

Nanoporous Poly(ether sulfone) Derived from a Block Polymer Precursor

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Abstract

We report a synthetic route to polylactide-*b*-poly(ether sulfone)-*b*-polylactide (PLA-*b*-PES-*b*-PLA) and nanoporous PES derived from the block polymer precursor. PLA-*b*-PES-*b*-PLAs were synthesized by combination of condensation polymerization and ring opening transesterification polymerization. Self-assembly behaviors of the resulting PLA-*b*-PES-*b*-PLAs were investigated with differential scanning calorimetry (DSC) and small angle X-ray scattering (SAXS) that indicated microphase separation between PLA and PES microdomains. PLA could be selectively removed from the PLA-*b*-PES-*b*-PLA under a basic condition resulting in nanoporous PES as evidenced by SAXS and scanning electron microscopy (SEM), suggesting its potential as an ultrafiltration membrane.

Introduction

Self-assembly of block polymers consisting of a sacrificial block can produce well-defined nanoporous polymers with robust control over pore size by selectively removing the sacrificial block [1]. Such nanoporous polymers are expected to be useful in application including catalyst, separation, and filtration. Particularly for filtration membrane application, nanoporous polymers should possess good mechanical properties that can stand high hydraulic pressure as well as high chemical stability [2]. To this end, we explored a synthetic route to novel block polymers composed of a high-performance condensation polymer block and a sacrificial polymer that can be converted into nanoporous polymers containing the condensation polymer framework. We chose poly(ether sulfone) (PES) as the condensation polymer and polylactide (PLA) as the sacrificial polymer and synthesized PLA-*b*-PES-*b*-PLA by combination of condensation polymerization and ring opening transesterification polymerization (ROTEP). PES is a well-known engineering polymer largely used as microfiltration and ultrafiltration membranes due to their good mechanical properties and high thermal stability [3]. Here we demonstrate high molecular weight PES comparable to commercial grades can be incorporated into block polymer architecture by introducing benzyl hydroxyl groups at the chain ends of PES and subsequent ROTEP of lactides. We also show that PLA-*b*-PES-*b*-PLA microphase-separates driven by incompatibility between PLA and PES, and PLA can be selectively etched from the block polymer precursor suggesting potential of our approach towards next-generation ultrafiltration membranes that combines advantages of conventional membrane materials and pore structure control via block polymer self-assembly.

Experimental

Materials. Bis(4-fluorophenyl)sulfone, 4,4-sulfonyldiphenol, potassium carbonate (K_2CO_3) were purchased from TCI. 4-Hydroxybenzyl alcohol, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), anhydrous dimethyl sulfoxide (DMSO), anhydrous *N,N*-dimethylformamide (DMF), anhydrous *N,N*-dimethylacetamide (DMAc), anhydrous toluene were purchased from Sigma-Aldrich. *d,l*-Lactide was provided from Purac and purified by crystallization from toluene. 4,4-Sulfonyldiphenol and bis(4-fluorophenyl)sulfone were purified by recrystallization from water and chloroform/hexane, respectively. K_2CO_3 was dried in vacuo at 150 °C for 24 h prior to use. Other commercially available reagent-grade chemicals were used without further purification.

Instrumentation. 1H nuclear magnetic resonance (NMR) spectra of synthesized materials were recorded on a Bruker Fourier Transform AC 400 spectrometer. Chemical shifts were expressed in part per million (ppm) with reference to the peak of residual DMSO (2.49 ppm for 1H). Molecular weights and molecular weight distributions of polymer were measured by size exclusion chromatography (SEC). The SEC traces were obtained with Agilent 1260 Infinity system using

DMF with 0.05 M LiBr as an eluent at 35 °C. The number and weight average molecular weights of the polymers were calculated relative to linear polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TA instruments TGA Q500 and DSC Q20 with a heating rate of 10 °C/min, respectively. Synchrotron small angle X-ray scattering (SAXS) experiments were performed at the 9A-SAXS beamline at Pohang Accelerator Laboratory. Samples were loaded into a cell sandwiched with Kapton tape and exposed to X-ray at rt or designated temperature controlled by a heating stage. Scanning electron microscopy was performed on a Nova230 microscope with a 5-10 kV accelerating voltage.

