

## Reduction Reaction to Thiol Group of Dithiobenzoate End Group in Polystyrene Polymerized by Reversible Addition–Fragmentation Chain Transfer

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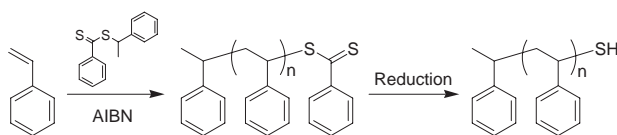
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A dithiobenzoate end group of polystyrene generated by reversible addition–fragmentation chain-transfer radical polymerization was reduced to a thiol group in various reduction methods, and the structure of the products was analyzed using <sup>1</sup>H NMR, IR, and MALDI-TOFMS. It was found that the side reactions including a dimerization of the polymers were observed and they can be prevented by a specific process.

Reversible addition–fragmentation chain-transfer (RAFT) radical polymerization, a kind of living radical polymerization, is known to be a useful method for not only the control of molecular weight and polydispersity of polymers but also synthesis of block copolymers.<sup>1</sup> The dithiobenzoate end group of the polymers produced by the RAFT polymerization can be functionalized to a thiol group using a reducing agent. There are several methods to reduce the end group of the polymers, for example metal hydrides reduction,<sup>2–7</sup> aminolysis,<sup>8–11</sup> and hydrolysis.<sup>12</sup> In their reduction methods, disappearance of the dithiobenzoate end group was confirmed. However, the reaction mechanism and the evidence of generation of the thiol end group are not discussed in detail. Besides, a dimerization of the reactant was observed as a side reaction in some papers.<sup>8–11</sup> The resulting polymers with the thiol end group can be used for functionalization of noble metal surface and metal nanoparticles. In this letter, we report on the structure of polystyrenes (PSTs) reduced by different reaction conditions using various reducing agents. We found that the use of NaBH<sub>4</sub> in water/THF as the reduction method produced PST with the controlled molecular weight, polydispersity, and end group.

PST with the dithiobenzoate end group was synthesized by the RAFT polymerization using styrene, azobisisobutyronitrile (AIBN), and 1-phenylethyl dithiobenzoate (PEDB) as the RAFT agent (Scheme 1).<sup>13</sup> Reduction reactions of the dithiobenzoate group were performed in four different methods using NaBH<sub>4</sub> in water/THF phase, NaBH<sub>4</sub> in water/toluene with tetraoctylammonium bromide (TOAB) as the phase-transfer reagent,<sup>14</sup> Super-Hydride (lithium triethylborohydride) in THF,<sup>2</sup> and propylamine in THF,<sup>11</sup> as shown in Table 1.

Disappearance of the dithiobenzoate group in each reduced



**Scheme 1.** Synthesis and reduction of PST with dithiobenzoate group.

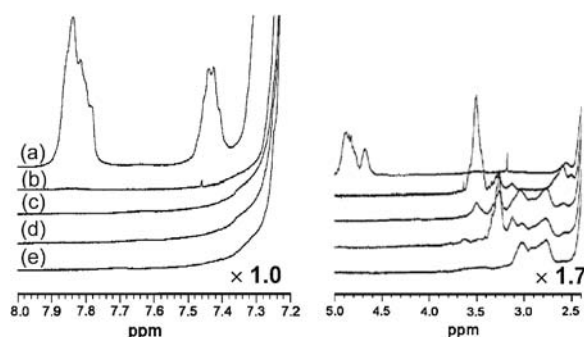
**Table 1.** Conditions of reduction reaction in the end groups<sup>a</sup>

Reactant <sup>b</sup> /Solvent (usage)	Additive (usage)	Reducing agent/Solvent (usage)
PST/THF (200 mg/5 mL)	—	NaBH <sub>4</sub> /water (179 mg/1 mL)
PST/toluene (200 mg/3 mL)	TOAB (344 mg)	NaBH <sub>4</sub> /water (179 mg/3 mL)
PST/THF <sup>c</sup> (200 mg/5 mL)	—	Super-Hydride/THF <sup>d</sup> (1 mL) under Ar
PST/THF (200 mg/5 mL) <sup>e</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /water (a few drops)	propylamine (1 mL) <sup>e</sup> under Ar

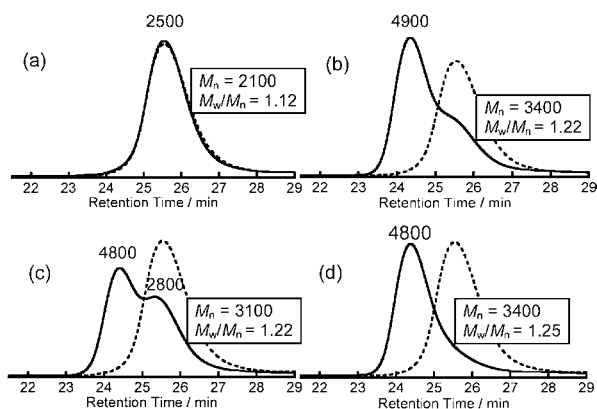
<sup>a</sup>All reactions were carried out for 1.5 days at room temperature. The resulting polymers were purified by reprecipitation. <sup>b</sup>Produced by bulk polymerization of styrene for 4 days at 60 °C ([PEDB] = 0.117 M, [AIBN] = 1.06 × 10<sup>-2</sup> M). *M<sub>n</sub>*(GPC) = 2100, *M<sub>w</sub>*/*M<sub>n</sub>* = 1.14. <sup>c</sup>Anhydrous THF. <sup>d</sup>1.0 M Super-Hydride in THF solution is commercially available. <sup>e</sup>Degassed by freeze–pump–thaw cycle before reaction.

