

Syntheses of well-defined poly(siloxane)-*b*-poly(styrene) and poly(norbornene)-*b*-poly(styrene) block copolymers using functional alkoxyamines

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Abstract

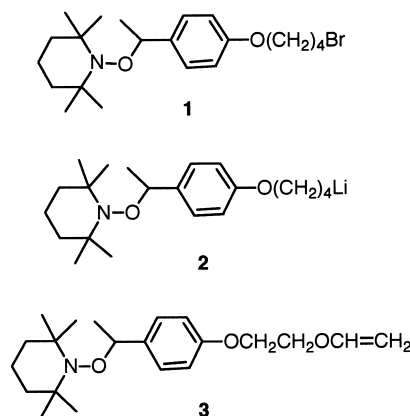
Functional alkoxyamines, 1-[4-(4-lithiobutoxy)phenyl]-1-(2,2,6,6-tetramethylpiperidinyl-*N*-oxyl)ethane (**2**) and 1-[4-(2-vinyloxyethoxy)phenyl]-1-(2,2,6,6-tetramethylpiperidinyl-*N*-oxyl)ethane (**3**) were prepared, and well-defined poly(hexamethylcyclotrisiloxane)-*b*-poly(styrene)[poly(D₃)-*b*-poly(St)] and poly(norbornene)-*b*-poly(St) [poly(NBE)-*b*-poly(St)] were prepared using the alkoxyamines. The first step was preparation of poly(D₃) and poly(NBE) macroinitiators, which were obtained by the ring-opening anionic polymerization of D₃ using **2** as an initiator and the ring-opening metathesis polymerization of NBE using **3** as a chain transfer. The radical polymerization of St by the poly(D₃) and poly(NBE) macroinitiators proceeded in the ‘living’ fashion to give well-defined poly(D₃)-*b*-poly(St) and poly(NBE)-*b*-poly(St) block copolymers.

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1. Introduction

Stable nitroxide-mediated ‘living’ free radical polymerization gives well-controlled polymers with low polydispersity indexes (M_w/M_n) [1–6]. Since this polymerization system can be initiated with nitroxide-based alkoxyamines, an employment of multifunctional alkoxyamine initiators having a functional group(s) to initiate different type of polymerization, e.g. cationic or anionic polymerization, is a promising approach to well-defined block copolymers which are difficult to prepare by the conventional methods. Many structurally interesting block polymer architectures have so far been prepared using this procedure [7–9]. Herein we report syntheses of well-defined poly(hexamethylcyclotrisiloxane)-*b*-poly(styrene) [poly(D₃)-*b*-poly(St)] and poly(norbornene)-*b*-poly(St) [poly(NBE)-*b*-poly(St)] using functional alkoxyamine initiators **2** and **3**.



Since alkoxyamine **2** bears a butyllithium-like unit as one of the functional groups, this alkoxyamine can be used as an initiator for a wide variety of anionic polymerization. In the present study, **2** was employed as an initiator for the polymerization of D₃, and the resultant poly(D₃) was used as a macroinitiator for radical polymerization of St. Poly(D₃)-*b*-poly(St) block copolymers were previously prepared by three methods: the ring-opening anionic polymerization (ROAP) of D₃ by a phenyllithium bearing a TEMPO-based alkoxyamine and the subsequent nitroxide-mediated radical

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polymerization (NMRP) of St initiated with the poly(D₃) macroinitiator [10], ROAP of D₃ by *sec*-butyllithium and the subsequent atom-transfer radical polymerization of St [11] or subsequent TEMPO-mediated free radical polymerization [12], and NMRP of St initiated with an poly(siloxane)-based azo compound [13]. In the first method, the ROAP of D₃ by the phenyllithium bearing TEMPO-based alkoxyamine gave poly(D₃) with a polydispersity index of 1.33, but the resulting polymerization of St initiated by the poly(D₃) macroinitiator gave a block copolymer with a broad polydispersity of 1.80 at 21% conversion. The second method utilizes the coupling reaction of the growing siloxy anion chains with hydrosilyl chlorides. The silylhydride end-capped polysiloxanes were then treated with vinyl compounds to introduce a halides [11] or an alkoxyamine moiety into the one end of polysiloxane chain [12]. Since the second method utilizes the polymer reaction to introduce a halide or an alkoxyamine moiety into one end of the polymer chain, the 100%-functionalized macroinitiators are impossible to obtain. The third method utilizes a polysiloxane-based azo compound as a macroinitiator, which was prepared by the reaction of an α,ω -diamino-poly(dimethylsiloxane) with 4,4'-azobis(4-cyanopentanoyl) dichloride. Since the azo macroinitiator does not have a constant structure, the resulting block copolymers showed broad polydispersities of 1.88–2.26. Since our approach (the first method) utilizes no polymer reaction, the procedure is more convenient and expected to give 100%-functionalized macroinitiators.

The combination of ring-opening metathesis polymerization (ROMP) [14] and living free radical polymerization is an alternating attractive method for preparation of block copolymers. Although preparation of block copolymers by the combination of ROMP and the atom transfer radical polymerization were previously reported by three groups [15–17], preparation of those by the combination of ROMP and NMRP has not been reported yet. Since NMRP does not use transition metals as a catalyst, if the macroinitiator prepared by ROMP are metal-free, the resultant block copolymers are metal-free. Since in the ROMP of norbornene (NBE) using RuCl₂(=C=CHBu-*t*)(PCy₃)₂ as a cocatalyst, vinyl ethers and vinyl sulfides function as a chain transfer agent [17–19], the polymerization of NBE in the presence of **3** yields a poly(NBE) having the moiety of **3** at the one end of the polymer chain. In this work we used the poly(NBE) as a macroinitiator for radical polymerization of St.

2. Experimental section

2.1. Measurements

¹H NMR spectra were recorded on a JEOL α 400 NMR spectrometer (400 MHz) using TMS as the internal standard. Size exclusion chromatography (SEC) measure-

ments were carried out with a Tosoh GPC 8020 series using TSK_{gel} G5000H_{HR}, MultiporeH_{XL}-M, and GMH_{HR}-L columns calibrated with the polystyrene standards, eluting with THF at 40 °C. Detection was made with a Tosoh refractive index detector RI8020.

