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Synthesis of High Molecular Weight and End-Functionalized Poly(styrene oxide) by Living Ring-Opening Polymerization of Styrene Oxide Using the Alcohol/Phosphazene Base Initiating System

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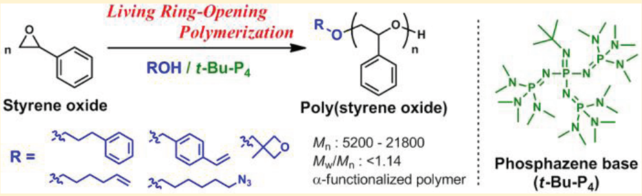
Supporting Information



ABSTRACT: The ring-opening polymerization (ROP) of styrene oxide (SO) was carried out using 3-phenyl-1-propanol (PPA) as the initiator and a phosphazene base, 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) (*t*-Bu-P_4), as the catalyst at room temperature. The polymerization proceeded in a living manner, which was confirmed by the kinetic and chain extension experiments, to produce the poly(styrene oxide) (PSO) with a controlled molecular weight (5200−21 800 g mol^{-1}) and narrow molecular weight distribution (<1.14). The ^1H NMR and MALDI-TOF MS measurements of the obtained PSO clearly indicated the presence of the PPA residue at the chain end. In addition, the *t*-Bu-P_4-catalyzed ROP of SO with functional initiators, such as 4-vinylbenzyl alcohol, 5-hexen-1-ol, 6-azide-1-hexanol, and 3-hydroxymethyl-3-methyloxetane, successfully afforded the corresponding end-functionalized PSO with precise molecular control. The *t*-Bu-P_4-catalyzed ROP of SO proceeded through the β- and α-scissions as the main and minor ring-opening manners on the basis of the microstructure of the PSOs analyzed by the ^{13}C NMR measurement, which was clarified in the model reactions corresponding to the initiation and propagation. For the thermal analysis of PSO, the glass transition temperature and 5% weight loss temperature were found to be 34 and 310 °C, respectively.

INTRODUCTION

Ethylene and propylene are fundamental and industrial chemicals because polyethylene and polypropylene are indispensable materials in our daily life. Additionally, they are versatile raw materials for various monomers; for example, ethylene oxide (EO) and propylene oxide (PO) are typical monomers, and their ring-opening polymerizations (ROPs) are well established, such as living polymerization systems, to afford various kinds of poly(ethylene oxide)s (PEO) and poly(propylene oxide)s (PPO). Furthermore, ROPs using anionic or coordination catalysts, such as potassium *tert*-butoxide,[1] potassium hydroxide/crown ether,[2] Al*i*Bu_3,[3,4] phenolate−aluminum complex,[5] and Et_2AlCl/porphyrin systems,[6] successfully afforded well-defined polyepoxides through living polymerization procedures.[7,8] However, these systems often required absolutely dry reagents, unstable and pyrophoric initiators, time-consuming and complicated handling techniques, and strict temperature control.

Möller et al. reported that 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2Λ^5, 4Λ^5-catenadi(phosphazene) (*t*-Bu-P_4) coupled with *n*-butyllithium or alcohol was efficient for the ROP of EO leading to the PEO having a predicted molecular weight and narrow polydispersity index.[9−11] The living characteristic was caused by the nature of *t*-Bu-P_4 possessing an extremely high basicity ($pK_{BH}{}^+(CH_3CN)$ = 42.7) comparable to alkyllithium compounds and a low nucleophilicity.[12] In particular, the assortment of *t*-Bu-P_4 and alcohol has advantages for the polymerization of epoxides due to the metal-free, stability toward H_2O and O_2, high solubility toward apolar solvents, and high catalytic activity under mild reaction conditions.[10,11]

Styrene is also one of the industrially important monomers for producing polystyrene and its copolymers, such as polyacrylonitrile-*co*-polybutadiene-*co*-polystyrene and ABS resin, and styrene oxide (SO) is one of the commercially available styrene derivatives. The ROP of SO has been attempted, and the conventional cationic and anionic ROPs of SO afforded only an oligomer despite the severe polymerization conditions, such as higher temperature, longer polymerization time, and vacuum conditions.[13−17] In addition, although the coordination ROP of SO needed highly complicated catalyst systems, which required time-consuming

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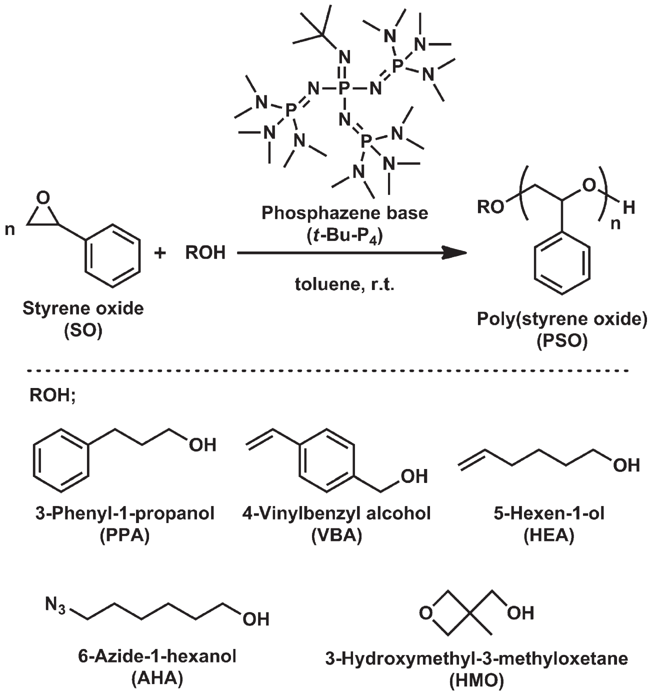
catalyst syntheses and rare-earth elements as a catalytic center, the molecular weights of the poly(styrene oxide)s (PSOs) were slightly higher than those obtained using conventional cationic and anionic catalysts.[18] Although high molecular weight PEOs and PPOs using nucleophilic catalysts are well-known, there is no report about the synthesis of a high molecular weight PSO (HMW-PSO) because the reactivity for the ring-opening addition of SO toward sodium methoxide was very low in comparison to those of EO and PO.[19,20] Thus, the synthesis of HMW-PSO is still a remaining task, and the controlled ROP of SO is a challenging issue.

