

MECHANISM-TRANSFORMATION SYNTHESIS AND CHARACTERIZATION OF POLY(STYRENE-*b*-2-ETHYL-2- OXAZOLINE) DIBLOCK COPOLYMER*

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Abstract By mechanism-transformation (anionic $\rightarrow$ cationic) poly(styrene-*b*-2-ethyl-2-oxazoline) diblock copolymer, PS-*b*-PEOx, was synthesized in two steps. The first step is the polymerization of styrene block capped with ethylene oxide and its tosylation; the second step is the cationic ring-opening polymerization of 2-ethyl-2-oxazoline. The products were thoroughly characterized by various methods, such as $^1\text{H-NMR}$, IR, DMA, TEM and SAXS. The results show that the copolymer obtained possesses high molecular weight and narrow molecular weight distribution.

Keywords Diblock copolymer, Mechanism-transformation polymerization, 2-Ethyl-2-oxazoline, Styrene, Characterization

INTRODUCTION

Poly (2-ethyl-2-oxazoline) (PEOx) has attracted attention because of its compatibility with many commodity polymers^[1,2]. Its monomer undergoes cationic polymerization with *p*-toluenesulfonate or methyl iodide as an initiator^[3], a mechanism not applicable to many other common monomers. Thus, synthesis of its block copolymers, for example, poly(styrene-*b*-2-oxazoline) block copolymer is difficult to obtain through a "living" cationic copolymerization. Mechanism-transfer polymerization^[4] makes possible the synthesis of block copolymer from monomers adaptable to different polymerization mechanisms. This paper describes for the first time the synthesis of poly(styrene-*b*-2-ethyl-2-oxazoline) diblock copolymers with high molecular weights and narrow MW distributions through mechanism transformation from anionic to cationic. This block copolymer no doubt finds wide application in compatibilization of many in-miscible blends.

EXPERIMENTAL

Chemical Reagents and Their Purification

2-Ethyl-2-oxazoline (EOx) (labeled purity >98%) from Aldrich Chem. Co. was dried over calcium hydride (CaH_2) and potassium hydroxide (KOH) for more than a month, and then distilled twice over CaH_2 and KOH under reduced pressure in a pure argon atmosphere. The amount collected at $50.1^\circ\text{C}/6.78 \times 10^3 \text{ Pa}$ was kept in a sealed ampoule at a low temperature (-20°C) before use.

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Styrene (St) (A. R.) was purified by reduced pressure distillation over CaH_2 and the amount collected at $56.4^\circ\text{C}/4.25 \times 10^3 \text{ Pa}$ was stored at low temperature.

n-Butyllithium (*n*-BuLi) was prepared and analyzed by a known method^[5].

Tetrahydrofuran (THF) (A.R.) dried over 5 Å molecular sieves and CaH_2 for more than two months was distilled, and then refluxed for two weeks over potassium grains until the biphenyl ketone (indicator) added appeared blue, and the amount collected at b.p. 66.3°C was kept in an ampoule before use. N, N-dimethylformamide (DMF) (A.R.) was dried by calcium chloride and 5 Å molecular sieves and then distilled twice under reduced pressure, and the amount was collected at $55.3^\circ\text{C}/2.92 \times 10^3 \text{ Pa}$ and sealed in an ampoule.

Ethylene oxide (A.R.) was dried over CaH_2 for two weeks, and then distilled twice over CaH_2 . The amount collected at 10.7°C was sealed in an ampoule and stored at -20°C before use. *p*-Toluenesulfonyl chloride (TsCl) (C.P.) obtained from the Beijing Chemical Plant was twice purified by recrystallization from 95% ethanol (A.R.). The purified TsCl (m.p. 68.3°C) was then dissolved in THF to make a concentration of 10% (w/v).

Highly pure argon, a product of Fushun Oxygen Plant, was purified by passing through columns of silica-gel and 5 Å molecular sieves.

Poly(2-ethyl-2-oxazoline) (PEOx) ($M_w = 2 \times 10^5$) from Aldrich Chem. Co. was purified as follows before use: it was dissolved in chloroform, precipitated in a large amount of ether, filtered, washed and dried.

Methanol (A.R.), ethanol (C.P.), ether (C.P.) and chloroform (A.R.) are all common reagents.

