

# Facile Synthesis of High Refractive Index Thiophene-Containing Polystyrenes

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**ABSTRACT:** High refractive index polymer films have been extensively investigated because of their wide application potentials. We now designed thiophene-containing polystyrenes as colorless and transparent high-refractive-index thin film. The copolystyrenes were synthesized by general radical polymerization with controlled mole ratios 0 : 10, 1 : 9, 3 : 7, 5 : 5, 7 : 3, 9 : 1, 10 : 0 (styrene : *p*-bromostyrene), respectively. Next, the thiophene-containing polystyrenes were synthesized by Suzuki-Miyaura coupling reaction. The chemical structures of synthesized thiophene-containing polystyrene in accordance with ratios were confirmed by using  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and FTIR. The effect of the thiophene units on refractive index

according to copolymer ratios were confirmed by using prism coupler. The thiophene-containing polystyrene showed improved refractive index ranging from 1.58 to 1.67 and birefringence in the range of 0.0001–0.0019. The thermal stability and thermal behaviors of thiophene-containing polystyrene also can be confirmed by TGA and DSC. The polymers have high glass transition temperature in the range of 108°C–177°C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 789–795, 2012

**Key words:** sulfur-containing polymer; optical material; high refractive index; Suzuki-Miyaura coupling reaction; polystyrene; polymer reaction

## INTRODUCTION

In recent years, high refractive index polymers have been extensively investigated<sup>1–11</sup> because of their wide potential application in display devices,<sup>12</sup> optical adhesives used in advanced organic light-emitting diodes (OLEDs),<sup>13</sup> antireflective coatings,<sup>14</sup> various semiconductors,<sup>15</sup> etc. According to the Lorentz-Lorenz equation, the refractive index of polymers depends on several factors such as molar refraction and molar volume.<sup>16</sup> Therefore, the introduction of an aromatic ring, sulfur atoms, and metal atoms, which have high polarizability, can aid in obtaining a high refractive index. Recently, several sulfur-containing polymers such as epoxy,<sup>17,18</sup> polyurethane,<sup>19</sup> polystyrenes,<sup>20</sup> and poly(methylmethacrylate)<sup>21–23</sup> have been developed for optical applications. Among them, polystyrenes have several advantages such as good transparency, low cost, and amenability to vary the functionaliza-

tion and processing. These features make polystyrenes<sup>24–41</sup> one of the most important candidates for optical applications.

In this study, copolymers including sulfur functions, i.e., copolystyrenes containing thiophene groups, were prepared to evaluate the influence of various factors on optical properties. The synthesized copolymers containing thiophene groups clearly show improved optical property as compared with polystyrenes<sup>42–44</sup> without any sulfur groups.

Thiophene derivatives would be promising candidates for realizing a high refractive index because of the high polarizability of thiophene units.<sup>45,46</sup> Ueda and coworkers reported the use of thiophene-containing polyimides for optical applications.<sup>47</sup> We reported a silyl-functionalized oligothiophene-based polymer with high refractive index.<sup>48,49</sup> These polymers show highly improved refractive index and optical transparency. Because of the abovementioned characteristics of thiophene units, the use of thiophene derivatives can be expected to result in a high refractive index.

In this study, we prepared high refractive index polystyrenes possessing a thiophene moiety by the Suzuki-Miyaura coupling reaction<sup>50–55</sup> of poly(styrene-*co*-4-bromostyrene). It is noted that this polymer reaction strategy presents a simple and strong tool for the design of high refractive index polystyrene.

Additional Supporting Information may be found in the online version of this article.

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TABLE I  
The Reaction Conditions and Results of Thiophene-Containing Polystyrene

Entry	S : B <sup>a</sup>	St <sup>b</sup>	Br-St <sup>c</sup>	M <sub>n</sub> <sup>d</sup>	Ratio <sup>e</sup>	Yield <sup>f</sup>	Co-PS <sup>g</sup>	Thio <sup>h</sup>	M <sub>n</sub>	Sub <sup>i</sup>	Yield <sup>j</sup>
1	10 : 00	5.4	0	45,000	0	68	0	–	45,000	0	
2	9 : 1	4.3	0.5	28,000	11.7	66	0.4	0.5	29,000	54.2	91
3	7 : 3	3.2	1.6	23,000	29.1	77	1.3	1.5	34,000	52.1	90
4	5 : 5	2.1	2.4	30,000	46.9	56	2.1	2.6	33,000	52.5	86
5	3 : 7	1.3	3.6	21,000	69.1	51	3	3.6	24,000	41.5	88
6	1 : 9	0.5	5.6	22,000	85.9	50	3.9	4.7	24,000	50.3	92
7	0 : 10	0	1.9	5000	100	50	4.3	4.3	7000	37.2	93

<sup>a</sup> The ratio indicates styrene monomer(S) and bromo styrene monomer(B) (*n* : *m*).