We now demonstrate that *t*-Bu-P_4 is used as an anionic organocatalyst for the ROP of SO as the epoxy monomer using various functional alcohols as the initiators, as illustrated in Scheme 1. This article describes (1) the structure of the obtained PSOs involving the end-functionality, (2) the regioselectivity for the α- and β-scissions of the epoxy group, (3) the kinetic and chain extension experiments, (4) a discussion on the living characteristics based on the model reactions corresponding to the initiation and propagation, and (5) the thermal stability and glass transition temperature of PSO.

Scheme 1. Synthesis of End-Functionalized Poly(styrene oxide) (PSO) by *t*-Bu-P_4-Catalyzed Ring-Opening Polymerization of Styrene Oxide (SO) Using Alcohol (ROH) as the Initiator



EXPERIMENTAL SECTION

Materials. Toluene (>99.5%; water content, <0.001%) was purchased from Kanto Chemical Co., Inc., and distilled over sodium benzophenone ketyl before use. Styrene oxide (SO; >98.0%, Tokyo Chemical Industry Co., Ltd.) was distilled over NaH prior to use. 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) (*t*-Bu-P_4, 1.0 M solution in *n*-hexane, Sigma-Aldrich Chemicals Co.), 2-propanol (>99.7%, Kanto Chemical Co., Inc.), and dichloromethane (>99.5%, Kanto Chemical Co., Inc.) were used as received. 3-Phenyl-1-propanol (PPA; >98.0%), 5-hexen-1-ol (HEA; >95.0%), and 3-hydroxymethyl-3-methyloxetane (HMO; >96.0%) were purchased from Tokyo Chemical Industry Co., Ltd., and distilled over CaH_2 prior to use. 4-Vinylbenzyl alcohol (VBA)[21] and 6-azide-1-hexanol (AHA)[22] were synthesized from 4-vinylbenzyl chloride and 6-bromo-1-hexanol, respectively, according to the literature.

Instruments. The ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-A400II instruments with $CDCl_3$ as the solvent. The polymerization was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) and a dry argon atmosphere (H_2O, O_2 < 1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively. The size exclusion chromatography (SEC) was performed at 40 °C in THF (1.0 mL min^{-1}) using a Jasco GPC-900 system equipped with set of Waters Ultrastyragel 7 mm columns (linear, 7.8 mm × 300 mm; exclusion limit, 1 × 10^7) and two Shodex KF-804 L columns (linear, 8 mm × 300 mm; exclusion

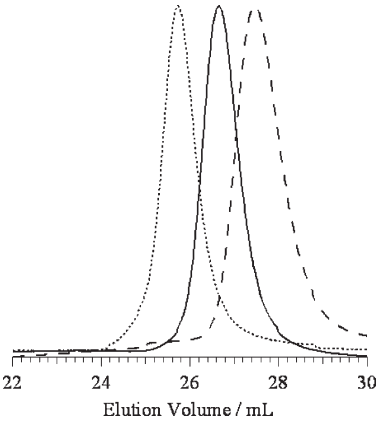


Figure 1. SEC traces of obtained PSOs produced with the $[SO]_0$/$[PPA]_0$ ratio of 50/1 (entry 1, dashed line), 100/1 (entry 2, solid line), and 200/1 (entry 3, dotted line) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Table 1. *t*-Bu-P_4-Catalyzed Ring-Opening Polymerization (ROP) of Styrene Oxide (SO) Using 3-Phenyl-1-propanol (PPA) as the Initiator[a]

entry	$[M]_0/[I]_0$	time (h)	conv (%)[b]	$M_{n,theo}$[b] (g mol^{-1})	$M_{n,NMR}$[b] (g mol^{-1})	M_w/M_n[c]	molar ratio of β-scission[d]
1	50	20	99.1	6 100	5 200	1.14	0.94
2	100	20	93.9	11 400	11 200	1.10	0.93
3	200	40	92.0	22 200	21 800	1.06	0.94
4	100 (1st)	20	96.8	11 800	10 300	1.12	
	100 (2nd)	+50	97.0	23 400	20 500	1.14	

[a] Polymerization condition: $[SO]_0$ = 5.0 (M); $[t\text{-Bu-P}_4]_0/[PPA]_0$ = 1; temp, rt. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Determined by SEC in THF using PSt standards. [d] Determined by ^{13}C NMR in toluene-d_8 at 80 °C using the methine peak of polymer main chain.