2.2. Materials

D₃ was commercially available and purified by distillation over CaH₂. Di-*tert*-butyl diperoxyoxalate (DBDP) was obtained by the reported method [20]. RuCl₂(=C=CHBu-*t*)(PCy₃)₂ was kindly gifted by Prof. F. Ozawa, Osaka City University [17–19]. 2,2,6,6-Tetramethylpiperidiny-*N*-oxyl (TEMPO) was commercially available and purified by sublimation. Column chromatography was carried out on silica gel 60 N (Kanto Chemical Co., Inc.).

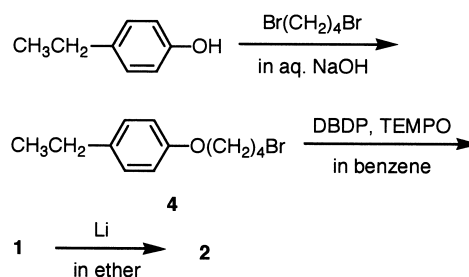
2.3. Syntheses of alkoxyamine **1** and **2** (Scheme 1)

2.3.1. 4-Ethylphenyl 4-bromobutyl ether (**4**)

A mixture of 4-ethylphenol (10 g, 0.082 mol) and 1,4-dibromobutane (53 g, 0.25 mol) in 2 N NaOH aq. solution (80 ml) was refluxed for 24 h. After water (100 ml) was added, the mixture was extracted with ether, and the combined ether extracts were washed with brine, dried over anhydrous MgSO₄, and evaporated. The residue was then twice chromatographed on silica gel. The first chromatography was carried out with 9:1 hexane–EtOAc, and the second chromatography was done with hexane. Compound **4** was obtained as a colorless oil in 75% yield (16 g, 0.062 mol). ¹H NMR (CDCl₃, ppm): δ 1.20 (t, *J* = 7.6 Hz, CH₃CH₂, 3H), 1.90–1.95 (m, OCH₂CH₂CH₂CH₂Br, 2H), 2.00–2.07 (m, OCH₂CH₂CH₂CH₂Br, 2H), 2.58 (q, *J* = 7.3 Hz, CH₃CH₂, 2H), 3.47 (t, *J* = 6.8 Hz, OCH₂CH₂CH₂CH₂Br, 2H), 3.93 (t, *J* = 6.3 Hz, OCH₂CH₂CH₂CH₂Br, 2H), 6.83 (d, *J* = 8.5 Hz, aromatic, 2H), 7.23 (d, *J* = 8.5 Hz, aromatic, 2H).

2.3.2. 1-[4-(4-Bromobutoxy)phenyl]-1-(2,2,6,6-tetramethylpiperidiny-*N*-oxyl)ethane (**1**)

A mixture of **4** (4.3 g, 16.7 mmol), TEMPO (0.87 g, 5.6 mmol), and DBDP (1.31 g, 5.6 mmol) in benzene (30 ml) was stirred at 38 °C for 5 h with stirring under N₂. After the mixture was evaporated under reduced pressure, the residue was chromatographed on silica gel with



Scheme 1.

benzene. Recrystallization from MeOH gave **1** as colorless prisms in 24% yield (0.56 g, 1.36 mmol); mp 45–47 °C. ¹H NMR (CDCl₃, ppm) δ 0.65, 1.01, 1.15, and 1.28 (each s, CH₃, 12H), 1.35–1.60 (m, (CH₂)₃, 6H), 1.45 (d, *J* = 6.4 Hz, CH(Ar)CH₃, 3H), 1.90–1.97 (m, OCH₂CH₂CH₂CH₂Br, 2H), 2.04–2.11 (m, OCH₂CH₂CH₂CH₂Br, 2H), 3.49 (t, *J* = 6.6 Hz, OCH₂CH₂CH₂CH₂Br, 2H), 3.98 (t, *J* = 5.9 Hz, OCH₂CH₂CH₂CH₂Br, 2H), 4.73 (q, *J* = 6.4 Hz, CH(Ar)CH₃, 1H), 6.83 (d, *J* = 8.5 Hz, aromatic, 2H), 7.23 (d, *J* = 8.5 Hz, aromatic, 2H). Anal. Calcd for C₂₁H₃₄BrNO₂ (411.18): C, 61.16%; H, 8.31%; N, 3.40%. Found: C, 61.25%; H, 8.13%; N, 3.45%.

2.3.3. 1-[4-(4-Lithiobutoxy)phenyl]-1-(2,2,6,6-tetramethylpiperidinyl-*N*-oxyl)ethane (**2**)

A mixture of **1** (0.25 g, 0.61 mmol) and lithium metal (8.5 mg, 1.22 mg atoms) in dry ether (2.0 ml) was stirred at room temperature for 3 h under N₂. A part of the ether solution was used for the polymerization of D₃.

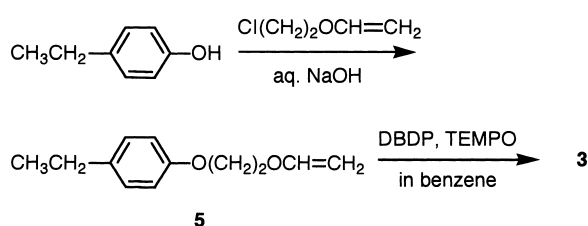
2.4. Synthesis of alkoxyamine **3** (Scheme 2)

2.4.1. 4-Ethylphenyl (2-vinyloxy)ethyl ether (**5**)

Sodium 4-ethylphenoxide, prepared from 4-ethylphenol (12.2 g, 0.10 mol) and NaH (4.0 g), was dissolved in dry DMF (50 ml), and 2-chloroethyl vinyl ether (10 g, 0.094 mol) was added. After the mixture was heated at 100 °C for 6 h under N₂, water (ca. 300 ml) was added, and the resultant mixture was extracted with ether. The combined ether extracts were washed with brine, dried over anhydrous MgSO₄, and evaporated. The residue was then chromatographed on silica gel with benzene to give **5** as a colorless oil in 78% yield (15.0 g, 78 mmol). ¹H NMR (CDCl₃, ppm): δ 1.20 (t, *J* = 7.6 Hz, CH₃CH₂, 3H), 2.57 (q, *J* = 7.6 Hz, CH₃CH₂, 2H), 4.00 (t, *J* = 4.9 Hz, ArOCH₂CH₂O or ArOCH₂CH₂O, 2H), 4.04 (dd, *J* = 6.8 and 2.0 Hz, CHH=CHO, 1H), 4.15 (t, *J* = 4.9 Hz, ArOCH₂CH₂O or ArOCH₂CH₂O, 2H), 4.23 (dd, *J* = 14.6 and 6.8 Hz, CHH=CHO, 1H), 6.52 (dd, *J* = 14.6 and 2.0 Hz, CHH=CHO), 6.84 (d, *J* = 8.8 Hz, aromatic, 2H), 7.09 (d, *J* = 8.8 Hz, aromatic, 2H).