Synthesis of Poly(ether sulfone) (PES). Bis(4-fluorophenyl)sulfone (5.079 g, 19.98 mmol), 4,4-sulfonyldiphenol (5.000 g, 19.98 mmol), K₂CO₃ (11.044 g, 79.91 mmol), and DMAc (50 mL) were added to a three-necked round bottomed flask (RBF) equipped with an overhead stirrer and a Dean-Stark trap under nitrogen atmosphere. Toluene was added to the reaction mixture and azeotropically distilled at 140 °C for 4 h. The temperature was raised to 160 °C and the mixture was stirred for 24 h. Then bis(4-fluorophenyl)sulfone (2.00 mmol) was additionally added and the mixture was further stirred for 4 h. The reaction mixture was cooled to rt and diluted with DMAc, and precipitated in water acidified with small amount of acetic acid. The polymer was obtained by filtration and dried in vacuo at 100 °C for 10 h. The polymer was further purified by reprecipitation in methanol (MeOH), filtration and drying in vacuo at 120 °C for 24 h.

Synthesis of PES macroinitiator (PES-OH). PES (8.000 g), 4-hydroxybenzyl alcohol (0.331 g, 2.67 mmol), K₂CO₃ (0.369 g, 2.67 mmol), and DMSO (160 mL) were added to one-necked RBF. The reaction mixture was stirred at 50 °C for 72 h. The reaction mixture was precipitated into acidified water. The polymer was collected by filtration, washed with water, and then dried in vacuo at 100 °C for 10 h. The polymer was further purified by reprecipitation in MeOH, filtration and drying in vacuo at 120 °C for 24 h.

Synthesis of PLA-*b*-PES-*b*-PLA. PES-OH in one-necked RBF was dissolved in DMF under nitrogen atmosphere. DBU was added to polymer solution and stirred for a few minutes. d,l-Lactide was added to the reaction mixture and stirred for 2 h at rt. The polymerization reaction was quenched by adding benzoic acid. The reaction mixture diluted with DMF was precipitated in methanol. The polymer was obtained by filtration and dried in vacuo at 100 °C for 24 h.

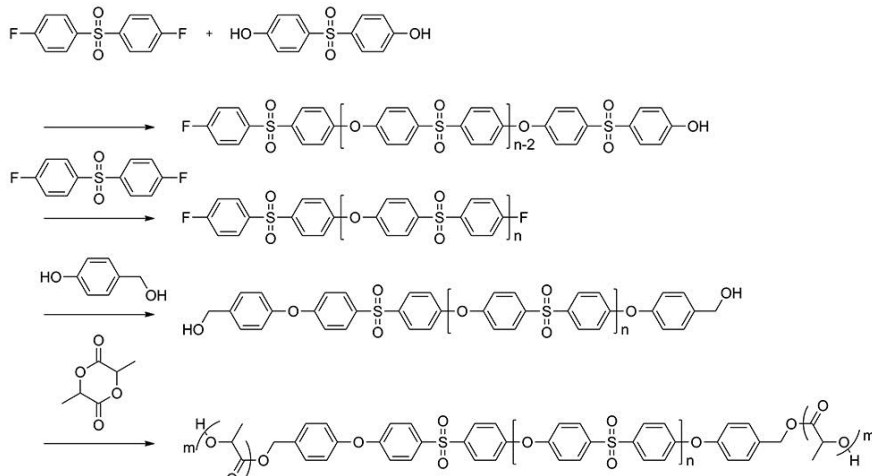
PLA-*b*-PES-*b*-PLA film. The polymer film was prepared by evaporation of DMF solution in polypropylene vials and drying under nitrogen at rt.

Nanoporous PES. A polymer film was placed in a polypropylene vial and a solution of 0.5 M NaOH (MeOH/water = 4/6 (v/v)) was poured over the sample. After 24 h at rt, nanoporous PES was obtained by draining solution and rinsed with water and MeOH several times. The nanoporous PES was dried in a desiccator under a flow of nitrogen for 1 day.

Result and Discussion

Synthesis. The whole route for synthesis of PLA-*b*-PES-*b*-PLA is depicted in Scheme 1. To ensure good mechanical properties of the resulting membranes, high molecular weight PES was synthesized by AA + BB type polymerization under stoichiometric condition using K₂CO₃ as a base following a modified literature procedure [4]. Subsequent end group modification with the AA type difluoro monomer and 4-hydroxybenzyl alcohol successfully produced telechelic PES possessing benzyl hydroxyl groups at both ends of the chain. The chemical structure of polymers was confirmed by ¹H NMR spectroscopy (Figure 1). The number-average molecular weight (M_n) and dispersity (\bar{D}) of PES and PES-OH estimated by SEC were 109 kg mol⁻¹ (\bar{D} = 1.46) and 107 kg mol⁻¹ (\bar{D} = 1.48), respectively.

