

## Synthesis of Dilithium $\alpha,\omega$ -Disulfonated Polystyrene by Anionic Polymerization

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**ABSTRACT:** The chain-end sulfonation of  $\alpha,\omega$ -dilithiopolystyrene prepared by lithium naphthalenide as a difunctional initiator using 1,3-propanesultone was studied by the characterization methodologies such as acid/base titration, colorimetric method using methylene blue, two-phase titration with Hyamine 1622, size exclusion chromatographic analysis infrared, and <sup>1</sup>H NMR spectroscopic analysis. The reactivity modification of  $\alpha,\omega$ -dilithiopolystyrene through the end-capping with 1,1-diphenylethylene prior to the sulfoalkylation in benzene-tetrahydrofuran (THF) (10:1, v/v) at 25°C with excess 1,3-propanesultone is suggested as a useful method for the preparation of the corresponding dilithium  $\alpha,\omega$ -disulfonated polystyrene in relatively high yield based on the results from the acid/base titration (>85%).

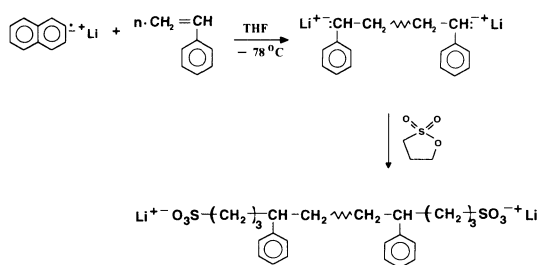
**KEY WORDS**  $\alpha,\omega$ -Dilithiopolystyrene / Difunctional Initiator /  $\alpha,\omega$ -Bis(1-lithio-1,1-diphenylethyl)polystyrene / Sulfoalkylation / 1,3-Propanesultone / Dilithium  $\alpha,\omega$ -Disulfonated Polystyrene / Size Exclusion Chromatography /

Ion-containing polymers have received a great attention in industry as well as academic field because of their unique chemical, thermal, rheological, and mechanical properties.<sup>1-6</sup> Physical properties of these materials have been investigated by studies to the solution behavior of polymers that contain many ionic groups along the polymer backbone and with a statistically random distribution. Investigation of the physical properties of the model ionic polymers with well-defined structures provides presumably the possibility to predict the real properties of a variety of ion-containing polymers.<sup>7-10</sup>

Living anionic polymerization has been known as the best methodology to prepare polymers with control of the major variables that affect polymer properties for a long time.<sup>11-14</sup> Because many of anionic polymerizations proceed in the absence of termination and chain transfer, the growing polymer chain is still active when all of the monomer is consumed.<sup>15</sup> Therefore, these carbanionic chain ends can be reacted with a variety of electrophilic reagents to produce a wide range of the chain-end functional groups.<sup>16,17</sup>

Termination of polymeric carbanion with sultones has been reported.<sup>7,18,19</sup> However,

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Scheme 1.

functionalization with sultones requires severe conditions; it should be carried out in THF and at  $-78^{\circ}\text{C}$  because sodium counterion carbanion is insoluble in hydrocarbon solvents such as benzene, cyclohexane, or toluene. Dilithium  $\alpha,\omega$ -disulfonated polystyrene had been prepared using an initiator with lithium counterion as shown in Scheme 1.

However, the functionalization yield was reported below 70% even at  $-78^{\circ}\text{C}$ .<sup>19</sup> The reason for the low yield in the reaction was a side reaction such as  $\alpha$ -lithiation of 1,3-propanesultone.<sup>9,20</sup> Furthermore, it was also found out that the reactivity of the chain-end affected functionalization yield.<sup>9</sup> Based on this consideration, a new route for synthesis of dilithium  $\alpha,\omega$ -disulfonated polymers is reported.