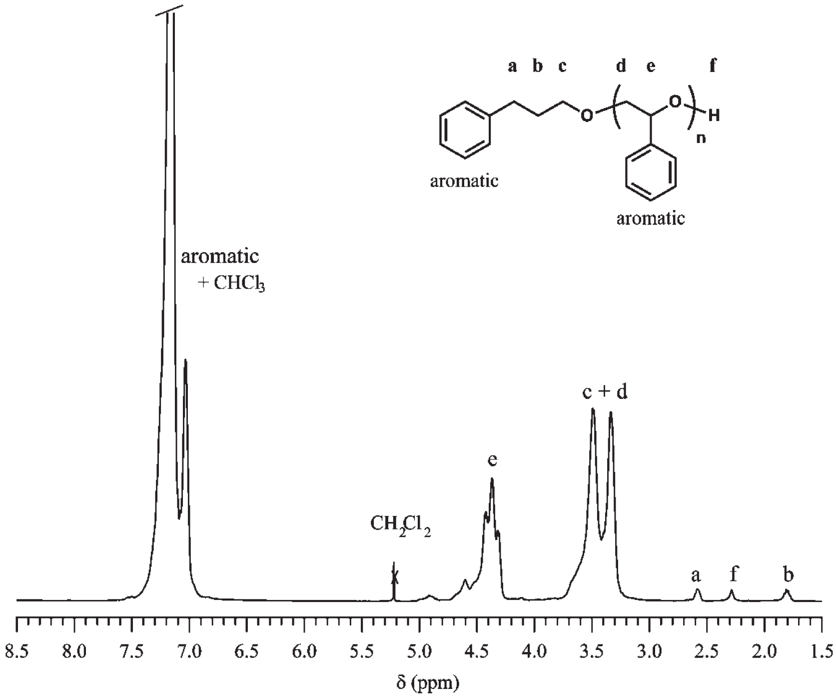
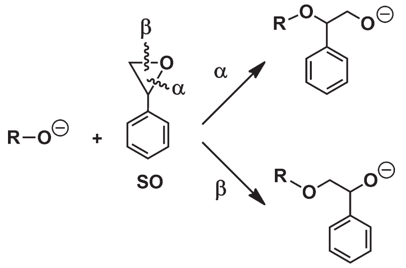


Figure 2. ^{1}H NMR spectrum of PSO (entry 2) in $CDCl_3$.

Scheme 2. Regioselectivity of SO through *α*- and *β*-Scissions



limit, 4 × 10^7). The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. The preparative HPLC was performed in MeCN/H_2O = 3/1 (2.5 mL min^{-1}) using a Jasco high performance liquid chromatography (HPLC) system (PU-980 Intelligent HPLC pump, RI-2031 Plus Intelligent RI detector, and DG-2080−53 3-Line degasser) equipped with a Kanto Chemical Mightysil RP-18 column (reverse phase column; 250 mm × 20 mm). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) of the obtained polymers was performed using an Applied Biosystems Voyager-DE STR-H equipped with a 337 nm nitrogen laser (3 nm pulse width). Two hundred shots were accumulated for the spectra at a 25 kV acceleration voltage in the reflector mode and calibrated using insulin (TAKARA BIO, Inc.) as the internal standard. For the MADLI-TOF MS measurement, the polymer (10 mg mL^{-1}) in THF, a matrix (Dithranol, 20 mg mL^{-1}) in THF, and a cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}) in methanol was mixed in the ratio of the polymer/matrix/cationizing agent of 5 μL/25 μL/5 μL, and 1 μL of mixed solution was deposited on the sample holder. The thermal gravimetric analysis (TGA) was done under a nitrogen atmosphere up to 500 °C at the heating rate of 10 °C min^{-1} using a Bruker AXS TG-DTA 2010. The differential scanning calorimetry (DSC) was done under a nitrogen atmosphere at −50 to 260 °C at the heating rate of 10 °C min^{-1} using a Bruker AXS DSC 3100.

Polymerization of Styrene Oxide. A typical procedure for the polymerization is as follows: *t*-Bu-P_4 (44.1 μL as 1.0 M solution in *n*-hexane, 44.1 μmol) was added to a solution of PPA (6.00 mg, 44.1 μmol) in toluene (0.31 mL). SO (1.00 mL, 4.41 mmol) was then added to the solution. After stirring for 20 h, the polymerization was quenched by the addition of benzoic acid (25 mg). The polymerization mixture was purified by decantation with CH_2Cl_2 and 2-propanol, and then the solvent was removed under vacuum to give a glassy white solid. The monomer conversion determined by the NMR measurement was 93.9%. $M_{n,NMR}$ = 11 200 g mol^{-1}; SEC (RI): M_w/M_n = 1.10. ^{1}H NMR ($CDCl_3$) ppm: 7.71−6.80 (m, 470H, aromatic), 5.04−4.05 (m, 93H, *C*H polymer backbone), 3.93−3.01 (m, 188H, CH_2O polymer backbone, Ph−$CH_2CH_2CH_2O$), 2.58 (m, 2H, Ph−CH_2), 2.29 (bs, 1H, OH), 1.81 (m, 2H, Ph−CH_2CH_2).

■ RESULTS AND DISCUSSION

Living Nature of *t*-Bu-P_4-Catalyzed ROP of SO Using PPA.

t-Bu-P_4 was used as the catalyst for the ROP of SO with 3-phenyl-1-propanol (PPA) as the initiator in toluene at room temperature. The reaction system was homogeneous with a change in color from yellow to orange during the polymerization. For the polymerization under the condition with the $[SO]_0/[PPA]_0/[t\text{-Bu-}P_4]_0$ ratio of 50/1/1, 100/1/1, and 200/1/1 (Table 1, entries 1, 2, and 3, respectively), the conversion of SO reached 92%, which was directly determined by the ^{1}H NMR spectra of the aliquots of the polymerization mixture in $CDCl_3$. The polymerization rate decreased with the increasing molar ratio of $[SO]_0/[PPA]_0$. The polymerization mixture was quenched by the addition of an excess amount of benzoic acid and purified by decantation with CH_2Cl_2 and 2-propanol to remove the catalyst residue and excess benzoic acid. After drying under vacuum, the product was obtained as a glassy white solid, which was soluble in

