Copolymerization of the Macromonomer Poly(ethylene oxide) with Styryl End Group and Styrene in the Presence of Poly(ε-caprolactone) with 2,2,6,6-Tetramethylpiperidinyl-1-oxy End Group by Controlled Radical Mechanism

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ABSTRACT: A copolymerization of macromonomer poly(ethylene oxide) (PEO) with a styryl end group (PEOS) and styrene was successfully carried out in the presence of poly(ε-caprolactone) (PCL) with 2,2,6,6-tetramethylpiperidinyl-1-oxy end group (PCLT). The resulting copolymer showed a narrower molecular weight distribution and controlled molecular weight. The effect of the molecular weight and concentration of PCLT and PEOS on the copolymerization are discussed. The purity of PEOS exerted a significant effect on the copolymerization; when the diol contents of PEO macromonomer were greater than 1%, the crosslinking product was found. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 2093–2099, 2004

Keywords: macromonomers; poly(ethylene oxide); styrene; poly(ε-caprolactone); radical polymerization; graft copolymers

INTRODUCTION

Molecular design of block, graft, and star copolymers with well-defined architecture has attracted much interest in polymer chemistry.1–4 These desired copolymers can be constituted by blocks with distinct differences in nature, such as flexible/rigid, crystalline/amorphous, hydrophilic/hydrophobic,5–7 and therefore have special properties and performance.

Because the controlled radical polymerization mediated by a stable radical such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) was accepted as a useful means to synthesize some well-defined copolymers with special architecture, many block and graft copolymers with different structures were developed. Stehling et al.8 reported the synthesis of polypropylene-graft-poly-styrene (PS) by a combination of metalallocene and controlled radical polymerization in the presence of TEMPO. In our previous study,9 TEMPO was introduced onto polymeric backbone of poly(methyl methacrylate-co-N,N-dimethylaminoethyl methacrylate [P(MMA-co-DAMA)]) to obtain a macro-initiator, and then a graft copolymer was successfully synthesized by copolymerization of styrene (St) by initiation of P(MMA-co-DAMA) macroinitiator.

In the preparation of polymeric hollow nanospheres, block copolymers have played very significant roles,10 especially the biodegraded seg-
ment-containing copolymers as poly(ε-caprolactone) (PCL), by which the “core” could be removed easily with enzyme after crosslinking of shell. To obtain the amphiphilic copolymer with biodegraded segment, PCL-b-(PS-g-PEO) (shown in Scheme 1) was prepared by copolymerization of poly(ethylene oxide) (PEO) with styryl end group (PEOS) and St in the presence of PCL with TEMPO end group (PCLT). This contribution focuses on the preparation of this new copolymer and the effect of copolymerization conditions on the copolymerization.

EXPERIMENTAL

Materials

Aluminum triisopropoxide was distilled in vacuo (10⁻² mmHg), dissolved in dry toluene, and then stored in −12 °C according to Duda’s method. ε-Caprolactone, St, and ethylene oxide (EO) were dried over CaH₂ for 24 h and then were distilled under reduced pressure before use. 4-Hydroxyl-TEMPO was purified by recrystallization with hexane. Benzoyl peroxide (BPO) was recrystallized from ethanol twice before use. 4-Chloromethylstyrene was distilled under reduced pressure to remove the stabilizer. All other reagents were purified by common purification procedures.

Preparation of the Prepolymer of PCL with TEMPO End (PCLT)

To a solution of 4-hydroxy-TEMPO (62 mg, 0.36 mmol) in 10 mL of toluene, 1 mL of a toluene solution of aluminum triisopropoxide (0.12 mol/L), 30 mL of dry toluene, and a definite amount of ε-caprolactone were added under a nitrogen atmosphere. The polymerization was kept at 25 °C for a given time and then was stopped by excess HCl aqueous solution (2 mol/L). The prepolymer PCLT was obtained by precipitation with hexane and then was purified by dissolution/precipitation with chloroform/ethanol twice.

Synthesis and Purification of Monomethoxy(poly(ethylene glycol)) (MPEG)

The preparation of MPEG with different molecular weight was carried out with sodium monomethoxyethylene oxide as an initiator. The typical synthesis procedure was as follows. Three hundred milliliters of dried tetrahydrofuran (THF), 4.7 mL of monomethoxyethylene oxide, and 1.4 g of sodium with fresh surface were introduced into a 500-mL, three-necked bottle under nitrogen and then were purged for 10 min. The mixture was stirred at 60 °C for 3 days and was filtrated. A solution of sodium monomethoxyethylene oxide was obtained, and the concentration was determined by titration with standard HCl (0.10 mol/L).