## EXPERIMENTAL

### Chemicals and Solvents

Benzene and tetrahydrofuran (THF) as solvents and styrene (KANTO Chem. Co., reagent grade) were carefully purified as described previously.<sup>9</sup> 1,1-Diphenylethylene (1,1-DPE; Aldrich Chem. Co., 97%) was stirred over Na–K alloy with degassing, followed by vacuum distillation into calibrated ampoules and dilution with benzene. 1,3-Propanesultone (Aldrich Chem. Co., 90 + %) was dried and degassed on the vacuum line, followed by dilution with benzene or THF. Lithium naphthalenide as the difunctional initiator was prepared in a high vacuum line from the reaction of naphthalene with lithium

wire in THF at  $-78^{\circ}\text{C}$  with stirring for 10 h, followed by filtration using a fritted glass and ampoullization. The ampoules were stored at  $-78^{\circ}\text{C}$  prior to use.

### Polymerization

Poly(styryl)lithium was prepared in benzene–THF (20:1, v/v) by using *n*-butyllithium as the initiator as described previously.<sup>9</sup> Anionic polymerization of styrene by difunctional initiator was carried out in benzene–THF (20:1, v/v) at  $25^{\circ}\text{C}$  for 24 h in all-glass, sealed reactors, using break-seals and standard high vacuum techniques.<sup>21</sup> At first, the initiator, monomer, and terminating agent ampoules were attached to 1 liter of a round bottom flask as the reactor prior to reaction using a hand torch, followed by complete evacuation in a high vacuum line. Appropriate amounts of benzene and THF (10:1, v/v) were distilled into the reactor, in which the volume ratio of monomer to solvent was usually 0.1–0.15, followed by delivery of the difunctional initiator and monomer by breaking the break-seal of the ampoules using a magnetic hammer. On adding monomer into the solution containing the difunctional initiator, the characteristic color of which is a dark green in THF, the color of the reaction solution turned into dark orange which indicated the formation of  $\alpha,\omega$ -dilithiopolystyrene in the mixture of benzene–THF (10:1, v/v). The reaction was carried out at room temperature for 24 h.

### Termination and Functionalization

An aliquot of  $\alpha,\omega$ -dilithiopolystyrene was taken, followed by termination of the aliquot with degassed methanol to produce homopolystyrene. The remaining  $\alpha,\omega$ -dilithiopolystyrene was crossover reacted with 1,1-DPE at  $25^{\circ}\text{C}$  for 24 h, at which the molar ratio of the chain-end concentration to 1,1-DPE was usually 0.1. The resulting  $\alpha,\omega$ -bis(1-lithio-1,1-diphenylethyl)polystyrene was terminated with 1,3-propanesultone/THF. Thus, dilithium  $\alpha,\omega$ -disulfonated polystyrenes were precipi-

tated in 5 times excess volume of methanol, followed by drying in vacuum at 25°C for at least 48 h. The  $\omega$ -sulfonated polystyrene with a relatively high molecular weight compared with that in the previous work was also synthesized as described previously.<sup>9</sup>

### Characterization

Size exclusion chromatographic (SEC) analysis of homopolystyrenes was performed at a flow rate of 1.0 ml · min<sup>-1</sup> in THF at 30°C using the Waters HPLC component system with four Ultrastrygel® columns (10<sup>5</sup>, 10<sup>4</sup>, 2 × 10<sup>3</sup> Å) after calibration with standard polystyrene samples (Polymer Lab.). SEC analysis of dilithium  $\alpha,\omega$ -disulfonated polystyrenes was carried out by using a ternary solvent as the eluent. The ternary solvent consisted of a mixture of 10:1 (v/v) of THF-dimethylformamide (DMF; Fischer Scientific Co., reagent grade; without further purification) containing 2 g · l<sup>-1</sup> of LiNO<sub>3</sub> after calibration with standard samples. The <sup>1</sup>H NMR spectrum was obtained in CDCl<sub>3</sub> on a Geol GSX-500 (500 MHz). FT-IR spectra of homopolystyrene and the functionalized polymer films on NaCl plates were obtained on a Nicolet Magna-IR spectrometer 750.