2.4.2. 1-[4-(2-Vinyloxyethoxy)phenyl]-1-(2,2,6,6-tetramethylpiperidinyl-*N*-oxyl)ethane (**3**)

A mixture of **5** (3.00 g, 15.6 mmol), TEMPO (1.22 g, 7.81 mmol), and DBDP (1.37 g, 5.85 mmol) in benzene (30 ml) was stirred at 38 °C for 3 h with stirring under N₂.

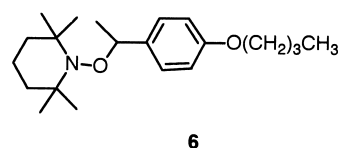


Scheme 2.

The mixture was then evaporated under reduced pressure and the residue was chromatographed on silica gel with benzene to give pure **3** in 37% yield (1.0 g, 2.88 mmol). Recrystallization from MeOH gave colorless microcrystals with mp 39–40 °C. ¹H NMR (CDCl₃, ppm): δ 0.63, 1.00, 1.15, and 1.28 (each s, CH₃, 12H), 1.35–1.60 (m, (CH₂)₃, 6H), 1.45 (d, *J* = 6.4 Hz, CH₃, 3H), 4.04 (t, *J* = 4.9 Hz, OCH₂CH₂OAr or OCH₂CH₂OAr, 2H), 4.06 (dd, *J* = 6.8 and 2.0 Hz, CHH=CHO, 1H), 4.20 (t, *J* = 4.9 Hz, OCH₂CH₂OAr or OCH₂CH₂OAr, 2H), 4.25 (dd, *J* = 14.6 and 2.0 Hz, CHH=CHO, 1H), 4.72 (q, *J* = 6.8 Hz, CH(Ar)CH₃, 1H), 6.55 (dd, *J* = 14.6 and 6.8 Hz, CH₂=CHO, 1H), 6.87 (d, *J* = 8.8 Hz, aromatic, 2H), 7.23 (d, *J* = 8.8 Hz, aromatic, 2H). Anal. Calcd for C₂₁H₃₃NO₃ (339.28): C, 72.58%; H, 9.57%; N, 4.03%. Found: C, 72.54%; H, 9.48%; N, 4.01%.

2.5. Synthesis of alkoxyamine **6**

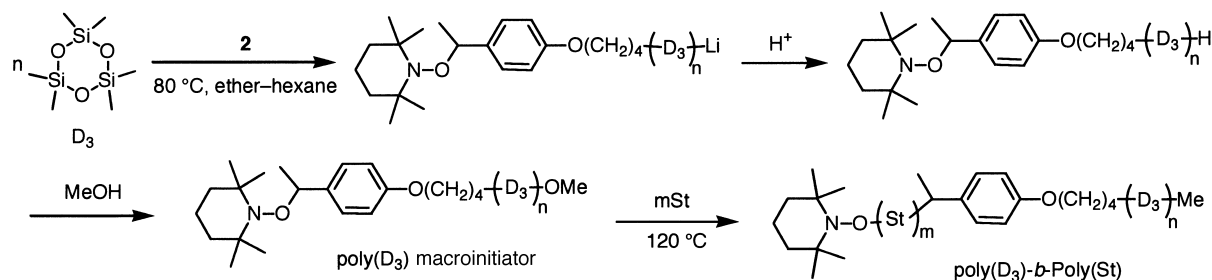
A mixture of 4-ethylphenyl butyl ether (1.00 g, 5.6 mmol), TEMPO (0.219 g, 1.40 mmol), and DBDP (0.492 g, 2.10 mmol) in benzene (10 ml) was stirred at 38 °C for 3 h with stirring under N₂. The mixture was then evaporated under reduced pressure and the residue was chromatographed on silica gel with 1:1 hexane–benzene to give pure **6** as a viscous oil in 21% yield (99 mg, 0.30 mmol). ¹H NMR (CDCl₃, ppm): δ 0.65, 1.01, 1.15, and 1.28 (each s, CH₃, 12H), 0.97 (t, *J* = 7.3 Hz, CH₃, OCH₂CH₂CH₂CH₃), 1.35–1.60 (m, (CH₂)₃, 6H), 1.46 (d, *J* = 6.4 Hz, CH₃, 3H), 1.45–1.52 (m, OCH₂CH₂CH₂CH₃, 2H), 1.72–1.79 (m, OCH₂CH₂CH₂CH₃, 2H), 3.94 (t, *J* = 6.3 Hz, OCH₂CH₂CH₂CH₃, 2H), 4.72 (q, *J* = 6.8 Hz, CH(Ar)CH₃, 1H), 6.83 (d, *J* = 8.8 Hz, aromatic, 2H), 7.22 (d, *J* = 8.8 Hz, aromatic, 2H).



2.6. Synthesis of poly(D₃)-*b*-poly(St) block copolymer (Scheme 3)

2.6.1. ROAP of D₃ with **2**

A mixture of D₃ (2.50 g, 11.2 mmol) in cyclohexane (2.0 ml) was refluxed over CaH₂ for 2 h under N₂, and 3.0 ml of the supernatant fraction of the mixture was transferred to a N₂ purged two-necked flask through a double septum with a syringe. After the ether solution of **2** (1.0 ml) and diglyme (0.005 ml) were added through a double septum with a syringe, the mixture was gently refluxed for 2.5 h with stirring under N₂ and poured into a large amount of MeOH to give poly(D₃) as a colorless viscous oil in 75% yield. The polysiloxane was once



Scheme 3.

purified by reprecipitation (THF/MeOH) $M_{n,NMR} = 6920$, $M_{n,SEC} = 8230$, $M_w/M_n = 1.12$.