Then, to a 100-mL sealed, degassed ampule, 25 mL of sodium monomethoxyethylene oxide with the concentration of 0.2 mol/L and 10 mL of EO were added by syringe. The polymerization was conducted at 60 °C for 24 h and was terminated by 1 mL of methanol. The crude product was precipitated with ethyl ether and was purified twice by a dissolution/precipitation procedure with dichloromethane/ether. The MPEGs were purified by crosslinking polysulfone film with definite pore size (manufactured by Shanghai Institute of Nuclear Research, Chinese Academy of Sciences) to remove the poly(ethylene glycol) (PEG) with hydroxyl groups at both ends (diol).
Preparation of the Macromonomer PEO-St (PEOS)

The macromonomer of PEO with styryl end group (PEOS) was prepared by the reaction of MPEG with chloromethylstyrene in the presence of NaH in THF in the literature and was purified by dissociation/precipitation with dichloromethane/ether. The yield of PEOS was about 78% by UV.

Copolymerization of PEO with St in the Presence of PCLT

A 100-mL ampule was charged with 1 mL of St, 1.4 mg of BPO, a definite amount of PCLT and PEOS, and 3 mL of p-xylene and was then sealed and degassed by three cycles of freeze-pump-thaw. The vessel was immersed in a preheated oil bath at 90 °C for 3 h, heated to 130 °C, and kept at this temperature throughout the reaction. The polymerization was quenched in liquid nitrogen after a given time. The resulting polymer was obtained by precipitation with petroleum ether and then purified by successive extraction by cold water and cyclohexane to remove the unreacted PEO-St as well as PCLT and possible St homopolymer.

Measurements

1H NMR spectra were recorded on a DMX 500-MHz spectrometer with tetramethylsilane as the internal standard and CDCl3 as the solvent. Gel permeation chromatography (GPC) was performed on an HP1100, for PCLT [columns: 79911GP-MXC, 79911GP-502 (Eligent)], THF as solvent and eluent, and monodistributed polystyrene as the calibration standard with a flow rate of 1.0 mL/min; for PEO [columns, G6,000 PW(XL), G3,000 PW(XL)], distilled water as solvent and eluent, and monodistributed PEO as the calibration standard with a flow rate of 1.0 mL/min. UV spectra were taken on a 756 MC ultraviolet–visible light spectrophotometer (Shanghai Third Analytical Instrument Factory, China). IR spectra were obtained on a Magna-550 Fourier transform infrared spectrometer.

RESULTS AND DISCUSSION

Effect of Impurity of MPEG on the Graft Copolymerization

The graft copolymerization was conducted in the bulk condition to obtain the copolymer with high molecular weight. However, the unsolvable products came into being when the monomer conversion was over 30%. Additional research revealed that there is about 1–10% PEG with a hydroxyl group at both ends (diol) in MPEG, whether it has been prepared by the researchers or purchased from other companies; Table 1 lists the corresponding data. Thus, PEG with styryl at both ends should be present when MPEG reacts with 4-(chloromethyl)styrene. PEG acted as a crosslinking agent in the copolymerization according to Scheme 2. To eliminate the crosslinking phenomena, MPEG was purified with polysulfone film with definite pore size to remove the diol, and then the copolymerization was conducted successfully in p-xylene.

Characterization of Copolymer

Figure 1 depicts the 1H NMR spectra of the graft polymer. The signals from 0.9 to 2.3 ppm were attributed to the methine and methylene protons, and the signals from 6.4 to 7.2 ppm were attributed to benzene ring protons in the PS block. The signals at 3.6 ppm were assigned to —OCH2CH2 protons in the PEO block, and the signals at 2.4 ppm for —CH2— and 4.1 ppm for —COOCH2— were assigned to protons in the PCL block. The formation of the copolymer could also be confirmed by IR; the absorptions at 1600, 758, and 700 cm−1 were assigned to the PS block. The ab-
sorptions at 1112 and 1029 cm\(^{-1}\) were assigned to the PEO block, and at 1734 cm\(^{-1}\) the absorption was assigned to carbonyl groups in the PCL block.