<sup>b</sup> This abbreviation means a volume of styrene monomer (ml).

<sup>c</sup> This abbreviation means 4-bromo styrene (ml).

<sup>d</sup> Measured by GPC with polystyrene standards (eluent : THF).

<sup>e</sup> Real ratios of bromogroups in copolymer (%).

<sup>f</sup> The yield is the amount of obtained copolymer with bromo styrene (%).

<sup>g</sup> The abbreviation means copolystyrene (mmol) and the calculated mole ratios of copolystyrene are 4-bromostyrene moiety in the copolymer.

<sup>h</sup> This abbreviated word is 2-thiophene bronc acid. The amount of 2-thiophene bronc acid is an excess (mmol).

<sup>i</sup> The attached thiophene ratios in the copolystyrene were calculated by integral value of <sup>1</sup>H-NMR (%).

<sup>j</sup> The abbreviation stands for the obtained thiophene-containing polystyrene after Suzuki-Miyaura coupling (%).

## EXPERIMENTAL

### Instruments

The <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) spectra were recorded by a JEOL LNM-EX 400 with CDCl<sub>3</sub> as solvent and using tetramethylsilane (TMS) as the internal standard. FT-IR spectra were recorded by using a JASCO FT-IR 460 plus spectrometer with KBr powder. The optical transmission spectra were measured by using a UV-vis spectrometer (Hitachi, U-3210) at room temperature. The in-plane (*n*TE) and out-of-plane (*n*TM) refractive indices of films were measured with a prism coupler (Metricon, model PC-2010) equipped with a half-wave plate in the light path and a He-Ne laser light source (wavelength: 633 nm). Gel permeation chromatography (GPC) was performed either by a JASCO UV-2075 detector and a JASCO RI-2031 detector (TOSOH TSK gel GMIXHX column) using tetrahydrofuran (THF) as the elute after calibration with polystyrene standards. Thermogravimetric analysis (TGA) was performed using a SII TG/DTA 6200 machine with a heating rate of 10°C/min in a nitrogen atmosphere. Differential scanning calorimetry (DSC) was measured by using a SII DSC 6220 (SEIKO instrument Inc.) machine and aluminum pan with a heating rate of 10°C/min in a nitrogen atmosphere.

### Materials

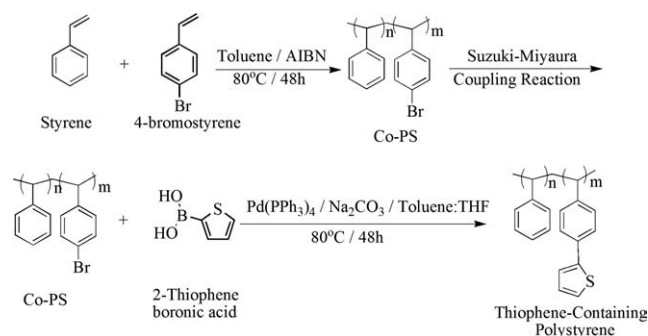
*p*-Bromostyrene and styrene were purified by vacuum distillation immediately before polymerization. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized in methanol before use. 2-Thiophene bronc acid and palladium catalyst (Pd(PPh<sub>3</sub>)<sub>4</sub>) were obtained from Tokyo Kasei (TCI).

### Synthesis of poly(styrene-co-4-bromostyrene)

Styrene, 4-bromostyrene, AIBN, and toluene were added to a round-bottom flask according to the proportion listed in Table I. Then, the mixture was heated to 80°C for 48 h and cooled to room temperature. The reaction mixture was diluted with toluene and the diluted reaction mixture was dropped into methanol when a white precipitate was obtained. The colorless precipitate was filtered and dried *in vacuo*. All copolystyrene samples were prepared by the same process. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.5–7.0 (m, bromo aromatic moiety), 6.7–6.2 (m, aromatic moiety), 2.0–1.5 (m 1H), 1.5–1.2 (m 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ 144, 143, 131, 129.5, 128.3, 127.5, 125.7, 119.5, 40 ppm.