2.6.2. Radical polymerization of *St* initiated with poly(D_3) macroinitiator

A styrene solution (0.50 ml) of the poly(D_3) macroinitiator (12 mmol l^{-1}) was put onto a Pyrex glass tube. After the content was degassed by three freeze-pump-thaw cycles, the tube was sealed off. After heating at 120 °C for the prescribed time, the mixture was poured into a large amount of MeOH. The resulting block copolymer precipitated was collected by filtered and dried in vacuum.

2.7. Synthesis of poly(NBE)-*b*-poly(*St*) block copolymer (Scheme 4)

2.7.1. ROMP of NBE with $RuCl_2(=C=CHBu-t)(PCy_3)_2$ in the presence of **3**

A mixture of NBE (0.50 g, 5.3 mmol) and **3** (0.074 g, 0.21 mmol) in CH_2Cl_2 (50 ml) was stirred at room temperature for 1 h under bubbling of N_2 . After $RuCl_2(=C=CHBu-t)(PCy_3)_2$ (0.043 g, 0.053 mmol) was added in one portion, the resulting mixture was stirred at the same temperature for 24 h under bubbling of N_2 and poured into a large amount of MeOH. The resulting poly(NBE) precipitated was collected by filtration and dried in vacuum. Yield 85%. The polymer was purified by reprecipitation (CH_2Cl_2 /MeOH). $M_{n,NMR} = 10\,000$, $M_{n,SEC} = 13\,500$, $M_w/M_n = 2.60$.

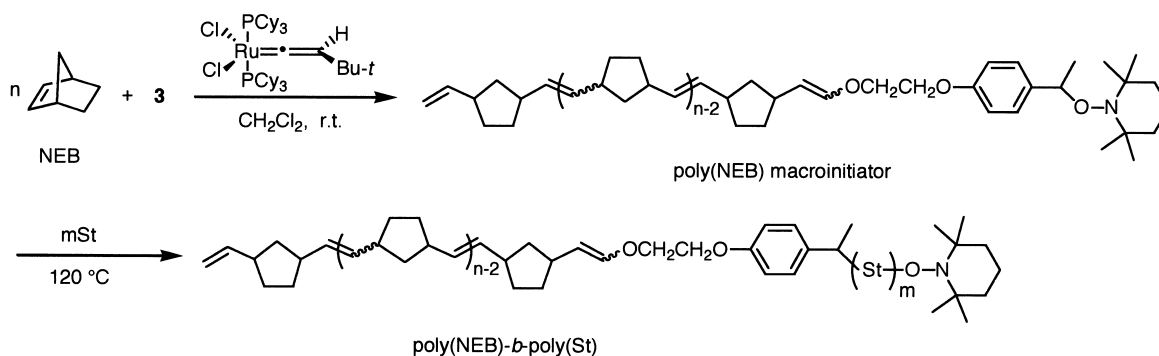
2.7.2. Radical polymerization of *St* initiated with poly(NBE) macroinitiator

A styrene solution (0.50 ml) of poly(NBE) (4.0 mmol l^{-1}) was put onto a Pyrex glass tube. After the content was degassed by three freeze-pump-thaw cycles, the tube was sealed off. After heating at 120 °C for the prescribed time, the mixture was poured into a large amount of MeOH, and the resulting copolymer precipitated was collected by filtration and dried in vacuum.

3. Results and discussion

3.1. Syntheses of functional alkoxyamines **1** and **3**

Alkoxyamine **1** was prepared according to Scheme 1. The reaction of 4-ethylphenol with an excess of 1,4-dibromobutane in aqueous alkaline solution gave 4-bromobutyl 4-ethylphenyl ether (**4**) as a colorless oil in 75% yield. The hydrogen abstraction from **4** was performed using di-*tert*-butyl diperoxyoxalate (DBDP) according to our previously reported method [10,21]. DBDP decomposes at a moderate rate at room temperature in hydrocarbons such as benzene to give *tert*-butoxyl radicals, with evolution of CO_2 [20]. Thus, a mixture of **4**, DBDP, and TEMPO in benzene was stirred at 38 °C for 5 h under nitrogen, and purification of the mixture by chromatography on silica gel afforded **1** as colorless prisms in 24% yield. We previously reported that the reaction of ethylbenzene or 4-bromoethylbenzene with DBDP in the presence of TEMPO gave the corresponding alkoxyamines in 88–90% yields [10,21].



Scheme 4.

Thus, the yield of **1** is low compared with the previous results. TLC analysis for the reaction mixture showed many spots. Since **4** has many reactive positions for hydrogen abstraction by *tert*-butoxyl radicals, it is likely that hydrogen abstraction takes place at many positions.

Lithiation of **1** was carried out by treating **1** with Li metal in dry ether at room temperature under N₂. To check whether the lithiation of **1** proceeded in a high yield or not, the mixture was quenched with H₂O and the resultant products were subjected to ¹H NMR measurements without any purification. The ¹H NMR spectra showed a complete disappearance of the triplet peaks due to –O(CH₂)₃CH₂Br at 3.49 ppm and the multiplet due to –OCH₂CH₂CH₂CH₂Br at 2.04–2.11 ppm, indicating that **1** was completely consumed in the reaction with Li. Compound **6**, a product produced by quenching of **2** with H₂O, was also independently prepared by the reaction of 4-ethylphenyl butyl ether with DBDP in the presence of TEMPO in the same manner as for **1**. The ¹H NMR spectrum of **6** obtained by quenching of **2** with H₂O was measured, which was essentially the same as that of the authentic sample, but some clear differences were observed. The triplet absorption peak due to –OCH₂CH₂CH₂CH₃ was considerably weak in intensity compared with that of the authentic sample and the absorption peaks due to –OCH₂CH₂CH₂CH₃ at 3.94 ppm was complex (that of the authentic sample is a triplet with *J* = 6.3 Hz). These differences indicate that the lithiation of **1** is not clean. The purity of **6** estimated by HPLC was 60%. However, the byproducts formed were removed in purification of poly(D₃) by reprecipitation.