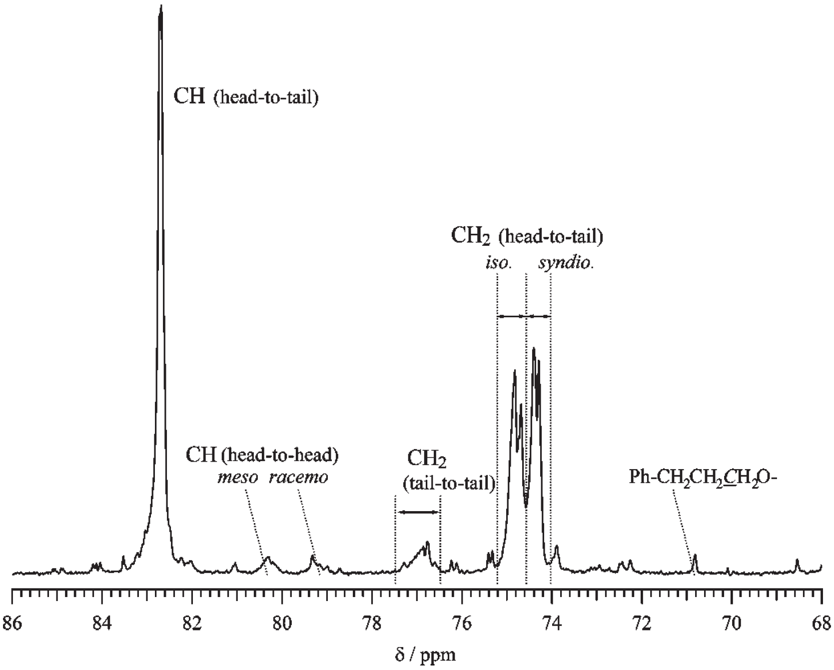


Figure 3. ^{13}C NMR spectrum of PSO (entry 2) in toluene-d_8.

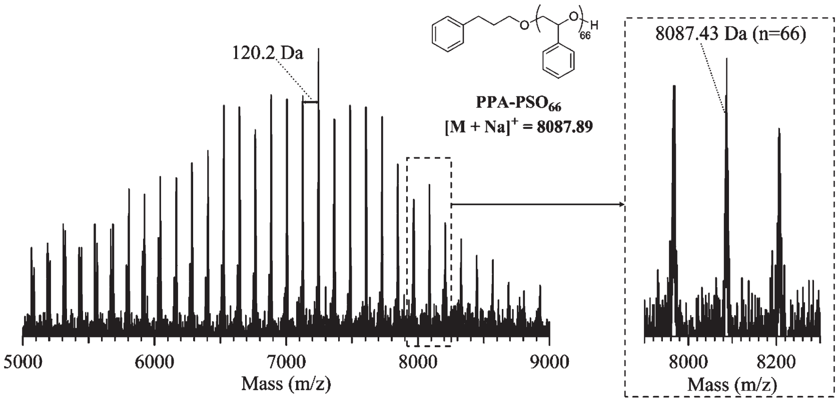


Figure 4. MALDI-TOF MS spectrum of PSO (entry 2).

chloroform, THF, toluene, DMF, DMSO, acetone, and diethyl ether and insoluble in methanol and water, which differed from the solvent solubility of polystyrene and poly(ethylene oxide). The SEC traces of the products displayed symmetrical monodisperse peaks with molecular weight distributions (M_w/M_ns) of 1.06−1.14, as shown in Figure 1.

In the ^{1}H NMR spectrum of the obtained polymer (Table 1, entry 2), as shown in Figure 2, the major signals in the range both from 3.01 to 3.93 ppm and from 4.05 to 5.04 ppm are assignable to the methylene and methine protons of the PSO main chain, respectively. The remaining strong signal in the range from 6.80 to 7.71 ppm is assigned to the aromatic protons of the PSO side chain. In addition, the minor signals at 1.81 and 2.58 ppm are assigned to the methylene protons of the initiator, while the broad signal at 2.29 ppm is assigned to the hydroxyl group of the polymer chain end. Furthermore, the signal of the styryloxy protons derived from the chain-transfer reaction during the polymerization was not observed in the region from 5.1 to 6.8 ppm.[23] These results indicated that the polymerization proceeded without side reactions, such as a chain-transfer reaction or backbiting reaction, to afford the PSO possessing the PPA residue. The number-average molecular weights ($M_{n,NMR}$s) of the obtained PSOs determined by the ^{1}H NMR spectra were 5200, 11 200, and 21 800 g mol^{-1} for entries 1, 2, and 3, respectively. The $M_{n,NMR}$ values of the obtained PSOs linearly increased with the increasing initial ratio of $[SO]_0/[PPA]_0$, which agreed with the theoretical molecular weights ($M_{n,theo}$s) predicted from the initial ratio of $[SO]_0/[PPA]_0$ and monomer conversions.

To obtain a more detailed structure of the obtained PSO is an important issue from the viewpoint of the regioselectivity for the ring-opening of SO, as illustrated in Scheme 2. In general, the ring-opening polymerization of epoxy monomers using anionic catalysts occurs through the β-scission of the epoxy group. Spassky et al. previously reported that the ROP of SO proceeded through β- and α-scissions as the main and minor ring-opening manners on the basis of the microstructure of the PSOs analyzed