### Synthesis of thiophene-containing polystyrene [poly(styrene-co-4-thienylstyrene)]

A 50-mL two-neck round-bottom flask was charged with 2 mL of 2N Na<sub>2</sub>CO<sub>3</sub> aqueous solution, 10 mL of THF, and 10 mL of toluene. The mixture solvent was bubbled with argon gas over a period of 1 h. Then, a 100-mL two-neck round flask equipped with a reflux condenser, an argon inlet/outlet, and a magnetic stirrer were charged with copolystyrene, 2-thiophene bronc acid, and Pd(PPh<sub>3</sub>)<sub>4</sub> in 20 mL of the mixture. The mixture was heated at 85°C for 48 h. Thiophene-functionalized copolystyrene was obtained by precipitation in methanol. The final product obtained as a white solid (0.73 g, 91.0%) was dried *in vacuo* at 50°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) δ 7.5–7.0 (m, bromo aromatic moiety), 6.7–6.2 (m, aromatic moiety), 2.0–1.5 (m 1H), 1.5–1.2 (m 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz) δ 144,143, 131, 129.5, 128.3, 127.5, 125.7, 124, 122, 40 ppm.



**Scheme 1** Synthetic route of thiophene-containing polystyrenes.

### Fabrication of thiophene-containing polystyrene films

The high refractive index films were fabricated using a viscous solution. The viscous solution was prepared as 40%. The synthesized copolystyrene (2 g) with a thiophene unit was dissolved in toluene. After solubilization, thin films were fabricated from the viscous solution using a spin coater. The thin films were prepared at controlled spin speeds (300 rpm, 800 rpm, 2000 rpm, and 2500 rpm for 30 s, respectively). Then, the obtained films, which were pale yellow in color, were placed on a heating stirrer. After completely removing the solvent from the films at 110°C, sulfur-containing polymer films with a light brown color were obtained.

## RESULTS AND DISCUSSION

### Synthesis

The synthetic routes for thiophene-containing polystyrenes [poly(styrene-*co*-4-thienylstyrene)] are shown in Scheme 1. The synthesis of copolystyrene was carried out via radical polymerization with AIBN as the initiator. Also, the thiophene-containing polystyrene with the refractive index was syn-

**TABLE II**  
The Refractive Index of Thiophene-Containing Polystyrene Series

Entry	Ratio <sup>a</sup>	$n_{av}$ <sup>b</sup>	$\Delta n$ <sup>c</sup>	$d$ <sup>d</sup>	Abbe's number
1	10 : 0	1.5837	0.0001	4.8	38
2	9 : 1	1.5894	0.0002	4.6	31
3	7 : 3	1.5963	0.0002	3.9	31
4	5 : 5	1.6239	0.0008	3.4	27
5	3 : 7	1.6285	0.0006	4.3	26
6	1 : 9	1.6580	0.0019	4.6	23
7	0 : 10	1.6669	0.0017	4.4	20

<sup>a</sup> Mole ratio (styrene : Br-styrene).

<sup>b</sup> Average refractive index at 633 nm.

<sup>c</sup> Birefringence.

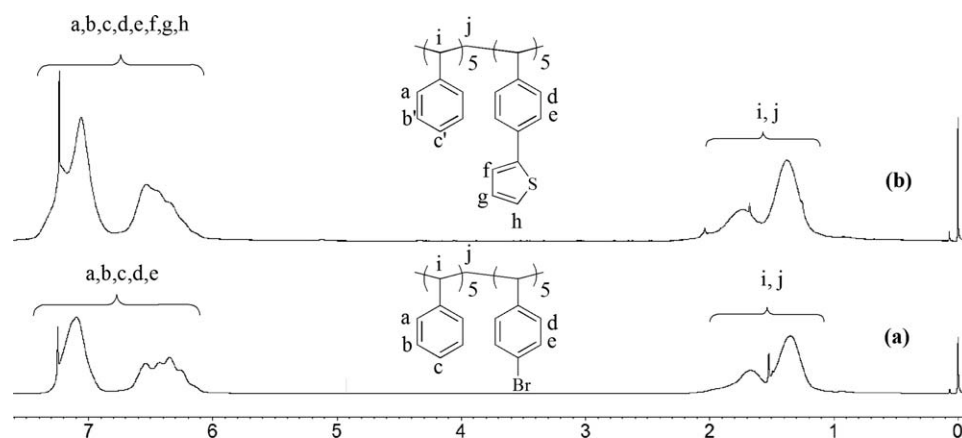
<sup>d</sup> Film thickness.

thesized by the Suzuki-Miyaura coupling reaction. The information of synthesis conditions are listed in Table I.