Alkoxyamine **3** was prepared according to Scheme 2. The reaction of sodium 4-ethylphenoxide with 2-chloroethyl 2-vinyl ether in dry DMF gave 4-ethylphenyl (2-vinyloxy)ethyl ether (**5**) as a colorless oil in 78% yield. Compound **5** was then treated with DBDP in the presence of TEMPO in the same manner as for **4**, and alkoxyamine **3** was obtained as colorless crystals in 37% yield. In this case also, the yield of alkoxyamine **3** was low, which was explained in the same manner as for the reaction of **4** with DBDP. The structures of **1** and **3** were confirmed by ¹H NMR and satisfactory elemental analyses.

3.2. Preparation of poly(D₃)-*b*-poly(St) block copolymer

The procedure for preparation of poly(D₃)-*b*-poly(St) block copolymer is described in Scheme 3. Anionic initiator **2** was prepared by treating **1** with lithium metal in dry ether under N₂. ROAP of D₃ initiated with **2** was carried out in ether–cyclohexane at the reflux temperature under N₂ in the presence of small amounts of diglyme [22]. After 2.0 h at the reflux temperature, the mixture was poured into methanol, and the resultant colorless viscous oil of poly(D₃) was purified by decantation (yield 75%).

The poly(D₃) was analyzed by ¹H NMR and SEC measurements. The ¹H NMR spectrum is depicted in Fig. 1(a). The strong singlet peak due to –Si(CH₃)₂O– is found

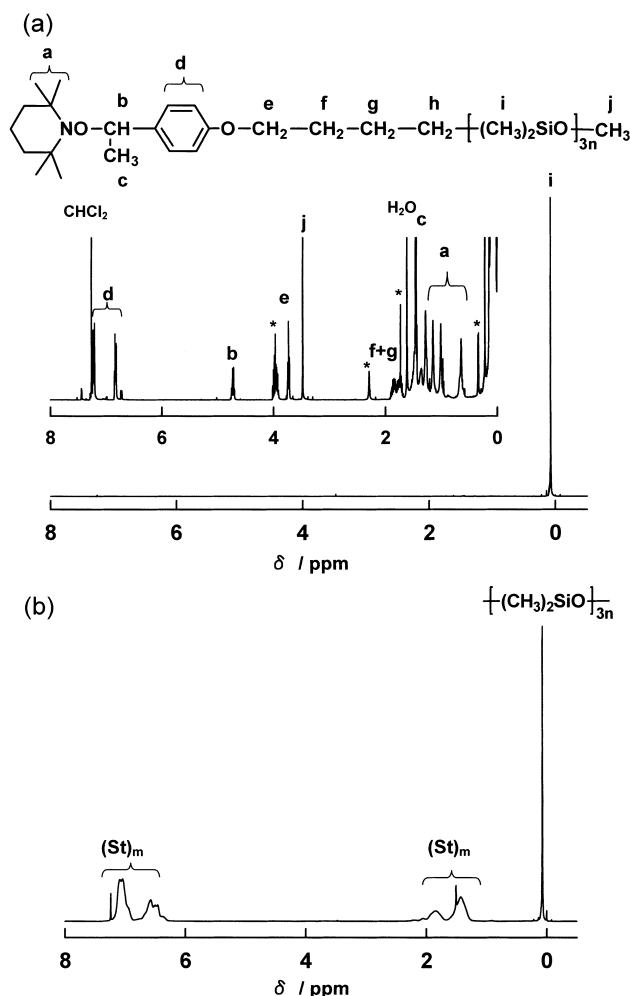


Fig. 1. (a) ¹H NMR spectra of poly(D₃) macroinitiator (a) and poly(D₃)-*b*-poly(St) block copolymer (b) in CDCl₃. The inset refers to a spectrum recorded at high gain. The asterisks indicate impurities. (b) ¹H NMR spectrum of poly(D₃)-*b*-poly(St) block copolymer at 42% conversion (*M*_{n,SEC} 35 400, *M*_w/*M*_n 1.27).

at 0.07 ppm. At high gain (see the inset), the peaks due to the alkoxyamine moiety are clearly observed. By comparing the intensity of the quartet peak due to –CH(Ar)CH₃ (H^b in Fig. 1(a)) at 4.73 ppm with that of the singlet peak for –Si(CH₃)₂O– at 0.07 ppm, the *M*_n for the poly(D₃) was estimated to be 6920. On the other hand, the *M*_n determined by SEC measurements was 8230, which was higher than that determined by NMR. Since the poly(St)s used as standards in the SEC measurements are highly different in flexibility from the poly(D₃), the SEC data (*M*_{n,SEC}) seem to be less reliable. We therefore used the NMR data (*M*_{n,NMR}) in further experiments.

Interestingly, the polydispersity index (*M*_w/*M*_n) for the poly(D₃) was satisfactory low (1.12), indicating that the ROAP of D₃ initiated with **2** proceeded in a living fashion. The initiation efficiency of **2** estimated from *M*_{n,NMR} was 0.56 (based on **1**), which agreed with the yield (60%) of **6** formed by quenching the solution of **2** with H₂O.

Bulk polymerization of St initiated with the poly(D₃)

macroinitiator was carried out at 120 °C. After the prescribed time, the polymerization mixtures were poured into a large excess of MeOH, and the resulting block copolymers were collected by filtration.

The $\ln([M]_0/[M]_t)$ vs time plots are shown in Fig. 2. A linear relationship between $\ln([M]_0/[M]_t)$ and time is established throughout the polymerization, indicating that the number of the propagating chains is constant. The conversion vs. M_n and the conversion vs. M_w/M_n plots are shown in Fig. 3(a) and (b). Fig. 3(a) exhibits that M_n s increase linearly with conversion and are in good agreement with the calculations obtained using Eq. (1)

$$M_n = \frac{[\text{St}]}{[\text{macroinitiator}]} \text{conversion} \times \text{MW}_{\text{st}} + M_{n,\text{macroinitiator}} \quad (1)$$

Fig. 3(b) shows that, although the M_w/M_n is high (1.45) at the initial stage of polymerization but decreases with conversion and keeps the low values (1.27–1.30) below 1.3 above 25% conversion. Accordingly, it can be concluded that the polymerization of St initiated with the poly(D₃) macroinitiator proceeded in the living fashion.