Using the polymer as a bifunctional macroinitiator, ROTEP of d,l-lactide in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) yielded the target triblock polymer PLA-*b*-PES-*b*-PLA [5,6]. ¹H NMR spectroscopy (Figure 2) and SEC data were all consistent with the block polymer formation. PLA-*b*-PES-*b*-PLAs with different volume fraction of PES (f_{PES}) could be obtained by adjusting the molar ratio of PES-OH to lactide. By TGA, f_{PLA} was determined from the percentage of the weight loss up to 380 °C and the rest was attributed to f_{PES} (Figure 3). Characterization details of PLA-*b*-PES-*b*-PLA are summarized in Table 1.



Scheme 1. Synthetic route of PLA-*b*-PES-*b*-PLA

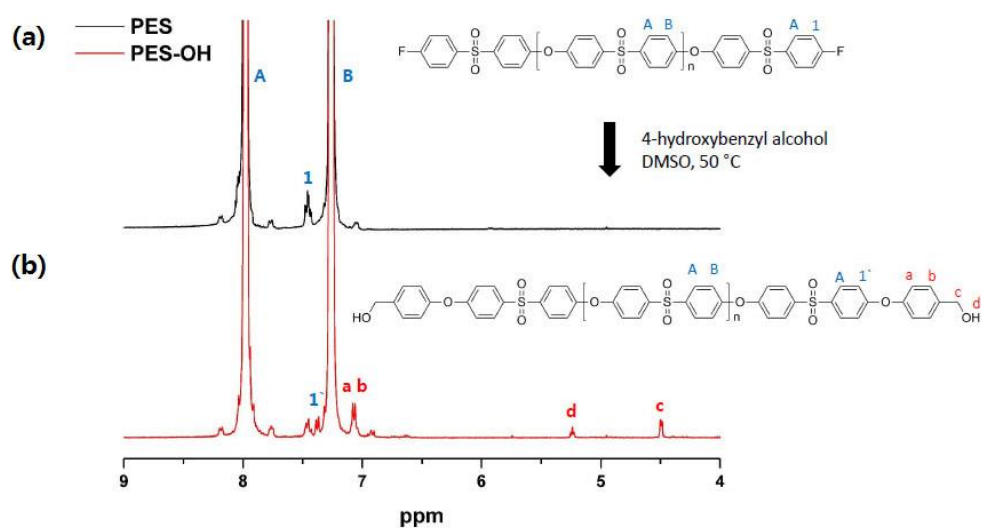


Figure 1. ^1H NMR spectra of the synthesized polymers (400 MHz, $\text{DMSO-}d_6$, 25 °C). (a) Fluorine-terminated PES (PES). (b) Benzyl hydroxyl-terminated PES (PES-OH).

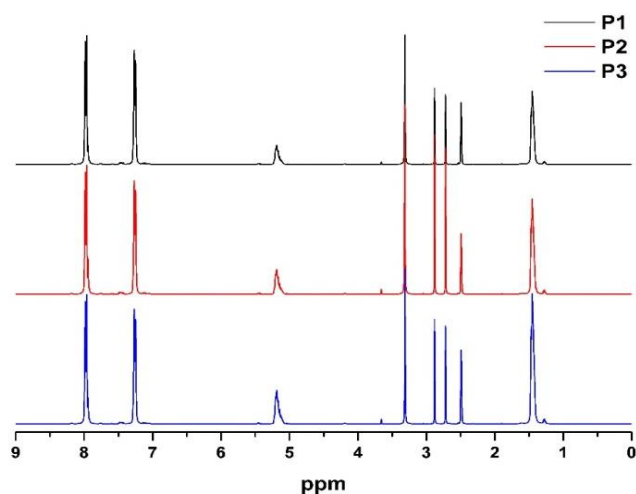


Figure 2. ^1H NMR spectra of PLA-*b*-PES-*b*-PLAs (400 MHz, $\text{DMSO-}d_6$, 25 °C).