Synthesis of The Polystyrene (PS) Block

The block precursor, *p*-toluenesulfonate-capped polystyrene (PS-OTs), was synthesized under water-and oxygen-free conditions in a specially designed flask. Styrene has been polymerized with *n*-BuLi for 1.5 h at -78°C in THF as the initiator. THF solutions of ethylene oxide and TsCl were successively added to terminate anions. The product was precipitated in a large amount of ethanol, filtered and dried. It was then extracted with ethanol for more than 48 h and then dried. The molecular weight of the end-product (PS-OTs) was analyzed by GPC and the content of the terminating group (-OTs) by ultraviolet absorption spectrophotometer in a very dilute solution of cyclohexane^[6], which shows an obvious absorption at $\lambda = 273 \text{ nm}$ contributed by -OTs groups.

Synthesis of Poly (styrene-*b*-2-ethyl-2-oxazoline) Diblock Copolymer (PS-*b*-PEOx)

In an ampoule, PS-OTs was dissolved in DMF, and then EOx monomer was added. After continuously stirring in an argon atmosphere at 110°C for 360 h, the polymerization was inhibited with methanol. The product was precipitated in ether, filtered and dried. After being extracted for 48 h successively with cyclohexane and methanol to remove homopolymers, it was dried in a vacuum and characterized.

Analysis and Characterization

UV spectra were recorded using a Beckman DU-700 spectrophotometer.

^1H -NMR spectra were recorded in CDCl_3 using a Variant Unity 400 instrument with TMS as an internal standard.

IR spectra were recorded using a BIORAD FTS-7 spectrometer, using specimens prepared by casting dilute chloroform solutions of PS-OTs or PS-*b*-PEOx on NaCl plates.

Molecular weights and MWD of polymers were measured by a Maxima-820 gel permeation chromatography (GPC) using chloroform as eluant.

Thermal behavior measurement was performed on a Perkin-Elmer DSC-7 instrument in a nitrogen atmosphere. All samples were scanned in the temperature range of $20\sim 140^\circ\text{C}$ at a heating rate of $20^\circ\text{C}/\text{min}$.

The morphologies of the copolymers were observed using a JEOL 2010 transmission electron

microscope (TEM). The specimens were films cast on glycerin from a 0.3 wt% chloroform solution of PS-*b*-PEOx fixed on copper grids and stained with OsO₄ vapor.

Small-angle X-ray scattering (SAXS) measurements were carried out on a Kratky Compact SAXS System (Austria Anont Paar Co.), and the scattering curves were corrected for background and then desmeared by Strobl's method^[7]. The data were presented on a consistent relative intensity I_{des} (arbitrary unit) versus the scattering vector magnitude $q = (4\pi / \lambda) \sin\theta$ (λ is the X-ray wavelength and 2θ is the scattering angle.)

RESULTS AND DISCUSSION

The Molecular Structure of The Block Copolymer

The ¹H-NMR spectra of PEOx, PS-OTs and PS-*b*-PEOx are shown in Fig. 1. It is difficult to see the characteristic peaks of TsO-groups in PS-OTs due to its similarity to polystyrene in molecular structure. However, PS-*b*-PEOx has the characteristics of both PS and PEOx. The IR spectra of PS-OTs and PS-*b*-PEOx are presented in Fig. 2. For PS-OTs, the absorptions at 1370, 1181 and 1110 cm⁻¹ are assigned to the sulfonate (-OTs) groups. The IR spectrum of PS-*b*-PEOx shows a strong band at 1620 ~ 1670 cm⁻¹ which is attributed to the amide groups. This indicates that the following scheme of transformation from the anionic polymerization of styrene to cationic polymerization of 2-ethyl-2-oxazoline is operative in the diblock copolymer synthesis:

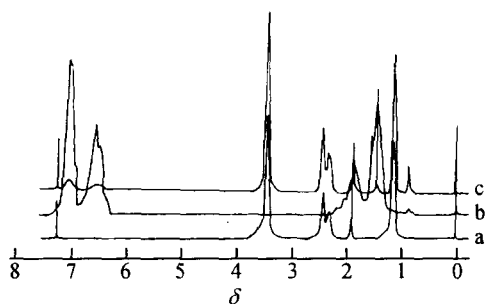
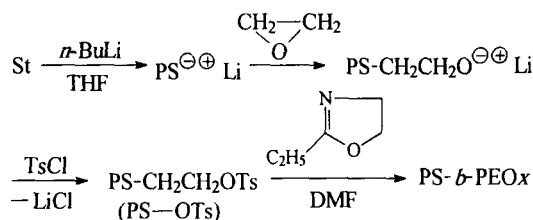