Colorimetric titrations of the sulfonated polystyrenes were performed by a two-phase colorimetric method and a methylene-blue modified method based on a standard curve generated using the methylene blue complex with sodium lauryl sulfate (Aldrich Chem. Co., 99%). The titration followed the procedures described previously.<sup>9</sup> Direct titration of the acidified polystyrene was performed by the acid-base titration method in benzene-methanol (9:1, v/v) using 0.01 N HCl methanol as a titrant after back titration with 0.01 N of the standard solution of potassium hydrogen phthalate (Fischer Scientific Co., 99.99%) dried at 105°C for 2 h.

## RESULTS AND DISCUSSION

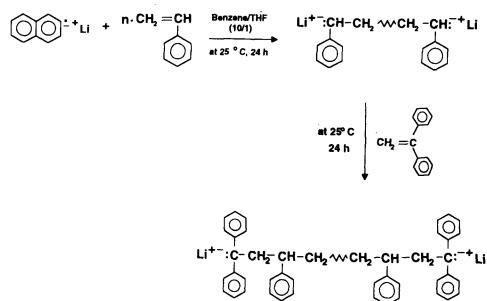
### Living Polymerization

As already described in Scheme 1, Lithium naphthalenide as the difunctional initiator generates 'living'  $\alpha,\omega$ -dilithiopolystyrene in benzene-THF (20:1, v/v) by an electron transfer mechanism at 25°C for 24 h. After the complete consumption of monomer, an aliquot of the living polymer is usually taken in a calibrated cylinder, followed by termination of the aliquot with degassed methanol to obtain the base homopolystyrenes. The remaining living polymer is crossover reacted with 1,1-DPE resulting in the formation of  $\alpha,\omega$ -bis(1-lithio-1,1-diphenylethyl)polystyrene as shown in Scheme 2. On adding 1,1-DPE to the living polymer system, the characteristic color of the polymer solution turns dark orange from orange indicating that the poly(styryl)lithium chain-end has changed to (diphenylalkyl)lithium phenomenologically. This observation can be performed through the UV/vis spectroscopic analysis (from 340 nm to 440 nm).

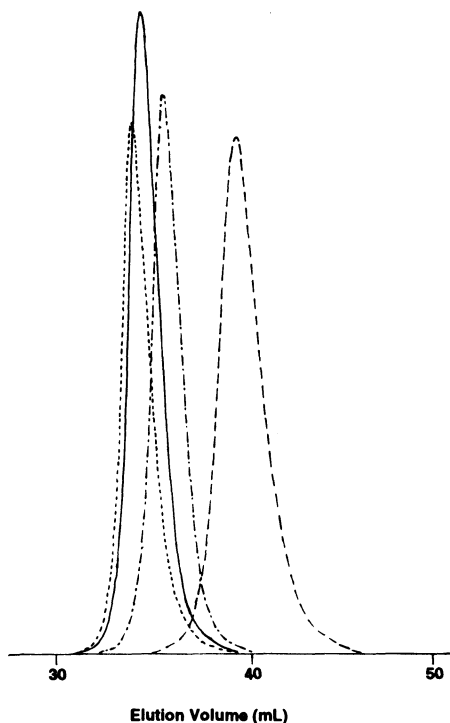
The molecular weights of the corresponding homopolystyrenes were in the range of 1.0 ~ 12.0 × 10<sup>4</sup> and molecular weight distributions were relatively narrow as shown in Table I. SEC results of the corresponding homopolystyrenes using THF as the eluent are shown in Figure 1.

### Functionalization and Characterization

#### $\alpha,\omega$ -Disulfoalkylation of the living polymers



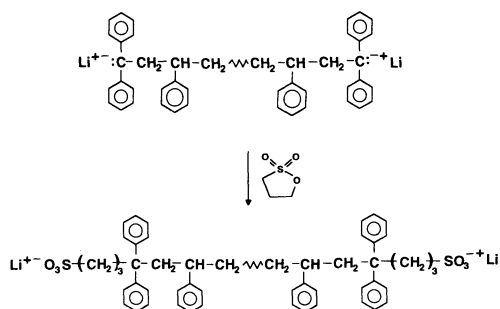
Scheme 2.



