature. This new grafting method has a universal significance for other graft copolymerization systems.

**Conclusion**

Decker-Forster reaction was performed successfully in the grafting of PEO with Schiff’s base end group onto chloromethylated PS. The grafting efficiency of PEO, is dependent on the molecular weight of PEO, and c-PS, chloromethylation degree of PS, reaction time and temperature. This new grafting method has a universal significance for other graft copolymerization systems.

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Tab. 1. Structural characterization of graft copolymer (reaction time: 24 h, temperature: 100 °C, solvent: xylene, $\overline{M}_w/\overline{M}_n$ for graft copolymers: 2.5–3.0)

<table>
<thead>
<tr>
<th>Copolymer sample</th>
<th>$\overline{M}_w \times 10^4$ (PS)</th>
<th>$-\text{CH}_2\text{Cl}$ a)</th>
<th>$\overline{M}_w \times 10^4$ (PEO) b)</th>
<th>Graft ratio c) in %</th>
<th>Average number of grafts per PS chain</th>
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<tbody>
<tr>
<td>1</td>
<td>0.86</td>
<td>20</td>
<td>0.87</td>
<td>58</td>
<td>11.6</td>
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<tr>
<td>2</td>
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<td>20</td>
<td>2.00</td>
<td>50</td>
<td>10.0</td>
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<tr>
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<td>25</td>
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<td>51</td>
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<tr>
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<td>38</td>
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</tr>
<tr>
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<td>3.00</td>
<td>20</td>
<td>0.87</td>
<td>54</td>
<td>10.8</td>
</tr>
</tbody>
</table>

a) Average fraction (in %) of chloromethylated sites in PS backbone; $\overline{M}_w/\overline{M}_n$ for PS: 1.17–1.21.

b) $\overline{M}_w/\overline{M}_n$ for PEO: 1.02–1.04.

c) Data from NMR.