The ¹H NMR spectrum of the poly(D₃)-*b*-poly(St) block copolymer is drawn in Fig. 1(b). The peaks due to the poly(St) units are observed at 1.42–2.05 and 6.36–7.10 ppm, along with the singlet peak due to –Si(CH₂)O– units at 0.07 ppm.

The SEC elution curves are depicted in Fig. 4. Every elution curves show a narrow unimodal molecular weight distribution and the peaks shift to a higher molecular region with conversion. Interestingly, in any SEC elution curve the corresponding peak due to the poly(D₃) homopolymer was not observed, indicating that all the poly(D₃) macroinitiators initiated the polymerization of St.

In the previous NMRP of St by the macroinitiator prepared by ROAP of D₃ using the phenyllithium-bearing

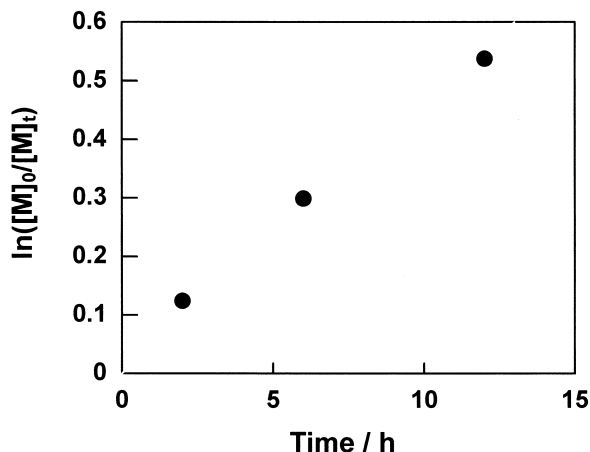


Fig. 2. The $\ln([M]_0/[M]_t)$ vs. time plots for the polymerization of St initiated with poly(D₃) macroinitiator. St 0.50 ml, poly(D₃) macroinitiator ($M_{n,\text{NMR}} = 6920$, $M_w/M_n = 1.12$) 12.0 mmol l⁻¹, temperature 120 °C.

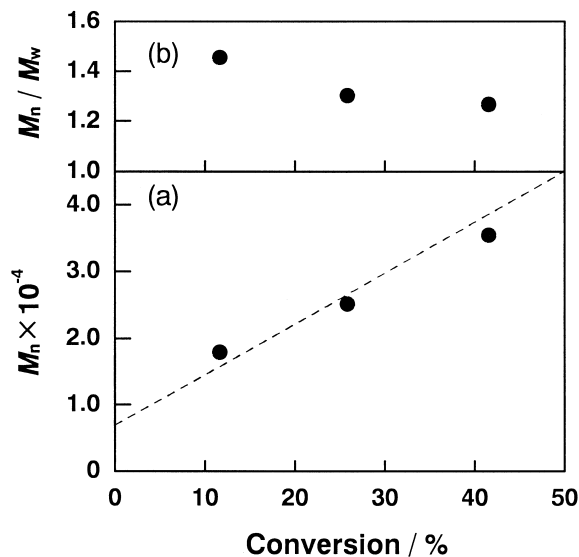


Fig. 3. (a) The $M_{n,\text{SEC}}$ vs. conversion plots and (b) the M_w/M_n vs. conversion plots for the polymerization of St initiated with poly(D₃) macroinitiator. St 0.50 ml, poly(D₃) macroinitiator ($M_{n,\text{NMR}} = 6920$, $M_w/M_n = 1.12$) 12.0 mmol l⁻¹, temperature 120 °C. The calculated molecular weights are shown in a dotted line.

TEMPO-based alkoxyamine [10], the block copolymers obtained showed a broad unimodal SEC elution curve with $M_w/M_n = 1.80$ at 21% conversion and a broad bimodal one at 53% conversion, indicating a poor livingness of the NMRP. Accordingly, it is obvious that alkoxyamine 2 is superior as an initiator to the phenyllithium-bearing TEMPO-based alkoxyamine for preparation of poly(D₃)-*b*-poly(St) block copolymer.

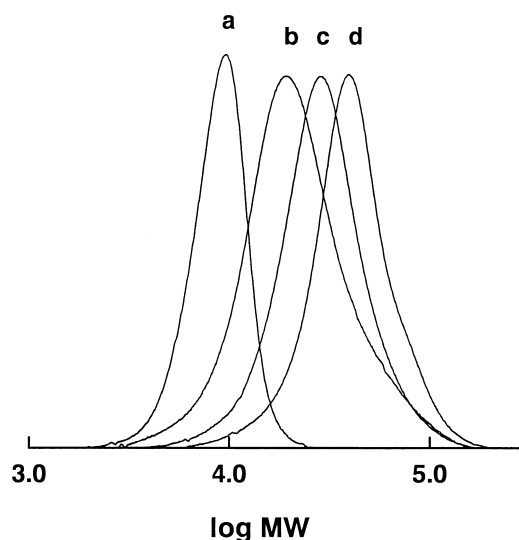


Fig. 4. SEC elution curves of poly(D₃)-*b*-poly(St) block copolymers. (a) poly(D₃) macroinitiator, $M_{n,\text{NMR}} = 6920$, $M_w/M_n = 1.12$; (b) conversion 12%, $M_{n,\text{SEC}} = 17900$, $M_w/M_n = 1.45$; (c) conversion 26%, $M_{n,\text{SEC}} = 25200$, $M_w/M_n = 1.30$; (d) conversion 42%, $M_{n,\text{SEC}} = 35400$, $M_w/M_n = 1.27$.