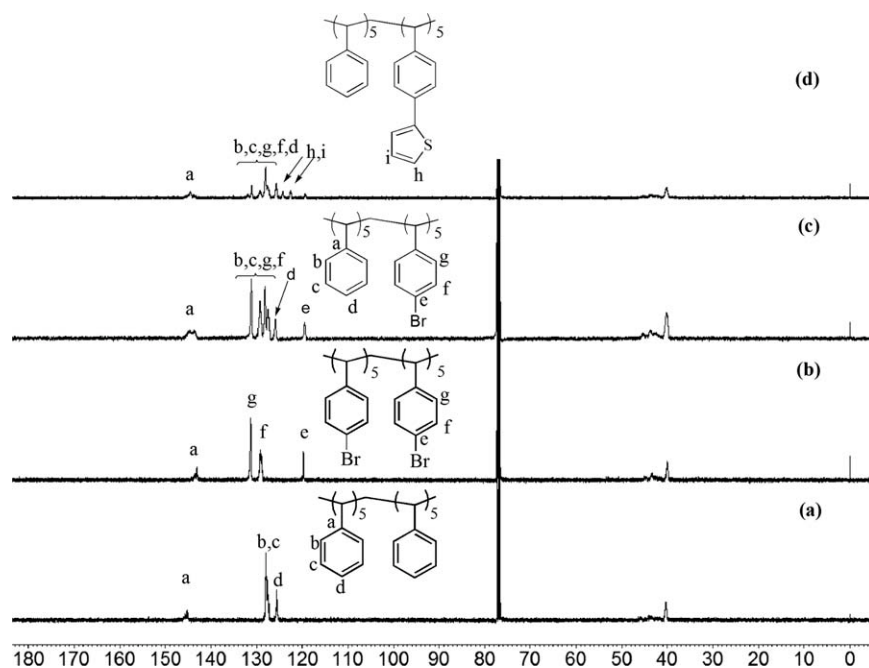
### Characterization

The structures of the obtained polymers were confirmed by the <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and FT-IR (Scheme S1) spectra. The <sup>1</sup>H-NMR spectrum of the thiophene-containing polystyrene (Table II, Entry 4,  $m : n = 5 : 5$ ) is shown in Figure 1. The peaks at 1.2–1.5 and 1.6–2.0 ppm were assigned to the methylene protons and the methin protons, respectively. The two broad peaks as combined aromatic ring of styrene and thiophene moieties appeared at around 6.2–6.7 ppm and 6.9–7.5 ppm, respectively. The slight chemical shift confirmed the presence of thiophene units in the synthesized copolymer. The substitution ratios of thiophene-containing copolymers were calculated from integral values of <sup>1</sup>H-NMR. The calculated ratio is summarized in Table I.

In addition, the peaks of thiophene unit were accurately confirmed on the <sup>13</sup>C-NMR. Figure 2 shows the series of <sup>13</sup>C-NMR spectra of copolymers. In the spectrum of polystyrene [Fig. 2(a)], the peaks



**Figure 1** <sup>1</sup>H-NMR spectra of (a) copolystyrene (5 : 5) and (b) thiophene-containing polystyrene (5 : 5).



**Figure 2**  $^{13}\text{C}$ -NMR spectra of polymers such as (a) homopolystyrene, (b) bromopolystyrene, and (c) copolystyrene (5 : 5), (d) thiophene-containing polystyrene (5 : 5).

corresponding to the *para*-aromatic carbons of benzene ring in styrene moiety were found at around 125 ppm. In addition, the *ortho*-aromatic carbon and *meta*-aromatic carbon appeared at 127 and 128 ppm, respectively. The peaks of all bromopolystyrene [Fig. 2(b)] were observed where carbon was connected to bromo groups, at around 120 ppm. Furthermore, the peaks of f and g carbon positions were clearly indicated at 129 and 131 ppm, respectively. As shown in Figure 2(c), the spectrum of 5 : 5 copolystyrene showed characteristic peaks originating from both carbon of styrene and bromostyrene moieties. The copolymer showed above peaks of two spectra. As a result of the Suzuki-Miyaura coupling reaction of product presented in the spectrum (d), two new peaks of thiophene moieties were observed at 122 ppm (i) and 124 ppm (h). According to the  $^{13}\text{C}$ -NMR spectra, we can confirm the presence thiophene ring in the copolymers. However, the characteristic peaks of polystyrene can be assigned as the C–Br bond present at 120 ppm. Complete substitution was not achieved because complete substitution results in the precipitation of the obtained polymer owing to low solubility because of thiophene groups.