**Figure 1.** Size exclusion chromatograms using THF as the eluent of homopolystyrenes in Table I prepared by di- and monofunctional initiators; (---) PS 1, (-·-·-) PS 2, (·-·-·) PS 3, and (—) PS 4.

can be performed by similar procedures to those in the case of  $\omega$ -sulfoalkylation as described previously.<sup>9</sup>  $\alpha,\omega$ -Bis(1-lithio-1,1-diphenylethyl)polystyrene by Scheme 2 presumably reacts with 1,3-propanesultone resulting in the generation of dilithium  $\alpha,\omega$ -disulfonated polymer as shown in Scheme 3.

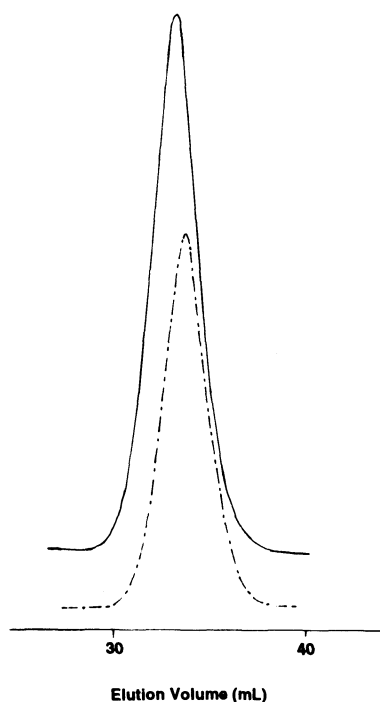
In the sulfonation process, increase of solution viscosity inside the reaction system is observed with the addition of a mixture of 1,3-propanesultone and THF. This is presumably due to the formation of an interpenetrating network or increase of the molecular weight by strong intermolecular association of the chain-end sulfonate groups. Increase of solution viscosity of the dilithium  $\alpha,\omega$ -disulfonated polymer in hydrocarbon in the case of low molecular weight is dominant compared with that of the higher molecular



**Scheme 3.**

weight of polymer. When the product was precipitated in a highly polar medium such as methanol, solubility in alcohol increased with decrease of molecular weight resulting in the formation of an emulsion as in the case of the surfactant.<sup>22</sup> This situation made its purification difficult. It is expected that the purification of the crude dilithium  $\alpha,\omega$ -disulfonated polymer should be performed by an analogous procedure to the  $\omega$ -sulfonated polystyrenes as described previously.<sup>9</sup>

The authors have already mentioned that SEC analysis of the  $\omega$ -sulfonated polystyrene should be performed using a ternary solvent system consisted of the mixture of THF-DMF (10:1, v/v) containing  $2\text{ g}\cdot\text{l}^{-1}$  of  $\text{LiNO}_3$ .<sup>9</sup> A comparison of SECs of PS 1 and the corresponding sulfonated SPS 1 using the ternary solvent as the eluent is shown in Figure 2. SEC of the dilithium  $\alpha,\omega$ -disulfonated polystyrene is monomodal. However, the apparent molecular weight of the dilithium  $\alpha,\omega$ -disulfonated polystyrenes is thought not to be acceptable because we have observed different elution volume in the SEC experiment of terminally-sulfonated polystyrene even in the ternary solvent depending on the amount of  $\text{LiNO}_3$ .<sup>9</sup> The molecular weight distribution is obtained from comparison with that of the corresponding homopolystyrene obtained by the SEC experiment using the ternary solvent as the eluent. The molecular weights of the dilithium  $\alpha,\omega$ -disulfonated polystyrenes were theoretically calculated on the basis of those



**Figure 2.** Comparison of size exclusion chromatograms of homopolystyrene and corresponding dilithium  $\alpha,\omega$ -disulfonated polystyrene in Table I using the ternary solvent as eluent; (—) PS 1 and (---) SPS 1.

of the corresponding homopolystyrenes.