PST was confirmed by IR spectrum,<sup>15</sup> UV–vis absorption spectrum (see Figures S1 and S2 in Supporting Information),<sup>16</sup> and <sup>1</sup>H NMR spectrum.<sup>17</sup> In these spectra, peaks derived from the RAFT end group disappeared certainly, but four <sup>1</sup>H NMR spectra in Figures 1b–1e are different from each other at 2.5–3.7 ppm.<sup>18</sup> This indicates that the structure of the end group of the reduced PSTs varies with the reduction methods and reaction conditions.

Gel permeation chromatograph (GPC) and matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOFMS) of the dithiobenzoate-terminated PST and the reduced PST are shown in Figures 2 and S3,<sup>16</sup> respectively.



**Figure 1.** <sup>1</sup>H NMR spectra of (a) PST synthesized by RAFT polymerization and PST reduced by (b) NaBH<sub>4</sub> in water/THF, (c) NaBH<sub>4</sub> in water/toluene with TOAB, (d) Super-Hydride in THF, and (e) propylamine in THF.

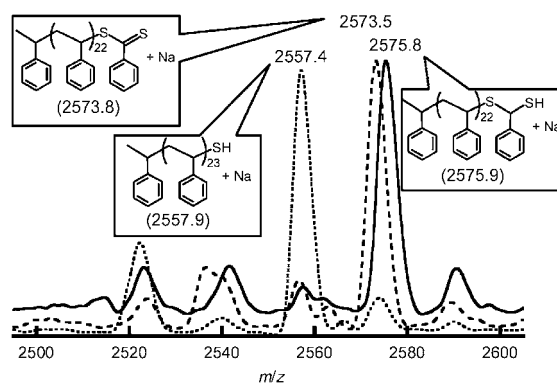


**Figure 2.** GPC elution curves of PST with dithiobenzoate end group (---) and PST reduced by (a) NaBH<sub>4</sub> in water/THF, (b) NaBH<sub>4</sub> in water/toluene with TOAB, (c) Super-Hydride in THF, and (d) propylamine in THF (—). GPC was performed at 40 °C in THF as the eluent. Standard polystyrenes were used as a calibration standard. Figures in the graph correspond to the molecular weight at the top of the peak.  $M_n$  and  $M_w/M_n$  of the polymer after the reduction are shown in box.

The results indicate that the reduction reaction certainly dimerized the polymer through a disulfide group except for the reduction using NaBH<sub>4</sub> in water/THF. The degree of dimerization reaction depends on the reaction conditions. The reaction with Super-Hydride in THF or propylamine in THF proceeded with very fast, whereas the reduction with NaBH<sub>4</sub> in water/THF was slow. Hence, it is thought that the dimerization reaction may be caused by strong reducing ambient.

Enlarged MALDI-TOFMS of PST with the dithiobenzoate group, PST reduced by NaBH<sub>4</sub> in water/THF, and PST reduced by Super-Hydride in THF are shown in Figure 3. The main peak of PST synthesized by RAFT accounts for ca. 52% of all MS peak intensity, and the peak corresponds to the structure with the dithiobenzoate end group. Other peaks produced during the measurement of MALDI-TOFMS can be assigned by referring to previous studies.<sup>9,19</sup> The peaks of PST with the thiol end group are confirmed in each polymer after the reduction. Especially, products reduced by NaBH<sub>4</sub> in water/THF clearly have the peaks of the polymer with the thiol end group as shown in Figure 3. This main peak accounts for ca. 57% of all MS peak intensity. In contrast, MALDI-TOFMS of PST produced by other reduction methods shows peaks that are related to not only the thiol end group but also other by-products including the dimerized polymer. As shown in Figure 3, the main peak of PST reduced by Super-Hydride in THF around  $m/z$  2575 appeared at two units larger than that of PST with the dithiobenzoate end group. Therefore, it is thought that the peak is derived from a product of the addition of two hydrogens to the dithiobenzoate end group. The MALDI-TOFMS of PST reduced by NaBH<sub>4</sub> in water/toluene with TOAB also shows the same peaks. These results indicate that the strong reduction reactions of the end group in the RAFT polymers generate not only thiolated or dimerized polymers but also other chemical species.

In conclusion, the reduction of PST polymerized by RAFT was performed using various reduction methods. PST with the dithiobenzoate end group was reacted to not only PST with the thiol group but also the dimerized PST through the disulfide



**Figure 3.** MALDI-TOFMS of PST with dithiobenzoate group (---), PST reduced by NaBH<sub>4</sub> in water/THF (···), and reduced by Super-Hydride in THF (—), and possible structures estimated from the results in this study. Dithranol and NaTFA were used as the matrix and the ionization reagent for analysis, respectively. The values in parentheses show the calcd  $m/z$  value including Na.

group and other minor species. However, these side reactions can be prevented by selecting the reduction condition using NaBH<sub>4</sub> in water/THF.

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