Table 1. Characterization of PLA-*b*-PES-*b*-PLAs

Entry	$M_{n,SEC}$ (kg mol ⁻¹) ^a	\bar{D} ^a	f_{PES} ^b
PES	113	1.49	-
PES-OH	95	1.46	-
P1	102	1.41	0.70
P2	104	1.40	0.64
P3	103	1.40	0.59

^aEstimated from SEC. ^bCalculated from TGA.

Microphase separation of PLA-*b*-PES-*b*-PLA. As PLA is known to decompose above 200 °C, DSC thermograms were obtained from 10 to 200 °C. P1, P2 and P3 all showed an endothermic transition corresponding to the glass transition of PLA at 49 °C, suggesting PES and PLA were microphase-separated regardless of f_{PES} (Figure 3).

Microphase separation behaviors of PLA-*b*-PES-*b*-PLAs were further investigated using SAXS. SAXS patterns of P1, P2 and P3 at 150 °C are shown in Figure 4. Based on the position of higher-order scattering peaks, we interpreted that all the samples possessed an asymmetric lamellar structure of PES and PLA. Higher-order scattering peaks were less clear in the SAXS data of P1 suggesting the polymer may lie close to the phase boundary between lamellar and cylindrical phases. Domain spacing (d) of the lamellar structures was calculated from the position of the principal peak (q^*) and summarized in Table 2.

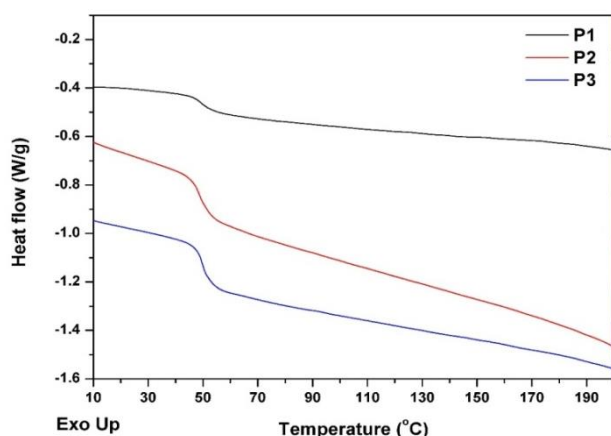


Figure 3. DSC thermograms of PLA-*b*-PES-*b*-PLAs (10 °C/min, N₂).

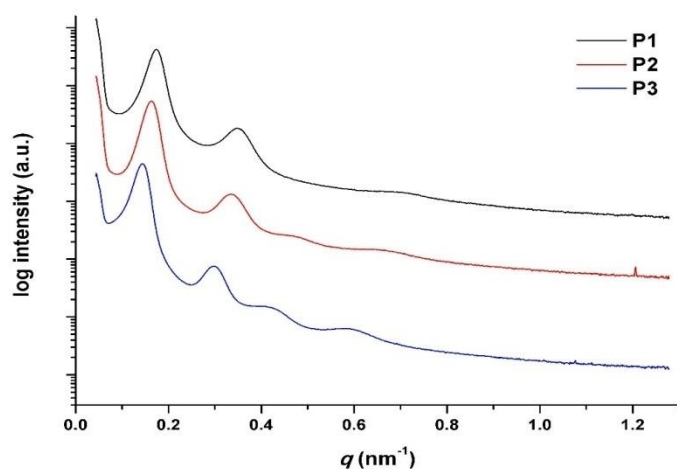


Figure 4. SAXS pattern of PLA-*b*-PES-*b*-PLAs (at 150 °C).

Table 2. SAXS results of PLA-*b*-PES-*b*-PLAs (at 150 °C)

Entry	q^* (nm ⁻¹)	D (nm)	Morphology
P1	0.173	36.3	Lamellar?
P2	0.164	38.3	Lamellar
P3	0.143	43.9	Lamellar

Nanoporous PES by PLA etching. PLA was selectively etched by immersing PLA-*b*-PES-*b*-PLA film in 0.5 M NaOH solution (water/methanol = 4/6). After etching, the peak corresponding to the methine proton of PLA (5.25 – 5.00 ppm) disappeared in the ¹H NMR spectra while peaks corresponding to benzyl protons (4.5 ppm) and hydroxyl proton (5.25 ppm) were recovered (Figure 5). The spectral data clearly corroborates the PLA removal from the block polymer precursor.