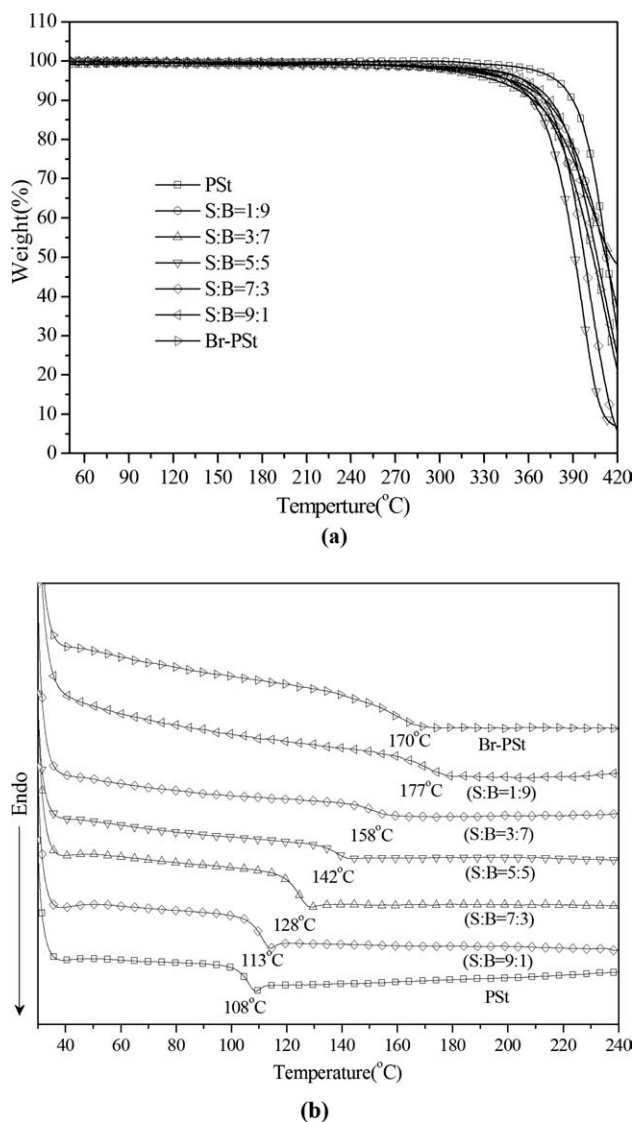
### Thermal properties

The thermal stability of the thiophene-containing polystyrenes was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure 3). The decomposition temperature ( $T_{d10}$ ) denotes 10% weight loss of thiophene-contain-

ing polystyrene series. The  $T_{d10}$  of the copolymer series was slightly high as compared to the degree of  $\pi$ - $\pi$  interaction. The substituted polystyrene with thiophene units were possible to interact easily with aromatic units of polymers because the  $sp^2$  bond of aromatic moiety has weak physical interaction, which has effect on its bond of polymer than Br units. The  $T_{d10}$  of the copolymers as were in the range of 360°C–372°C, suggesting that  $T_{d10}$  was not affected by the moiety substitution. However, all the thiophene-containing polystyrenes showed similar decomposition temperatures because the substituted copolystyrene contained an organic unit.

The thermal properties of the thiophene-containing polystyrenes were investigated by DSC under nitrogen atmosphere. From the DSC curve, the heating rate was found to be 10°C/min and an endothermal peak was observed in the case of all polymers. The glass transition temperatures of the copolymers were 108°C (10 : 0), 113°C (9 : 1), 128°C (7 : 3), 142°C (5 : 5), 156°C (3 : 7), 177°C (1 : 9), and 170°C (0 : 10) (PSt: Br-PSt), respectively. The observed thermal behavior can be explained by the mobile hindrance of the bulky side chain of the cyclic structure and the  $\pi$ - $\pi$  interaction between the benzene groups of the polystyrenes and the  $\pi$ -bond of thiophene moieties.<sup>15</sup> Moreover, all Br-PSt compounds were found to be thermally stable at around 170°C because of their exceptionally low molecular weight as compared with the thiophene-containing polystyrene series. In addition, all Br-PSt showed slightly low substituted ratios of thiophene units than other