Based on molecular weight, the functionality of each sulfonated polymer was characterized using a variety of the titration methods such as a two-phase titration, and a colorimetric method as already described previously.<sup>9</sup> The acid-base titration followed similar procedures as in the case of polymeric acid titration.<sup>23</sup> The two-phase titration and colorimetric method give relatively large error.<sup>9</sup> A small amount of sultone affected determination of functionalization yield by the two-phase titration and colorimetric titration.<sup>9</sup> However, the acid/base titration provides relatively reliable information on functionalization yield because the sultone does not affect acid/base titration. On the basis of these considerations, the functionalization yields obtained from our sulfonation process are relatively high (over 85%) compared with that obtained from the direct sulfonation<sup>19</sup> as shown in Table I. The sulfonation yield of dilithium  $\alpha,\omega$ -disulfonated polystyrene with relatively low molecular weight (SPS 1) was expected to be underestimated (see SPS 2 and 4 except

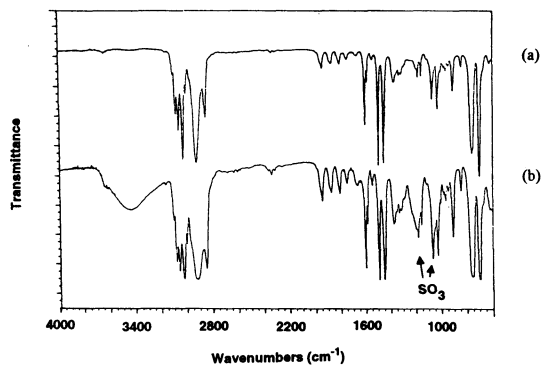
**Table I.** Results of the chain-end sulfonations of living polystyrenes using lithium naphthalenide as a difunctional initiator and *n*-butyllithium

| Sample             | $\bar{M}_n$<br>( $\times 10^3$ ) | $\frac{\bar{M}_w}{\bar{M}_n}$ | Functionality ( <i>f</i> ) |                     |                     |
|--------------------|----------------------------------|-------------------------------|----------------------------|---------------------|---------------------|
|                    |                                  |                               | Acid/base titration        | Two-phase titration | Colorimetric method |
| PS 1               | 18.5                             | 1.13                          |                            |                     |                     |
| SPS 1 <sup>a</sup> | 19.1 <sup>c</sup>                |                               | 1.71                       | 1.85                | 1.68                |
| PS 2               | 63.0                             | 1.09                          |                            |                     |                     |
| SPS 2 <sup>a</sup> | 63.6 <sup>c</sup>                |                               | 1.94                       | 2.20                | 2.03                |
| PS 3               | 115.0                            | 1.07                          |                            |                     |                     |
| SPS 3 <sup>a</sup> | 115.6 <sup>c</sup>               |                               | 1.97                       | 1.86                | 1.31                |
| PS 4               | 102.0                            | 1.07                          |                            |                     |                     |
| SPS 4 <sup>b</sup> | 102.3 <sup>c</sup>               |                               | 1.09                       | 1.57                | 0.90                |

<sup>a</sup> Dilithium  $\alpha,\omega$ -disulfonated polystyrene (difunctional polystyrene).

<sup>b</sup>  $\omega$ -Sulfonated polystyrene (monofunctional polystyrene).

<sup>c</sup> Theoretical molecular weight calculated based on that of the corresponding homopolystyrene obtained from SEC analysis using THF as the eluent.

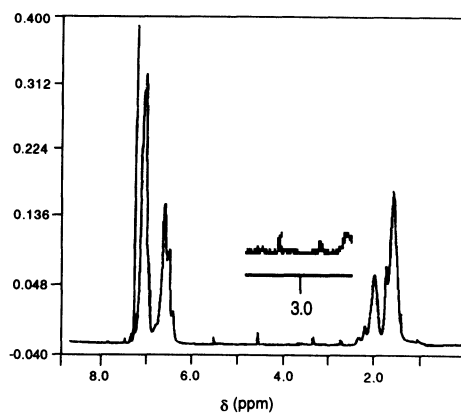


**Figure 3.** Comparison of infrared spectra of homopolystyrene (PS 1) and corresponding dilithium  $\alpha,\omega$ -disulfonated polystyrene (SPS 1) in Table I.