Fig. 1 ¹H-NMR spectra of polymer samples
a. PEOx; b. PS-OTs; c. PS-*b*-PEOx

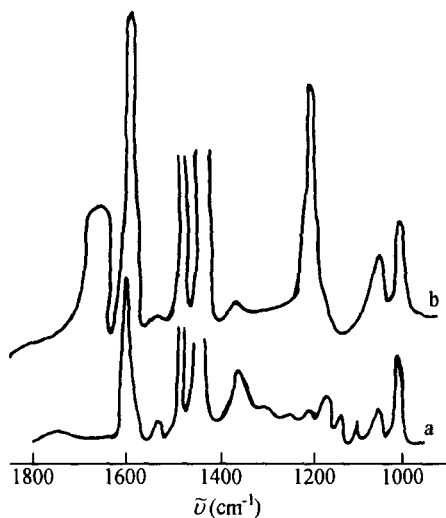
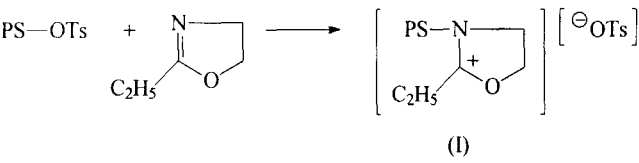


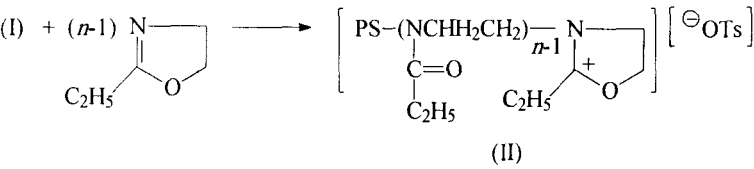
Fig. 2 IR spectra of PS-OTs (a) and PS-*b*-PEOx (b)

Data of the number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) of PS block and PS-*b*-PEOx (Table 1) indicate the M_n s are high and the distributions are narrow. GPC curves of the block copolymers only have a single peak, but they are wider than that of the corresponding polystyrene blocks as a result of the later cationic polymerization of EOx^[2]. The second step follows the manner:

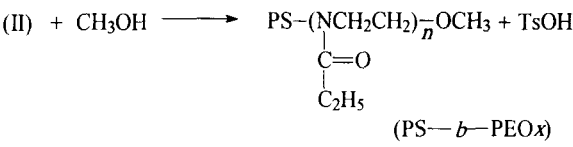
Initiation:



Propagation:



Termination:



The Microdomain Structure of the Copolymer

Two distinct glass transition temperatures (T_g) are shown on the DSC curve of the diblock copolymer (Fig. 3). This means that PS-*b*-PEO*x* is a microphase separation system, in which every phase has its own character. It also proves that the copolymer has two blocks in it; one is PS block ($T_g = 102^\circ\text{C}$) and the other PEO*x* block ($T_g = 58^\circ\text{C}$)^[3].

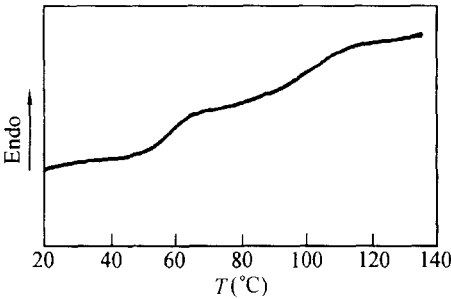


Fig. 3 DSC curve of PS-*b*-PEO*x* sample

Table 1. Data of molecular weight of PS block and the subsequent block copolymer

Sample	$10^{-4} \cdot M_n$		M_w / M_n	
	PS block	Copolymer	PS block	Copolymer
SEO1-1	1.05	3.22	1.07	1.45
SEO1-2	1.05	2.07	1.07	1.32
SEO2-1	2.32	2.95	1.09	1.47
SEO2-2	2.32	3.51	1.09	1.51

Depending on the relative fractions of the blocks in a block copolymer, spherical, cylindrical, ordered bi-continuous double diamond (OBDD), or lamellar microdomain morphology occurs^[8,9]. TEM provides a favorable opportunity to directly view the supermolecular structure in the range of 1 ~ 100 nm. The TEM photographs of PS-*b*-PEO*x* diblock copolymers are shown in Fig. 4a ~ d. It can be seen that two-phase structures are formed, the PEO*x* blocks having been stained black and the unstained PS blocks white. When the two blocks have about the same length, the block copolymer (SEO1-2) shows lamellar morphology (Fig. 4b). With increasing PS block content, the

morphology of the copolymers (SEO2-1, SEO2-2) changes to a honeycomb-like (Fig. 4c) or spherical structure with PEOx blocks dispersed in microdomains of PS blocks (Fig. 4d). In contrast, when the PEOx block content increases up to 67.4 mol%, the morphology of the copolymer (SEO1-2) shows spheres of PS block dispersed in the PEOx microdomains (Fig. 4a).

