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Controlled monomer insertion into polymer main chain: synthesis of sequence ordered polystyrene containing thiourethane and trithiocarbonate units by the RAFT process†

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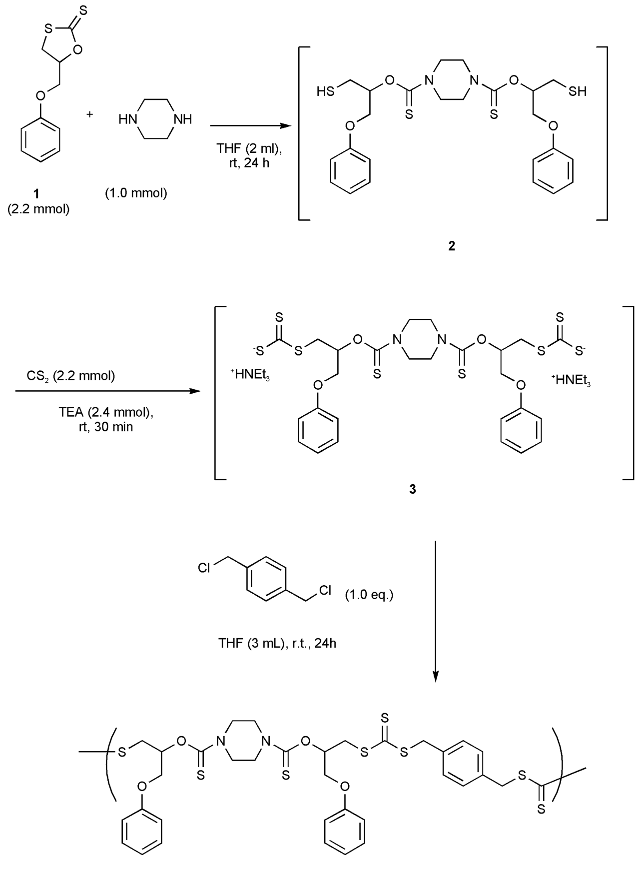
A polymer having a trithiocarbonate moiety in the main chain was applied as a polymeric precursor to the synthesis of a sequence ordered polymer by insertion polymerization of styrene into the main chain by a RAFT mechanism.

Appropriate design of the spatial arrangement of functional groups is quite important in fabrication of functional materials. Especially, distance between sequentially spaced functional groups would be one of the most important factors to determine material properties.[1] Herein, we report a novel strategy to synthesize a sequence-ordered polymer, whose repeating thiocarbonyl unit in the main chain can be arranged with a desired distance by radically induced well-defined insertion of styrene into the polymer main chain. Our strategy involves synthesis of a polymeric precursor having a trithiocarbonate moiety in the main chain, and insertion of styrene into the main chain through reversible-addition fragmentation-chain-transfer, the RAFT process, which is highly reliable and now widely applied to living radical polymerization.[2] Clouet *et al.* have reported an analogous system based on a photo-iniferter process using thiuram disulfide moiety as a reversibly dissociating group, but the molecular weight of the inserted polystyrene segment is not satisfactorily controlled.[3]

The polymeric precursor **4** having trithiocarbonate moiety was synthesized from dithiol **2**, which was prepared by the reaction of a five-membered cyclic thiocarbonate (**1**) with piperazine (Scheme 1). The cyclic thiocarbonate **1** was synthesized by the reaction of glycidyl phenyl ether with carbon disulfide (CS_2) under mild conditions,[4,5] and it readily underwent a ring-opening reaction with piperazine. We had reported that analogously formed bis(thiourethane thiol)s[5] could be applied as bifunctional monomers for polyaddition and polycondensation to afford a wide variety of sulfur-containing polymers.[6] Thus we carried out the reaction of dithiol **2** with CS_2 to obtain bifunctional trithiocarbonate anion **3**. This *in-situ* prepared **3** was successively treated with dichloro-*p*-xylene to accomplish polycondensation to afford the corresponding polymer **4** successfully,[7] having a unimodal profile in size exclusion chromatography (SEC) eluted with THF by polystyrene calibration. Incorporation of a trithiocarbonate moiety into the polymer main chain was confirmed by the appearance of the corresponding IR absorption at 1062 cm^{-1} and a ^{13}C-NMR signal at 221.9 ppm. The presence of a thiourethane moiety was also confirmed both by IR and ^{13}C-NMR spectroscopic studies, in which absorption at 1171 cm^{-1} and a signal at 185.9 ppm were observed, respectively. Quantitative incorporation of CS_2 was confirmed by elemental analysis of the polymer **4**.

