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Syntheses of AB_2 3- and AB_4 5-miktoarm star copolymers by combination of the anionic ring-opening polymerization of hexamethylcyclotrisiloxane and nitroxide-mediated radical polymerization of styrene

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Abstract

AB_2 3- and AB_4 5-miktoarm star copolymers were prepared by combination of the anionic ring-opening polymerization (AROP) of hexamethylcyclotrisiloxane (D_3) and the TEMPO-mediated radical polymerization of styrene (St). Initially, two kinds of dendritic multifunctional initiators were prepared. One has a 4-bromobutoxy group and two TEMPO-based alkoxyamines and the other has a 4-bromobutoxy group and four TEMPO-based alkoxyamines. Treatment of the multifunctional initiators with *tert*-butyllithium gave the corresponding lithiobutoxy derivatives, and AROP of D_3 by the lithiobutoxy derivatives gave poly(D_3) with M_w/M_n of 1.07–1.12. Nitroxide-mediated radical polymerization of St by the poly(D_3)s at 120 °C gave AB_2 3- and AB_4 5-miktoarm star copolymers with M_w/M_n of 1.15–1.28. Their structures were analyzed by means of ^1H NMR and SEC measurements.

Keywords: Living radical polymerization; Miktoarm star copolymer; Polysiloxanes

1. Introduction

Miktoarm star copolymers have attracted much attention in recent years because they show the interesting unique properties regarding microphase separation in solid state as well as in solution [1–3]. Therefore, those possess potential importance as new functional materials. Although miktoarm star copolymers have been synthesized mainly by the anionic polymerization [1–4], the recent development in the living radical polymerization (LRP) [5–9] has brought about a drastic change in the synthetic methodology for miktoarm star copolymers for the last 5 years [10–34]. The radical polymerization technique is more convenient than the anionic polymerization technique because it does not require strict purification of monomers and solvents and allows the presence of a variety of functional groups. There are two methods for the syntheses of miktoarm star copolymers by the LRP technique: the core-first method and the arm-first method. Although the arm-first method provides a convenient approach to miktoarm star copolymers, it does not afford well-defined miktoarm star copolymers [12,23,24]. On the other hand, the core-first method requires the design and syntheses of appropriate multifunctional initiators, but it provides well-defined structures with the constant arm numbers and constant arm lengths [10–11,13–22,25–34]. In a series of the studies on design and syntheses of well-defined polymeric architectures using the LRP technique [35–41], we synthesized star polymers, miktoarm star copolymers by the core-first method. In the present paper, we report the first successful syntheses of polysiloxane-containing AB_2 3- and AB_4 5-miktoarm star copolymers by combination of the anionic ring-opening polymerization (AROP) of hexamethylcyclotrisiloxane (D_3) and the nitroxide mediated radical polymerization (NMRP) of styrene (St) using dendritic tri- and pentafunctional initiators (Chart 1). It is well known that polysiloxanes are materials that show unique properties such as high chain flexibility, low surface energy, and low solubility parameter, etc. Consequently, the syntheses of polysiloxane-containing polymeric architectures are highly important for designing new materials. Some polysiloxane-containing miktoarm star copolymers were prepared using the anionic polymerization technique. Isono et al. prepared ABC 3-miktoarm star copolymer by the anionic polymerizations of D_3, St, and *t*-butyl acrylate [42], and Hadjichristidis, et al. reported the syntheses of AB_2 and ABC

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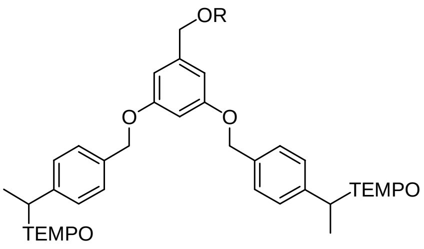
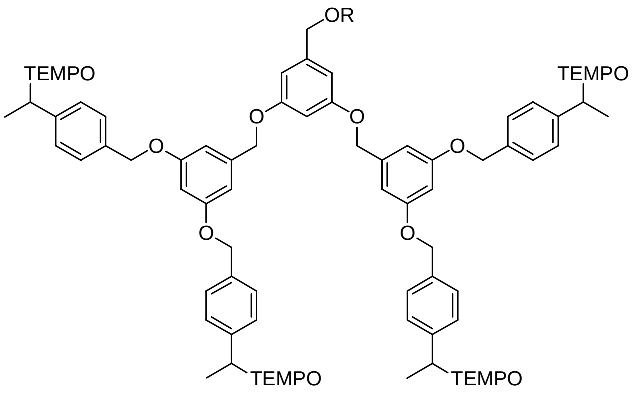


[G-1]-OH: R = H
[G-1]-O(CH$_2$)$_4$Br: R = (CH$_2$)$_4$Br
[G-1]-O(CH$_2$)$_4$Li: R = (CH$_2$)$_4$Li



[G-2]-OH: R = H
[G-2]-O(CH$_2$)$_4$Br: R = (CH$_2$)$_4$Br
[G-2]-O(CH$_2$)$_4$Li: R = (CH$_2$)$_4$Li

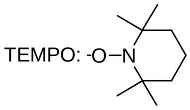


Chart 1.