for SPS 3 in Table I). That not only the 1,3-propanesultone is soluble but the low molecular weight fraction of sulfonated polymer forms an emulsion in methanol as already mentioned provides evidence for underestimation. An appropriate portion (*ca.* 5 wt%) of the dilithium  $\alpha,\omega$ -disulfonated polystyrene, SPS 1, was found in the alcoholic filtrate during precipitation and filtration although the presence of unreacted sultone could not be excluded completely. The usual precipitation in methanol in the case of a relatively low molecular weight of sulfonated polystyrenes will not be effective for purification of the product.

Sulfonic acid salts show a strong infrared band in the region of  $1150\sim 1250\text{ cm}^{-1}$  and a medium intensity absorption near  $1050\text{ cm}^{-1}$ .<sup>9,18,24</sup> Figure 3 shows the typical FT-IR spectra of the homopolystyrene (Figure 3a) and corresponding dilithium  $\alpha,\omega$ -disulfonated polystyrene (Figure 3b). The dilithium  $\alpha,\omega$ -disulfonated polystyrene shown in Figure 3b exhibits a broad and strong IR absorption band from  $1150\sim 1250\text{ cm}^{-1}$  and a medium intensity absorption band at  $1052\text{ cm}^{-1}$ . These absorption bands were used to confirm the presence of the sulfonate group in polymers.

The  $^1\text{H}$  NMR spectrum of the crude dilithium  $\alpha,\omega$ -disulfonated polystyrene, SPS 1 in Table I, is shown in Figure 4. In spite of



**Figure 4.**  $^1\text{H}$  NMR spectrum of dilithium  $\alpha,\omega$ -disulfonated polystyrene (SPS 1) in Table I.

the use of the product with relatively low molecular weight, it is difficult to assign typical methylene protons on the  $\alpha$  carbon to the lithium sulfonate group because of the relatively high molecular weight of the sulfonated polystyrene. However, the chemical shift of the protons ( $\delta=2.3\text{ ppm}$ ) adjacent to the sulfonate group and trace of the chemical shift of the methylene unit ( $\delta\sim 3.8\text{ ppm}$ ) adjacent to the diphenylmethyl group can be observed in that region.<sup>9</sup> The chemical shifts observed at  $\delta\sim 2.6, 3.2,$  and  $4.5\text{ ppm}$  may be assigned to the methylene units in the unreacted sultone.

## CONCLUSIONS

$\alpha,\omega$ -Dilithiopolystyrenes with a relatively narrow molecular weight distribution were successfully synthesized using lithium naphthalenide as the difunctional initiator. Their molecular weights were also controlled by the molar ratio of monomer to the initiator. Based on the results from the acid/base titration, sulfoalkylation of the  $\alpha,\omega$ -dilithiopolystyrenes with 1,3-propanesultone provides the corresponding dilithium  $\alpha,\omega$ -disulfonated polystyrenes in relatively high yield ( $>85\%$ ) after reactivity modification of the living chain-end using 1,1-diphenylethylene. The

sulfonated polystyrene with a low molecular weight was found to form the emulsion-like solution in methanol during precipitation and filtration. The chemical shift ( $\delta=2.3$  ppm) of the methylene unit ( $-\text{CH}_2-\text{SO}_3$ ) adjacent to the chain-end sulfonate group could be tentatively assigned in the  $^1\text{H}$  NMR spectrum and FT-IR absorption bands at  $1150\sim 1250\text{ cm}^{-1}$  and  $1052\text{ cm}^{-1}$  provide evidence for the presence of the sulfonate groups in the chain. However, SEC analysis of the dilithium  $\alpha,\omega$ -disulfonated polystyrene using a ternary mixture of THR-DMF (10:1, v/v) containing  $2\text{ g}\cdot\text{l}^{-1}$  of  $\text{LiNO}_3$  provides analogous results to the previous work.<sup>9</sup> Studies on the solution properties of these disulfonated polystyrenes are in progress and will be reported in a future publication.

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