3.3. Preparation of poly(NBE)-*b*-poly(St) block copolymer

The procedure for preparation of poly(NBE)-*b*-poly(St) block copolymer is described in Scheme 4. The ROMP of NBE with $\text{RuCl}_2(=\text{C}=\text{CHBu}-t)(\text{PCy}_3)_2$ in the presence of **3** was carried out according to a previously reported procedure [17–19]. In this metathesis polymerization, alkoxyamine **3** functions as a chain transfer agent; namely, the reaction of **3** with $\text{RuCl}_2(=\text{C}=\text{CHBu}-t)(\text{PCy}_3)_2$ yields $\text{RuCl}_2(=\text{CHOCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{-TEMPO})$, $(\text{PCy}_3)_2$ which initiates ROMP of NBE to give the poly(NBE) macroinitiator having the **3** unit at one end of the resulting polymer chain. A mixture of NBE, $\text{RuCl}_2(=\text{C}=\text{CHBu}-t)(\text{PCy}_3)_2$, and **3** in a 100:1:4 molar ratio was stirred in CH_2Cl_2 at room temperature for 20 h under N_2 , and the mixture was poured into a large amount of MeOH to give poly(NBE) as a gray powder in 85% yield. The poly(NBE) was purified by reprecipitation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

The poly(NBE) macroinitiator was analyzed by the ^1H NMR and SEC measurements. The ^1H NMR spectrum is depicted in Fig. 5(a). The assignments of the protons of poly(NBE) were performed according to a previous report [17]. Upon recording at high gain, the peaks due to the phenylalkoxyamine protons were detected. By comparing the intensity of the quartet peak due to $-\text{CH}(\text{Ar})\text{CH}_3$ (H^a in Fig. 5(a)) at 4.73 ppm with those of the singlet peaks due to $=\text{CH}-(1,3\text{-cyclopentylene})-\text{CH}=(\text{H}^d$ in Fig. 5(a)) at 5.20 and 5.34 ppm, the M_n was determined to be 10 000. On the other hand, the M_n determined by SEC measurements was 13 500, indicating a large discrepancy between $M_{n,\text{NMR}}$ and $M_{n,\text{SEC}}$. This is due to the use of the poly(St) standards different in flexibility from poly(NBE) in the SEC measurements, similar to the case of poly(D_3) described above. We therefore used the M_n s determined by the NMR method in further study. Unfortunately, the polydispersity indexes for the poly(NBE)s obtained were always high (>2.0). This means that, even if the resultant St polymerization initiated with poly(NBE) macroinitiator successfully proceeded in a living fashion, the resultant poly(NBE)-*b*-poly(St) would show a relatively high polydispersity index.

The radical polymerization of St initiated by the poly(NBE) was carried out at 120 °C. After the prescribed times, the mixtures were poured into a large amount of MeOH, and the resulting block copolymers were collected by filtration.

The ^1H NMR spectrum of poly(NBE)-*b*-poly(St) block copolymer is drawn in Fig. 5(b). The broad multiplets observed in 6.3–7.2 ppm are assigned to the aromatic protons of the poly(St) units, and four peaks at 5.20, 5.34, 2.42, and 2.78 ppm are assigned to H^d and H^g in the poly(NBE) units, respectively. The peaks due to $-\text{CH}_2-\text{CH}(\text{Ph})-$ of the poly(St) units and the peaks due to H^e and H^f in the poly(NBE) units overlap with each other in 1.20–2.10 ppm.

The $\ln([M]_0/[M]_t)$ vs. time plots are depicted in Fig. 6. A linear relationship between $\ln([M]_0/[M]_t)$ and time is

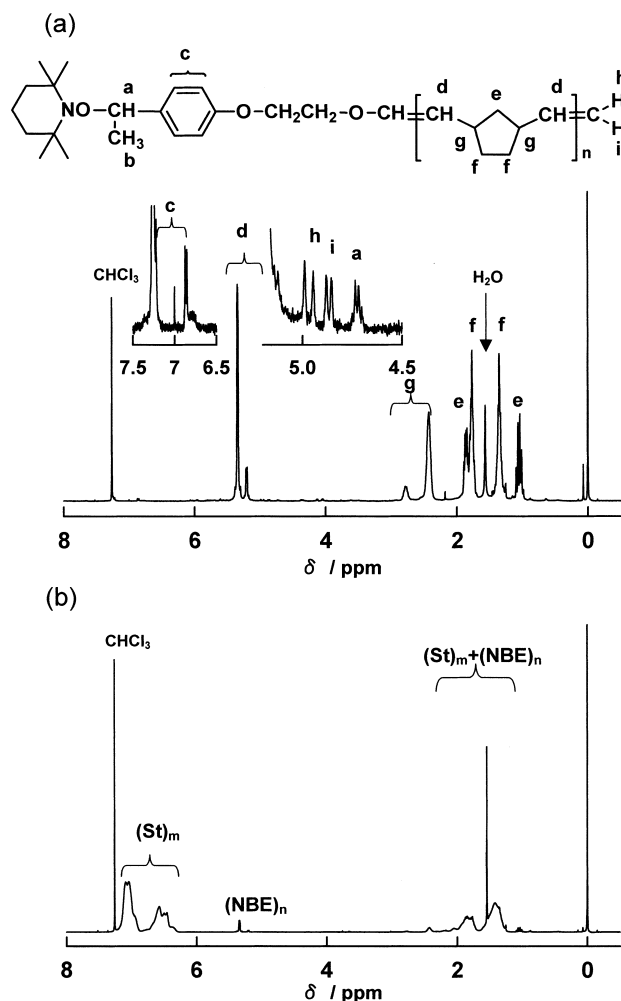


Fig. 5. (a) ^1H NMR spectra of poly(NBE) macroinitiator and (b) poly(NBE)-*b*-poly(St) block copolymer in CDCl_3 . The inset refers to a spectrum recorded at high gain. The asterisks indicate impurities. (b) ^1H NMR spectrum of poly(NBE)-*b*-poly(St) block copolymer at 73% conversion ($M_{n,\text{NMR}} = 164\,000$, $M_w/M_n = 2.06$).