3-miktoarm star copolymers by the anionic polymerizations of D$_3$ and St, and isoprene [43]. However, the syntheses of polysiloxane-containing miktoarm star copolymers via the LRP technique have never been reported.

2. Experimental section

2.1. General

^{1}H NMR spectra were measured with a JEOL α-400 spectrometer (400 MHz). Chemical shifts (δ) are expressed in ppm downfield from TMS as the internal standard. High resolution (HR) FAB mass spectra were recorded on a JEOL JMS-AX500 spectrometer. Preparative HPLC purification was performed with a Japan Analytical Industry LC-908 preparative recycling HPLC instrument with CHCl$_3$ as the eluant. Size exclusion chromatography (SEC) was carried out with a Tosoh 8020 series using TSKgel G5000H$_{HR}$, MultiporeH$_{XL}$-M, and GMH$_{HR}$-L columns calibrated with polystyrene standards, eluting with THF at 40 °C. Detection was made with a Tosoh refractive index detector RI8020.

2.2. Materials

[**G-1**]-OH and [**G-2**]-OH were prepared by our previously reported method [37,39, 40]. 2,2,6,6-Tetramethylpiperidinyl-*N*-oxyl (TEMPO) was commercially available (Aldrich) and purified by sublimation. *tert*-Butyllithium (*t*-BuLi) was obtained from Kanto Chemical as heptane solution (concentration 1.60 M). Commercially available D$_3$ was refluxed in toluene for 12 h in the presence of CaH$_2$ and, after filtration, the toluene was evaporated and the residue was sublimed prior to use. St was purified prior to use by the usual method. THF and diethyl ether were distilled from benzophenone/Na. Column chromatography was carried out on silica gel (Kanto Chemical N60).

2.3. Synthesis of [G-1]-O(CH$_2$)$_4$Br

NaH (0.23 g, 9.6 mmol), washed with anhydrous THF, was added to a solution of [**G-1**]-OH (4.49 g, 6.54 mmol) in anhydrous THF (10 mL). After the mixture was stirred for 30 min at room temperature, the THF was removed under reduced pressure. 1,4-Dibromobutane (7.06 g, 32.7 mmol) and dry DMF (3.5 mL) were added and the resultant mixture was stirred at 60 °C for 48 h under N$_2$. After water (50 mL) was added, the mixture was extracted with ether, and the combined ether extracts were dried over anhydrous MgSO$_4$. After filtration, the ether was evaporated under reduced pressure and the residue was chromatographed on silica gel with 1:7 EtOAc–hexane to give [**G-1**]-O(CH$_2$)$_4$Br in 58% yield (3.07 g) as a colorless viscous oil. The oil was further purified with a preparative recycling HPLC instrument using CHCl$_3$. HRFABMS: *m/z* calcd for $C_{47}H_{69}\ {}^{79}BrN_2O_5\ (M+1)^+$ 821.4468. Found: 821.4443. Calcd for $C_{47}H_{69}\ {}^{81}BrN_2O_5\ (M+1)^+$ 823.4468. Found: 823.4459. ^{1}H NMR (CDCl$_3$): δ 0.68, 1.02, 1.16, 1.29 (s, CH$_3$, 24H), 1.37–1.60 (br m, (CH$_2$)$_3$, 12H), 1.47 (d, $J = 6.6$ Hz, CHCH_3, 6H), 1.75 (quint, $J = 6.4$ Hz, OCH$_2$CH$_2$CH_2CH$_2$Br or OCH$_2$CH_2CH$_2$CH$_2$Br 2H), 1.98 (quint, $J = 6.4$ Hz, OCH$_2$CH_2CH$_2$CH$_2$Br or OCH$_2$CH$_2$CH_2-CH$_2$Br, 2H), 3.44 (t, $J = 6.4$ Hz, OCH_2CH$_2$CH$_2$CH$_2$Br, 2H), 3.48 (t, $J = 6.4$ Hz, OCH$_2$CH$_2$CH$_2$CH_2Br, 2H), 4.44 (s, benzylic, 2H), 4.79 (q, $J = 6.6$ Hz, CHCH$_3$, 2H), 5.00 (s, benzylic, 4H), 6.54 (t, $J = 2.0$ Hz, aromatic, 1H), 6.59 (d, $J = 2.0$ Hz, aromatic, 2H), 7.33 (d, $J = 8.4$ Hz, aromatic, 4H), 7.36 (d, $J = 8.4$ Hz, aromatic, 4H).

2.4. Synthesis of [G-2]-O(CH$_2$)$_4$Br

NaH (60% in oil) (0.050 g, 2.1 mmol), washed with anhydrous THF, was added to a solution of [**G-2**]-OH (2.00 g, 1.35 mmol) in anhydrous THF (5.0 mL). After the mixture was stirred at room temperature for 30 min, THF was removed under reduced pressure. 1,4-Dibromobutane (1.46 g, 6.75 mmol) and dry DMF (3.0 mL) were then added, and the resultant mixture was stirred at 60 °C for 48 h under N$_2$. After water (50 mL) was added, the mixture was extracted with ether and the combined ether extracts were dried over anhydrous MgSO$_4$. After filtration, the ether was evaporated under