Figure 6 shows SAXS data of the samples after PLA etching. Scattering intensity increased abruptly after PLA etching because of much higher electronic contrast between air and PES than that of PLA and PES. However, loss of higher-order scattering peaks accompanied with appearance of large scattering intensity at the small-angle regime indicated pore collapse, as expected from the geometry of the lamellar structure. SEM images shown in Figure 7 were consistent with SAXS data.

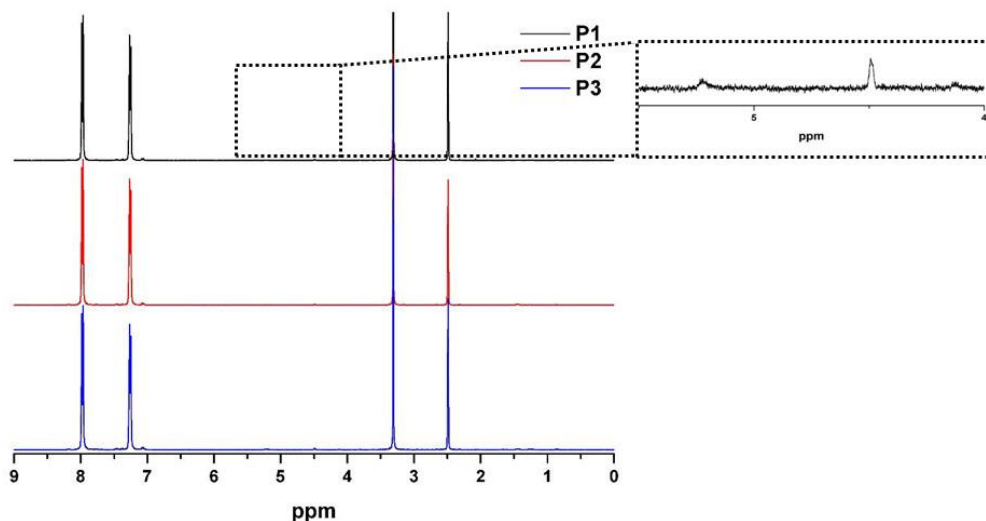


Figure 5. ¹H NMR spectrum of the materials after basic treatment (400 MHz, DMSO-*d*₆, 25 °C)

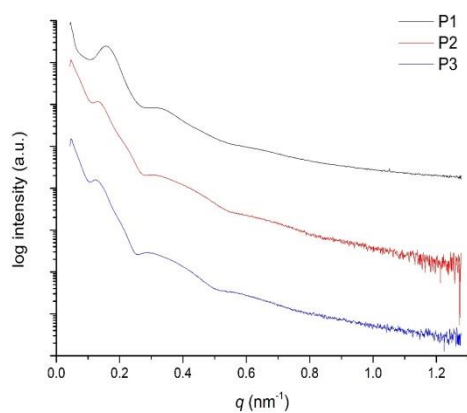


Figure 6. SAXS data of nanoporous PES at 25 °C.

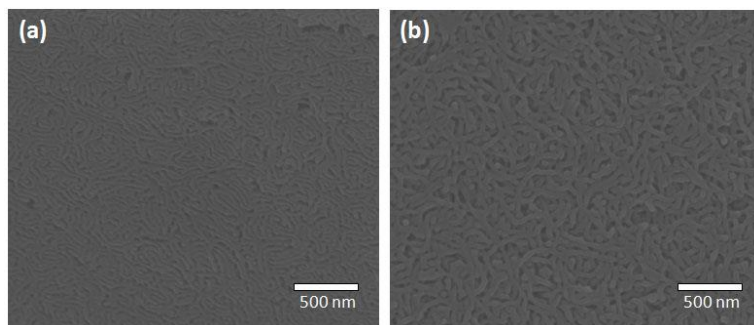


Figure 7. SEM images of nanoporous PES. (a) P2. (b) P3.

Summary

In this study, we established a synthetic route to PLA-*b*-PES-*b*-PLA by combination of condensation polymerization and ROTEP. DSC and SAXS result clearly showed PLA-*b*-PES-*b*-PLAs synthesized in this study microphase-separated into a lamellar morphology. PLA was selectively removed from PLA-*b*-PES-*b*-PLA suggesting potential of this class of materials as precursors to nanoporous PES membranes for ultrafiltration.

Reference

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