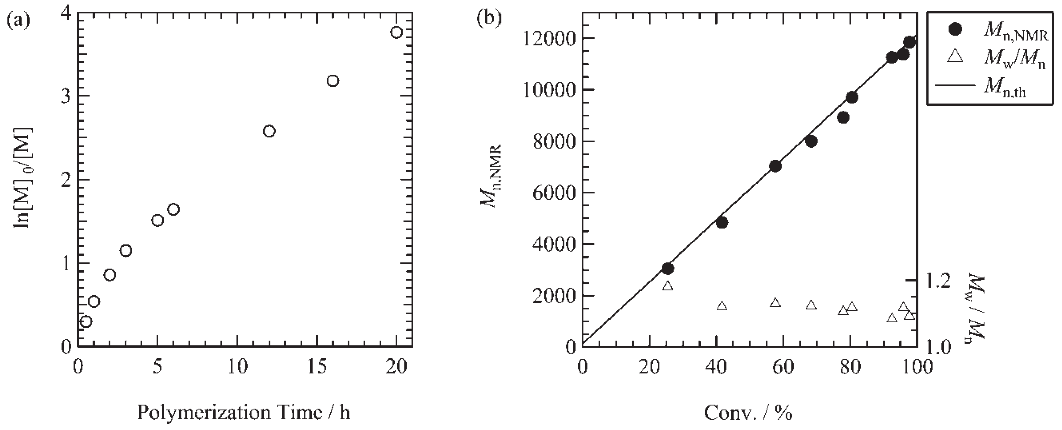


Figure 5. (a) Kinetic plots and (b) dependence of $M_{n,NMR}$ and M_w/M_n on monomer conversion for the *t*-Bu-P$_4$-catalyzed ROP of SO using PPA in toluene at room temperature ($[SO]_0/[PPA]_0/[t\text{-Bu-P}_4]_0 = 100/1/1$).

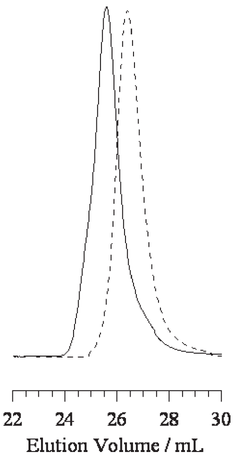


Figure 6. SEC traces of the first PSO sequence (dashed line) and postpolymerization (solid line) (entry 4) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Table 2. *t*-Bu-P$_4$-Catalyzed ROP of SO Using Functional Alcohols[a]

entry	initiator (I)	conv (%)[b]	$M_{n,theo}$[b] (g mol^{-1})	$M_{n,NMR}$[b] (g mol^{-1})	M_w/M_n[c]
5	VBA	95.8	11 600	11 400	1.08
6	HEA	97.0	11 800	10 900	1.13
7	AHA	92.1	11 200	12 900	1.12
8	HMO	93.4	11 300	10 800	1.10

[a] Polymerization condition: $[SO]_0 = 5.0$ (M); $[SO]_0/[I]_0/[t\text{-Bu-P}_4]_0 = 100/1/1$; time, 20 (h); temp, rt. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Determined by SEC in THF using PSt standards.

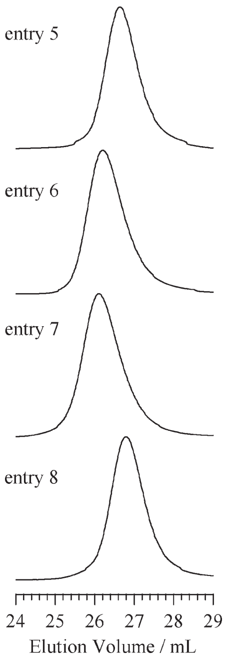
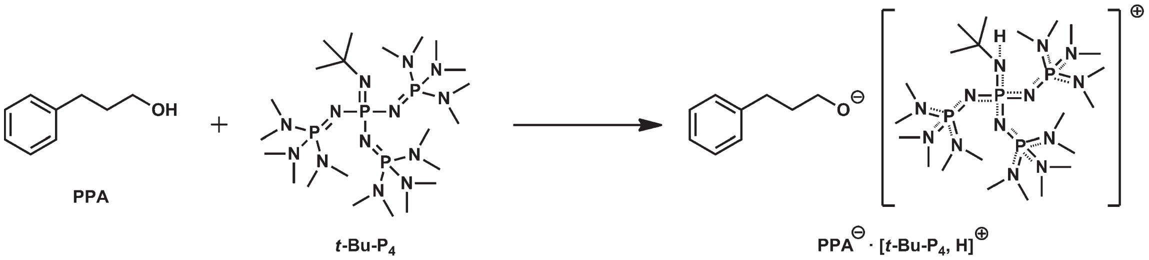


Figure 7. Synthesis of end-functionalized PSOs by the *t*-Bu-P$_4$-catalyzed ROP of SO using 4-vinylbenzyl alcohol (VBA, entry 5), 5-hexen-1-ol (HEA, entry 6), 6-azide-1-hexanol (AHA, entry 7), and 3-hydroxymethyl-3-methyloxetane (HMO, entry 8) (eluent, THF; flow rate, 1.0 mL min^{-1}).

by the ^{13}C NMR measurement.[16] For the ^{13}C NMR spectrum of PSO in toluene-d_8, as shown in Figure 3, the peaks due to the methine and methylene carbons of the PSO backbone are observed in the region of 70−85 ppm, in which the $PhCH_2CH_2CH_2O-$ group originated from PPA is confirmed at 70.81 ppm. The large methylene and methine signals due to the head-to-tail linkage appear at 73.76−75.45 and 81.76−83.47 ppm, respectively, in which the methylene signal with a multiplet peak is caused by the isotactic and syndiotactic sequences on the polymer main chain because of using the racemic SO.[24] In addition, the small methylene signals at 76.44−77.45 ppm were assignable to the tail-to-tail linkage, and the small methine signals at 79.32 and 80.30 ppm were assignable to the meso and racemo head-to-head linkages, respectively, indicating α-scission of the epoxy group. The estimated molar ratio of the head-to-tail linkage using the ^{13}C NMR measurement was determined to be 0.94 for entries 1 and 3 and 0.93 for entry 2, indicating that the content of the head-to-head linkage was independent of the molecular weight of PSO; i.e., the *t*-Bu-P$_4$-catalyzed ROP of SO using PPA proceeded through the β-cleavage pathway along with a slight α-cleavage.