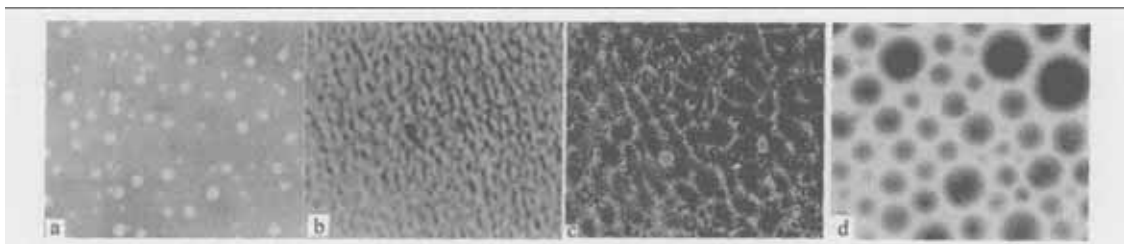


Fig. 4 TEM micrographs of PS-*b*-PEOx samples
a. SEO1-1; b. SEO1-2; c. SEO2-1; d. SEO2-2

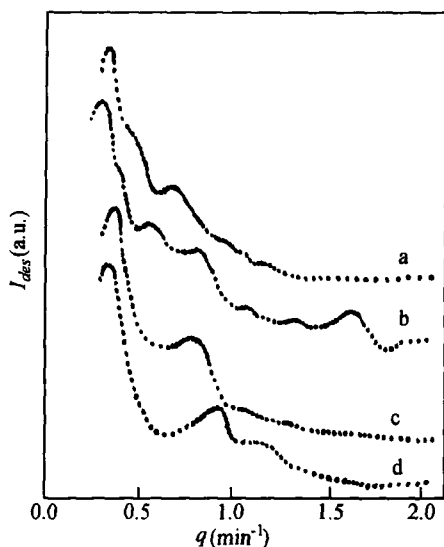


Fig. 5 SAXS curves of PS-*b*-PEOx samples
a. SEO1-1; b. SEO1-2; c. SEO2-1; d. SEO2-2

SAXS allows determination of lattice symmetry in the microdomains of a block copolymer^[10]. The SAXS curves of the four copolymers with different compositions are shown in Fig. 5. Several sharp Bragg scattering peaks can be seen on it. Generally, the position, number, shape and strength of the peaks on SAXS curves are related to the microdomain structures and arrangement of lattices in the domains. On the curve of sample SEO1-1 (Fig. 5a), the corresponding scattering vector magnitude of the second peak, q_2 , doubles the first one, q_1 , i.e. $q_1:q_2 = 1:2$, and the third peak caused by separated microdomains scattering is weak and wide. By equating on the spherical microdomain, $q_i R = 5.765i$ ($i = 1, 2, \dots$), the average size of the domains is estimated to be $R = 18.6$ nm. Comparing it with the results of TEM, it is suggested that the spherical microdomains are arranged in body-centered isometric lattices. For sample SEO1-2, the first four peak positions on its SAXS curve (Fig. 5b) have the following relation: $q_i/q_1 = 1:i$ ($i = 1, 2, 3, 4, \dots$), which is a lamellar structure arranged in hexagonal lattices. For SEO2-1, only two scattering peaks are shown on its SAXS curves, and their positions follow the relation: $q_1:q_2 = 1:2.3$ (Fig. 5c), which corresponds to a microdomain structure between lamellar and cylindrical structures. This is in line with the results

observed by TEM. The sample SEO2-2 also has only two obvious scattering peaks, whose positions are related by $q_1:q_2 = 1:2.7$ (Fig. 5d) on its SAXS curves. Related to the TEM results, it is concluded that the copolymer has a morphology between spherical and cylindrical structures.

CONCLUSIONS

By mechanism-transformation from an anionic polymerization to a cationic block, copolymers PS-*b*-PEO_x of high molecular weight were prepared. The synthesis of the block copolymers, as evidenced by various methods, such as ¹H-NMR, IR, GPC, DMA, TEM and SAXS, proved that this is a practicable method to prepare a block copolymer from monomers not adapted to a single polymerization mechanism. This extends the means of studying the effect of molecular parameters of block copolymers on compatibilization of in-miscible blends.

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