**Controllability of Copolymerization**

Table 2 lists the data of the copolymerization of PEO\(_8\) and St in the presence of the PCL\(_T\). In all cases, the molecular weight of the copolymer increased with polymerization time and the polydispersity \((M_w/M_n)\) was around 1.4. Figure 2(a) is a plot of the molecular weight versus conversion and (b) is the first-order relationship of \(\ln([M_0]/[M])\) with polymerization time (where \([M_0]\) is the initial monomer concentration and \([M]\) is the monomer concentration at a given time). Therefore, in our system

![Scheme 2](image)

**Figure 1.** \(^1\)H NMR spectrum of graft copolymer, CDCl\(_3\) as solvent. Polymerization conditions: 1 mL of St, [PEO-St]/[St] = 1/50, [PCL\(_T\)]/[BPO] = 1.3, 130 °C.
the copolymerization was completed on a controlled radical polymerization mechanism.

**Effect of Molecular Weight of PCLₜ and PEOₜ on Copolymerization**

From the data listed in Table 2, the molecular weight of PCLₜ and PEOₜ exerted a remarkable effect on the copolymerization. In the same conditions, when PCLₜ and PEOₜ with high molecular weight were used, the monomer conversion and the average side-chain number of PEOₜ were lower than that of PCLₜ and PEOₜ with low molecular weight. It was suggested that in the conditions of the same molar concentration, PCLₜ and PEOₜ with higher molecular weight showed relatively

**Table 2. Copolymerization Data of the PEO–St with St in the Presence of PCLₜ**

<table>
<thead>
<tr>
<th>PCLₜ (g/mol)</th>
<th>PEOₜ (g/mol)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>(M_n) (g/mol)</th>
<th>(M_w/M_n)</th>
<th>(N_g)^b</th>
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</table>

[\(PCLₜ\)] = 0.02 mmol, \(M_w/M_n\) ranged from 1.17 to 1.20; \([PCLₜ]/[BPO]\) = 1.3:1, \(M_w/M_n\) of PEOₜ ranged from 1.05 to 1.09, \([\text{St}]/[\text{PEOₜ}]\) = 50:1.

\(^a\) Calculated by the gravimetric method.

\(^b\) Calculated by \(N_g = (M_n - M_{PCL})/W_g/M_{PEO}\), where \(M_n\), \(M_{PCL}\), and \(M_p\) stand for the molecular weight of copolymer, PCLₜ, and PEOₜ; \(W_g\) is the weight composition of PEOₜ in the copolymer; and \(N_g\) is the average PEOₜ chain number.

Figure 2. (a) \(M_w\) as a function of conversion and (b) linear plot of \(\ln([M_0]/[M])\) as a function of polymerization time. Polymerization conditions: PEO-St (\(M_n = 3000\)), 1 mL of St, [PEO-St]/[St] = 1/50, [PCLₜ]/[BPO] = 1.3, 130 °C.
lower diffusion ability as well as higher system viscosity, and it caused the low polymerization rate, low conversion, and low side-chain number.

**Effect of Concentration of PCLT on Copolymerization**

The concentration of PCLT also affected the controllability of the copolymerization. When the concentration of PCLT increased (as shown in Table 3), the $M_w/M_n$ of the copolymer was narrower and the molecular weight decreased. In the TEMPO-mediated polymerization, there was equilibrium between the propagation radical and the dormant compound formed by coupling of TEMPO with the former. When the concentration of PCLT increased, the equilibrium shifted to the formation of dormant compounds, so the addition reaction of propagation radical with PEOS and St was restricted, leading to the narrow distribution. As for the molecular weight of copolymer in this case, which could be expressed by the formulas $X_n = [M]/[\text{dormant}]$ (where $X_n$ is the number polymerization degree, $[M]$ is the total concentration of PEOS and St, and $[\text{dormant}]$ is the dormant compound concentration), it is obvious that when the dormant compound concentration increased, the molecular weight of copolymer decreased. However, if the concentration of PCLT is beyond 0.1 mol, the $M_w/M_n$ of copolymer is wider and the molecular weight larger. It may attributed to the PCLT chain entanglements in high concentration leading to envelopment of TEMPO of PCLT.

**CONCLUSIONS**

A new graft copolymer (PCL-PS-g-PEO) was prepared by copolymerization between macromonomer PEOS with a styryl end group and St with PCL with TEMPO end group as a macronitiator. The copolymerization was controllable, and the resulting copolymer showed a narrow molecular weight distribution and controlled molecular weight. The molecular weights of PCL and PEO and the concentration of PCL significantly affected the copolymerization.

**REFERENCES AND NOTES**