In order to provide direct evidence for the PSO structure obtained from the *t*-Bu-P$_4$-catalyzed ROP of SO using PPA, we

Scheme 3. A Generation of $PPA^{-}\cdot[t\text{-Bu-P}_4\text{,H}]^{+}$ as Initiating Species for the ROP of SO



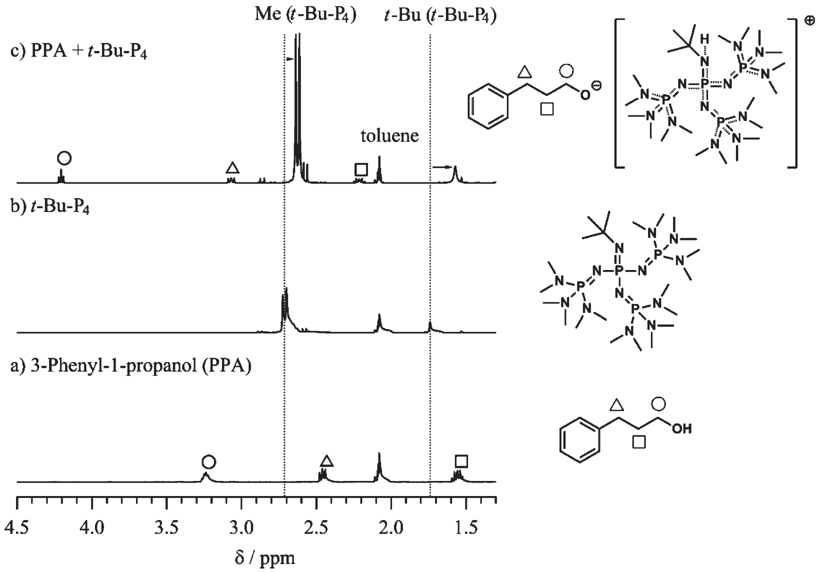


Figure 8. ^{1}H NMR spectra of (a) PPA, (b) t-Bu-P_4, and (c) their 1:1 mixture in toluene-d_8.

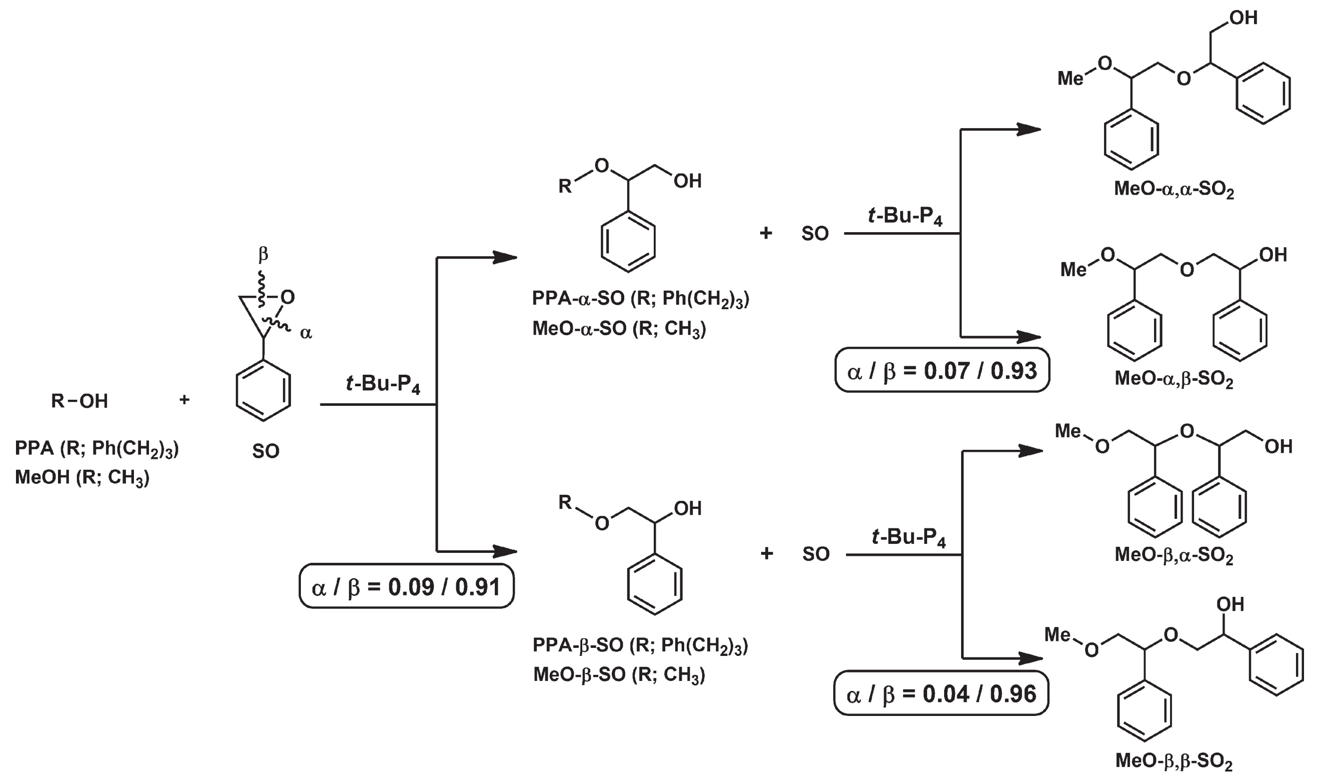
carried out a MALDI-TOF MS measurement, as shown in Figure 4. The MALDI-TOF MS spectrum of the obtained PSO shows only one series of peaks, which has a regular interval of 120.15 for the molar mass that corresponds to the SO unit. In addition, the series of peaks for the obtained polymer is assignable to the expected PSO structure having the 3-phenylpropoxyl group and the hydroxyl group at each chain end because the peak of the resultant polymer at m/z of 8087.43 corresponds to the 66-mer of PSO initiated from PPA (8087.89, calculated for $[M + Na]^+$). This result means that the t-Bu-P_4-catalyzed ROP of SO using PPA proceeded in a living manner without any side reactions, such as backbiting and chain-transfer reactions.