**Figure 3** Thermal properties of copolymers (a) TGA curves, (b) DSC curves.

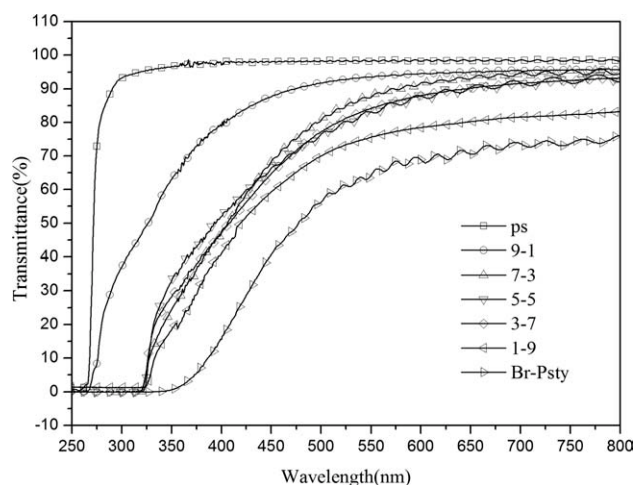
polymers. Thus, the thermal behavior of substituted thiophene moieties was affected on chain mobility owing to  $\pi$ - $\pi$  interaction. Therefore, the thermal behavior of all thiophene-containing polystyrene definitely showed increased glass transition temperatures.

### Optical properties

Figure 4 shows the optical properties of the thiophene-containing polymers. It is found that transmittance decreases with increasing mole ratios. As a result, the nonsubstituted polystyrene showed a high transmittance exceeding 98% at the cutoff wavelength ( $\lambda_{\text{cutoff}}$ ) of 550 nm. However, the transmittance decreased with increasing thiophene ratios. The results of transmittance measurements are listed in Table II.

The refractive indexes of polymer coatings on quartz glass were measured at 633 nm and were found to be in the range of 1.58–1.67. The refractive indexes increased with increasing thiophene ratios. In addition, we can also suggest that the copolystyrene with the Br group of *p*-bromostyrene, which has a large atomic refraction, may affect an increased refractive index compared with a general carbon molecule of copolystyrene. However, the atomic refraction of thiophene is well-known to be larger than Br groups. Thus, it means that the larger atomic refraction of thiophene in sulfur-containing polystyrene is higher than copolymer including Br groups.

The observed  $n_{\text{av}}$  values are apparently high as compared with homopolystyrenes. The highest substituted polymer (Table II, Entry 7) shows the highest  $n_{\text{av}}$  value (1.67) among the synthesized copolymers. The refractive indexes clearly increased with increasing thiophene content. It is well known that the refractive index of polymers depends on several factors such as molecular volume fraction, molecular polarizability, and the degree of molecular packing. In particular, the high polarizability of thiophene units affects the properties of thiophene-containing polymers according to the increasing thiophene ratios. Additionally, the change in the birefringence of the corresponding copolymers also indicates that birefringence is related to their highly flexible structure and the chain packing in their structure. Polystyrene showed significant low birefringence (Table II, Entry 1) compared with the prepared copolymers with various ratios because of the  $\pi$ - $\pi$  interaction between benzene rings. However, the thiophene-containing polymers showed higher birefringence than that of polystyrene because residual Br groups disturbed the  $\pi$ - $\pi$  interaction between nonsubstituted benzene ring and thiophene groups in copolymer chains, and the unreacted sites interferes with the



**Figure 4** Optical transmission spectra of thiophene-containing polystyrene series.

$\pi$ - $\pi$  interaction and chain packing effect, compared with pure polystyrene.<sup>56</sup>

These results indicate that the benzene ring of the polystyrene unit and the thiophene moiety do not degrade the optical transparency because of the  $\pi$ -bond of the thiophene moiety. The trends in optical transmittance depend on the thiophene unit.

## CONCLUSIONS

In conclusion, we successfully prepared polystyrenes possessing thiophene moiety in the side chain prepared from poly(styrene-*cop*-bromostyrene) with various feed ratios by the Suzuki-Miyaura coupling reaction. The obtained polymers exhibited good optical and thermal properties. In particular, the highest thiophene-substituted polystyrene showed the highest refractive index ( $n_{av} = 1.67$ ) with low birefringence (0.0017). Moreover, the thermal stability of the polymers was increased, which can be attributed to the bulky side chain and the  $\pi$ - $\pi$  interaction<sup>57-65</sup> between the benzene ring in the polystyrene and the substituted thiophene ring. Thus, it was considered that the presented synthetic strategy for high refractive index polystyrene could be applied as a development of widely applicable optical polymeric material.

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