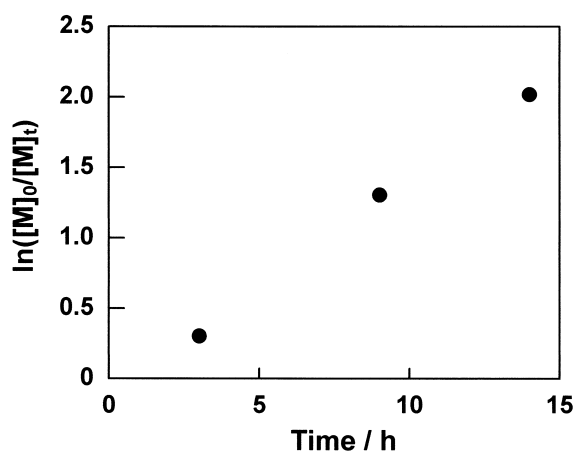


Fig. 6. The $\ln([M]_0/[M]_t)$ vs. time plots for the polymerization of St initiated with poly(NBE) macroinitiator. St 0.50 ml, poly(NBE) macroinitiator ($M_{n,\text{NMR}} = 10\,000$, $M_w/M_n = 2.60$) 4.0 mmol l^{-1} , temperature 120 °C.

established throughout the polymerization, indicating that the number of the propagating chains is constant. The M_n vs. conversion and M_w/M_n vs. conversion plots are shown in Fig. 7(a) and (b). In Fig. 7(a), both $M_{n,SEC}$ and $M_{n,NMR}$ are plotted against conversion. The $M_{n,NMR}$ s were determined by comparing the intensity of the peaks due to H_d in the poly(NBE) units with those of the peaks due to the aromatic protons of the poly(St) units. Although the $M_{n,SEC}$ s deviate largely from the calculated M_n s obtained using Eq. (1), the $M_{n,NMR}$ s are in satisfactory agreement with the calculations and increase linearly with conversion. Fig. 7(b) shows that, although the M_w/M_n is high (2.23) in the initial stage of polymerization but decreases considerably with conversion. However, it is still high even at high conversion (1.99 at 87% conversion). This is in part ascribed to the broad molecular weight distribution (2.60) of the poly(NBE) used as a macroinitiator. Other possible reason for the broad polydispersity may be the influence from the side reactions which increase the polydispersity indexes of the resultant polymers. The side reactions can be appreciably suppressed by use of high concentrations of alkoxyamines [23–25]. In this sense, if the polymerization of St was carried out using the poly(NBE) macroinitiator in a higher concentration (in the present study, 4.0 mmol l^{-1}), more well-controlled poly(NBE)-*b*-poly(St) block copolymers with lower polydispersity indexes might be obtained.

In Fig. 8, the SEC elution curves for the block copolymers obtained are shown, together with that of the poly(NBE) macroinitiator. Every elution curves show an unimodal molecular weight distribution, and the peaks shift to a higher molecular region with conversion. No peak due

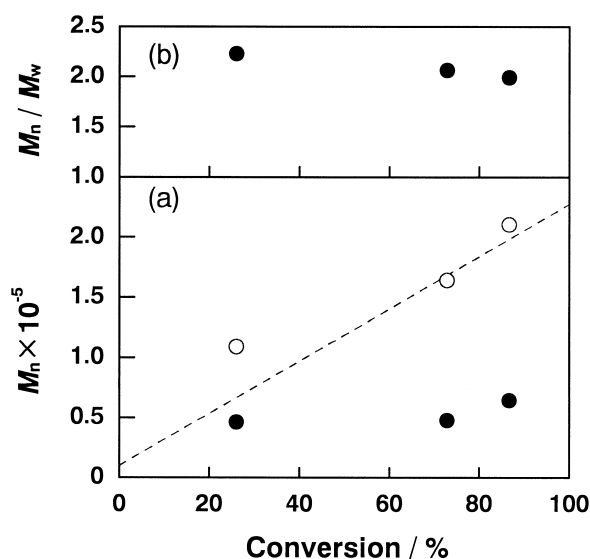


Fig. 7. (a) The M_n vs. conversion plots and (b) the M_w/M_n vs. conversion plots for the polymerization of St initiated with poly(NBE) macroinitiator. St 0.50 ml, poly(NBE) macroinitiator ($M_{n,NMR} = 10\,000$, $M_w/M_n = 2.60$) 4.0 mmol l^{-1} , temperature 120°C . (●) $M_{n,SEC}$ vs. conversion plots; (○) $M_{n,NMR}$ vs. conversion plots. The calculated molecular weights are shown in a dotted line.

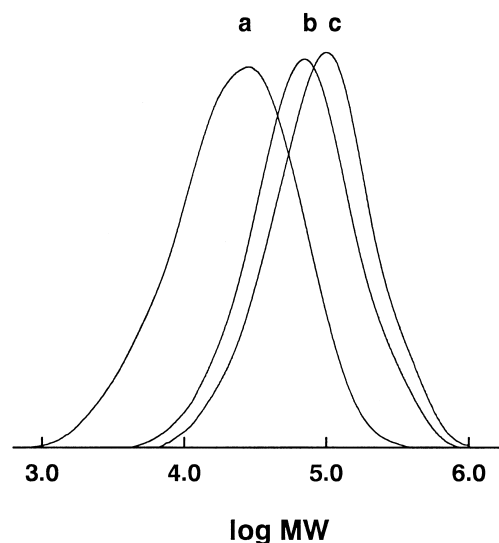


Fig. 8. SEC elution curves of poly(NBE)-*b*-poly(St) block copolymers. (a) poly(NBE) macroinitiator, $M_{n,NMR} = 10\,000$, $M_w/M_n = 2.60$; (b) conversion 26%, $M_{n,NMR} = 109\,000$, $M_w/M_n = 2.23$; (c) conversion 87%, $M_{n,NMR} = 210\,000$, $M_w/M_n = 1.99$.

to the poly(NBE) homopolymer is found in any elution curve, indicating that all the poly(NBE) macroinitiator chains initiated the polymerization of St, similar to the case of the poly(D_3) macroinitiator.

4. Conclusion

In the present study two kinds of block copolymers, poly(D_3)-*b*-poly(St) and poly(NBE)-*b*-poly(St), were prepared by the combination of ROAP of D_3 and NMRP of St and ROMP of NBE and NMRP of St, respectively. The NMRPs of St initiated with poly(D_3) and poly(NBE) macroinitiators proceeded in the living fashion to give well-defined poly(D_3)-*b*-poly(St) and poly(NBE)-*b*-poly(St), respectively. It is concluded that the present method using the functional alkoxyamines **2** or **3** is a nice approach to well-defined poly(D_3)-*b*-poly(St) and poly(NBE)-*b*-poly(St) block copolymers. Furthermore, since **2** has a capability to initiate a wide variety of anionic monomers, a variety of well-defined block copolymers will be obtained by using **2** as a multifunctional alkoxyamine via combination of anionic and radical polymerization.

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