The analysis of the PSO structure based on the ^{1}H and ^{13}C NMR and MALDI-TOF MS measurements strongly supported the fact that the t-Bu-P_4-catalyzed ROP of SO using PPA proceeded through a living mechanism. To confirm the living nature, we carried out kinetic and postpolymerization experiments with the $[SO]_0/[PPA]_0/[t\text{-Bu-P}_4]_0$ ratio of 100/1/1. The kinetic plots displayed a linear increase with the polymerization time, as shown in Figure 5a, though a slight decrease in the slope was observed after 3 h, which was caused by the decrease in the SO concentration and the viscosity increase of the polymerization mixture. Furthermore, the molecular weight of the obtained PSO linearly increased with the reaction time and the monomer conversion was ca. 100%, as shown in Figure 5b. More importantly, the number-average polymerization degrees of the obtained PSOs, which were estimated from the ^{1}H NMR analysis, were in good agreement with those calculated from the initial ratio of $[SO]_0/[PPA]_0$ and the monomer conversion. In addition, the polydispersity indices of the obtained PSOs had low values ranging from 1.08 to 1.14.

The chain extension experiment also supported the living nature of the t-Bu-P_4-catalyzed ROP of SO using PPA. Figure 6 shows SEC traces for the chain extension experiment. A PSO with an $M_{n,NMR}$ of 10 300 g mol^{-1} and an M_w/M_n of 1.12 was first prepared by the 96.8% conversion using the $[SO]_0/[t\text{-Bu-P}_4]_0/[PPA]_0$ of 100/1/1. The polymerization was further carried out by the subsequent addition of an equimolar amount of SO to afford a PSO with an $M_{n,NMR}$ of 20 500 g mol^{-1} and an M_w/M_n of 1.14, indicating that the chain end group of PSO possessed a truly living nature. Thus, the ROP of SO using t-Bu-P_4 was revealed to proceed through a living mechanism and produced a precisely controlled PSO at room temperature.

Synthesis of the End-Functionalized PSOs. To provide an intrinsic advantage of the t-Bu-P_4-catalyzed ROP of SO using an alcohol as the initiator, we focused on the synthesis of the end-functionalized PSOs using functional initiators. We selected 4-vinylbenzyl alcohol (VBA), 5-hexen-1-ol (HEA), 6-azide-1-hexanol (AHA), and 3-hydroxymethyl-3-methyloxetane (HMO) as the functional initiators, as shown in Scheme 1. They possess well-known clickable and polymerizable groups because the synthesis of α-end-functionalized polymers using the usual

Scheme 4. **t-Bu-P$_4$-Catalyzed Model Reactions Corresponding to the Initiation and Propagation of SO Using ROH in Toluene**



anionic polymerization required time-consuming and nonstraightforward syntheses to prepare a tailor-made initiator. Table 2 lists the synthetic results of the α-end-functionalized PSOs. All the t-Bu-P$_4$-catalyzed ROP of SO using VBA, HEA, AHA, and HMO proceeded in a well-controlled manner to afford the corresponding PSOs with predictable molecular weights and narrow molecular weight distributions, as shown in Figure 7. The $M_{n,NMR}$ values of the obtained PSOs estimated by the ^{1}H NMR measurements showed good agreement with the $M_{n,theo}$ values calculated from the $[SO]_0/[I]_0$. In addition, the introduction of these functional groups at the α-chain end of PSOs was confirmed by an ^{1}H NMR analysis (see Supporting Information). Thus, we revealed that t-Bu-P$_4$ was an efficient organocatalyst for the ROP of SO affording well-defined polyether-based materials.

Living Mechanism for t-Bu-P$_4$-Catalyzed ROP of SO Using Alcohol. The alcohol was acted as the initiator for the t-Bu-P$_4$-catalyzed ROP of SO to produce well-defined PSOs with an alcohol residue as the end-functional group though PSO with a high polydispersity was obtained by the polymerization of SO using t-Bu-P$_4$ in the absence of alcohols. Thus, we added SO to the mixture of PPA and t-Bu-P$_4$ (see Experimental Section). Therefore, we were the first to elucidate the interaction between PPA and t-Bu-P$_4$, as shown in Scheme 3.

In order to clarify the interaction, we measured the ^{1}H NMR spectra for PPA, t-Bu-P$_4$, and their mixture, as shown in Figures 8a, 8b, and 8c, respectively. For the mixture (Figure 8c), the downfield shift of the peaks marked with ○, △, and □ in PPA was observed from 3.25 to 4.20 ppm for the methylene protons (○) adjacent to the hydroxyl group, from 2.46 to 3.07 ppm for the methylene protons (△) adjacent to the aromatic ring, and from 1.56 to 2.21 ppm for the center methylene protons (□), while the upfield shift for t-Bu-P$_4$ was observed from 2.71 to 2.62 ppm for the t-butyl protons and from 1.74 to 1.57 ppm for the methyl protons. These results indicated that PPA was deprotonated by t-Bu-P$_4$ to form PPA$^-\cdot[t\text{-Bu-P}_4\text{,H}]^+$, as shown in Scheme 3, which should be formed and act as the initiating species for the ROP of SO.