Insertion of styrene into **4** (15 eq. to trithiocarbonyl moiety) was carried out in the presence of *tert*-butyl peroxide (TBPO, 1 eq. to trithiocarbonate moiety) in a sealed glass ample at 120 °C for 2 h (Scheme 2).[8] After 2 h, the SEC peak of the polymer shifted toward the higher molecular weight region, indicating successful insertion of styrene into the polymer main chain. The ^1H NMR spectrum of **5** exhibited broad signals at 1.20–2.60 ppm, which were assignable to the main chain of polystyrene (See ESI† Fig. 1). Fig. 2 of the ESI† illustrates the ^{13}C NMR spectra of **4** and **5**, before and after the styrene insertion experiment. The ^{13}C NMR spectrum of **5** showed signals at 220.5 and 186.2 ppm, which were assignable to the trithiocarbonate and thiourethane carbon atoms, respectively.[9] The incorporated trithiocarbonate moiety could be cleaved by treatment with *n*-butylamine to afford the corresponding polystyrene **6** with thiol end groups (Scheme 2),[2b,10] whose structure was confirmed by NMR spectroscopy. The molecular weight of **6** agreed well with the theoretical value (M_n = 2900), and the



4 M_n = 5,200, M_w/M_n = 1.52

Scheme 1

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† Electronic supplementary information (ESI) available: ^1H and ^{13}C-NMR spectra of polymer precursor **4** and polymer **5**. See http://www.rsc.org/suppdata/cc/b2/b205523f/

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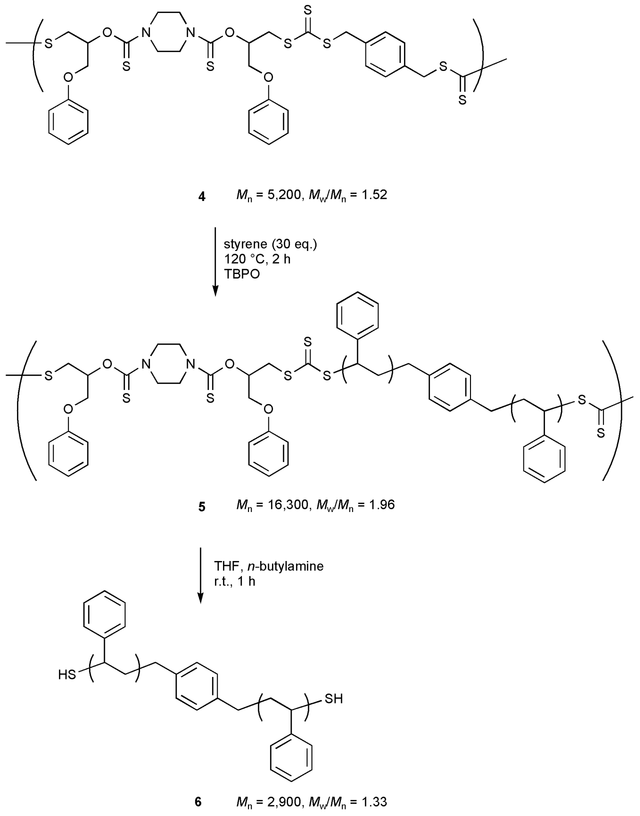

Scheme 2

molecular weight distribution was narrow (M_w/M_n = 1.33). It is indicated that the insertion polymerization proceeded in a controlled manner *via* the RAFT process.