For the t-Bu-P$_4$-catalyzed ROP of SO using PPA, the regioselectivity was mainly the β-scission along with a slight α-scission. For the sodium alkoxide catalyzed reaction of SO and alcohol, the regioselectivity of the α- and β-scissions varied with the basicity and bulkiness of the alkoxide. O'Hagan et al. reported that a mixture of α- and β-adducts had the ratio of 1:4, 1:9, and 1:3 using sodium methoxide, isopropoxide, and *tert*-butoxide, respectively.[25] To clarify the regioselectivity in the t-Bu-P$_4$-catalyzed ROP of SO, we carried out the model reactions corresponding to the initiation and propagation reactions, as shown in Scheme 4. For the initiation model, the reaction of PPA and SO ($[PPA]_0/[SO]_0 = 2.0$) was carried out in toluene at room temperature. After removing the unreacted PPA and oligomers, a mixture of α- and β-adducts as the minor and major products, respectively, was obtained in the molar ratio of PPA-α-SO and PPA-β-SO of 0.09:0.91. For the propagation model, we used the adducts of MeOH and SO, MeO-α-SO and MeO-β-SO, instead of PPA-α-SO and PPA-β-SO, respectively, to prevent the difficult isolation and characterization of the predicted products. The reaction of MeO-α-SO and SO produced a mixture of MeO-α,α-SO$_2$ and MeO-α,β-SO$_2$ in the ratio of 0.07:0.93, and that of MeO-β-SO and SO produced a mixture of MeO-β,α-SO$_2$ and MeO-β,β-SO$_2$ in the ratio of 0.04:0.96, meaning that there was no essential difference in the regioselectivity between the primary and secondary alkoxides that originated from MeO-α-SO and MeO-β-SO, respectively. This result differed from that for the

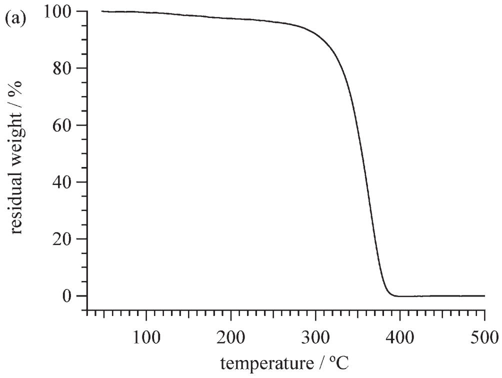


Figure 9. Thermogravimetric analysis (TGA, entry 1) of PSO under a nitrogen atmosphere.

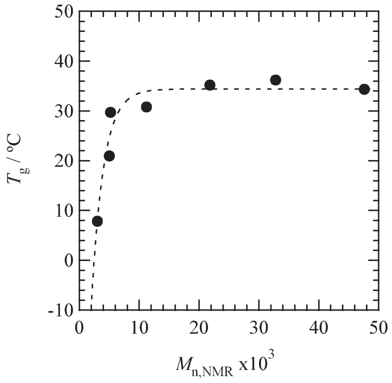


Figure 10. Plots of T_g vs $M_{n,NMR}$ of PSO.

regioselectivity in the sodium alkoxide-catalyzed reaction of SO and alcohol, which was caused by the characteristics of the protonated *t*-Bu-P_4, [*t*-Bu-P_4,H]$^+$, as the countercation. Möller et al.[10] and Penczek et al.[7] reported that the delocalization of the positive charge by the resonance effect occurred to form the phosphazenium cation. This nature of *t*-Bu-P_4 resulted in the regioselectivity for the *t*-Bu-P_4-catalyzed ROP of SO.

Thermal Property of PSO. There is no report on the thermal property of high molecular weight PSO (HMW-PSO). Thus, we synthesized well-defined HMW-PSOs with the $M_{n,NMR}$ (M_w/M_n) of 32 800 g mol^{-1} (1.07) and 47 600 g mol^{-1} (1.09) and completed the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of HMW-PSO under a nitrogen atmosphere, as shown in Figures 9 and 10, respectively. For the TGA measurement (Figure 9), the 5% weight-loss temperature ($T_{d,5\%}$) was recorded at ca. 310 °C, which was independent of the molecular weight of PSO. In addition, the glass transition temperature (T_g) of the obtained PSOs exhibited a molecular weight dependence, as shown in Figure 10. The T_g of PSO increased with the increasing molecular weight in the region from 3000 to 11 200 g mol^{-1} and finally reached a constant temperature of 34.4 °C, which was much higher than that of poly(ethylene oxide) (−63 °C) and lower than that of polystyrene (100 °C).

CONCLUSIONS

The strong organic base, i.e., the phosphazene base of *t*-Bu-P_4, effectively catalyzed the ring-opening polymerization (ROP) of styrene oxide (SO) using an alcohol to produce the poly(styrene oxide)s (PSOs) having predicted molecular weights and narrow molecular weight distributions. The results of the kinetic, chain-extension experiments and MALDI-TOF MS measurement revealed that the *t*-Bu-P_4-catalyzed ROP of SO proceeded in a living manner, in which the alcohol acted as the initiator. The α-functionalized PSOs could be obtained using various functional initiators, such as 4-vinylbenzyl alcohol, 5-hexen-1-ol, 6-azide-1-hexanol, and 3-hydroxymethyl-3-methyloxetane. The regioselectivity of the *t*-Bu-P_4-catalyzed ROP of SO was revealed by the model reactions corresponding to the initiation and propagation reactions; i.e., SO was polymerized preferentially by the β-scission together with α-scission. The thermal properties of PSO were recorded at 310 and 34.4 °C for the $T_{d,5\%}$ and T_g, respectively. To the best of our knowledge, the present report is the first and comprehensive research involving the syntheses of a high molecular weight PSO and end-functionalized PSO, the living nature and regioselectivity, and the thermal property.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental detail of model reactions corresponding to the initiation and propagation reactions and ^{1}H NMR specra of the end-functionalized PSOs. This material is available free of charge via the Internet at http://pubs.acs.org.

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