The ability of the RAFT process to control the insertion polymerization was also demonstrated by studying the M_n dependence of 5 on the styrene conversion. Insertion polymerization of styrene (150 eq. to trithiocarbonate moiety) was carried out in the presence of **4** and TBPO (1 eq. to trithiocarbonate moiety) at 120 °C. As shown in Fig. 1, the M_n of **5** increased almost linearly respective to the conversion of styrene. The molecular weight of polystyrene **6**, obtained by treatment of the corresponding **5** with *n*-butylamine, increased almost linearly respective to the styrene conversion, maintaining narrow polydispersity indexes. These results indicate that the present polymerization is free from termination reaction, and styrene is inserted into the polymer in a living fashion.

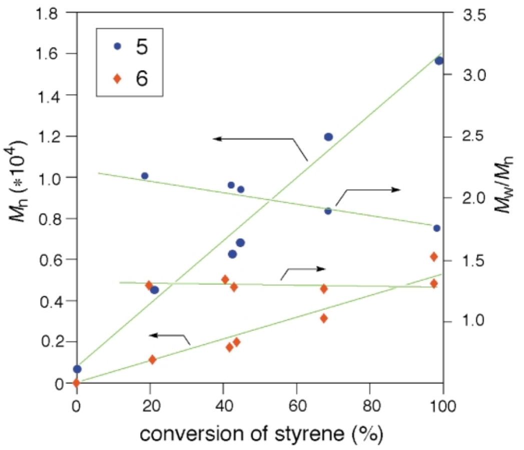

Fig. 1 Relationships between M_n of **5** and conversion in the insertion polymerization of styrene (in bulk, at 120 °C).

In summary, the present study has demonstrated a successful synthesis of a sequentially ordered polymer by controlled insertion of styrene into the polymeric precursor **4** having a trithiocarbonate moiety in the main chain. Extension of this study using various monomers as well as expanding structural diversity of a polymeric precursor will be reported in a forthcoming paper.

Notes and references

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7 Synthesis of **4**; to a solution of 5-phenoxymethyl[1,3]oxathiolane-2-thione (**1**) (0.50 g, 2.2 mmol) in THF (2 mL) was added piperazine (0.086 g, 1.0 mmol) at ambient temperature under nitrogen. After the resulting mixture was stirred for 24 h, CS_2 (0.168 g, 2.2 mmol) and triethylamine (TEA, 0.223 g, 2.4 mmol) were added to the mixture. To the mixture was added a solution of dichloro-*p*-xylene (0.17 g, 1.0 mmol) in THF (3 mL) at ambient temperature, and the reaction mixture was further stirred under nitrogen for 24 h. The resulting yellowish transparent reaction mixture was poured into water, and it was extracted three times with CH_2Cl_2. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to obtain yellow oil, which was poured into a large amount of diethyl ether. The precipitate was separated by filtration, and dried *in vacuo* to obtain polytrithiocarbonate (**4**) in 95% yield. ^{1}H NMR ($CDCl_3$): δ 3.62–3.73 (4H, br s), 4.04–4.07 (4H, br s), 4.22–4.28 (4H, br s), 4.55 (2H, br s), 6.88–7.28 (18H, br s). ^{13}C NMR ($CDCl_3$): δ 36.8, 41.2, 44.3, 48.29, 67.2, 114.7, 121.5, 128.9, 129.6, 134.5, 134.6, 134.7, 135.2, 137.1, 158.3, 186.3, 222.1. IR: 1062, 1171 cm^{-1}. EA: Calcd for $C_{34}H_{36}O_4N_2S_8$. C, 51.48; H, 4.57; N, 3.53; S, 32.34. Found C, 51.21; H, 4.42; N, 3.79; S, 32.62%.

8 To a 5 mL glass ample containing TBPO (0.028 g, 0.19 mmol) were fed **4** (0.16 g, 0.2 mmol) and styrene (0.31 g, 3.0 mmol). It was degassed, sealed off under vacuum, and heated at 120 °C for 2 h. After the glass ample was cooled to room temperature, polymer **5** was isolated by precipitation with hexane.

9 ^{1}H, ^{13}C-NMR spectrum are available as ESI.†

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