# Novel Two-Step Synthesis of Polybenzothiazoles via New Precursor Polyamides from 2,5-Bis[[(methoxycarbonyl)ethyl]thio]-1,4-phenylenediamine and Aromatic Dicarboxylic Acid Chlorides

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ABSTRACT: A series of aromatic polyamides of high molecular weight was synthesized by the low-temperature solution polycondensation of 2,5-bis[[(methoxycarbonyl)ethyl]thio]-1,4-phenylenediamine with aromatic diacid chlorides. The aromatic polyamides with pendant [(methoxycarbonyl)ethyl]thio groups had inherent viscosities in the range of 1.32-2.24 dL·g$^{-1}$. The introduction of bulky and polar pendant [(methoxycarbonyl)ethyl]thio groups in the polyamides improved the solubility in organic solvents. The soluble precursor polyamides were subjected to thermal cyclization at 360 °C in an inert atmosphere to convert them to the corresponding polybenzothiazoles with high molecular weights. The mechanism of the thermal cyclization is discussed based on the pyrolysis GC–MS analysis of the polyamides. The precursor polyamides were also characterized by X-ray diffraction studies. Dynamic mechanical analysis showed that the polyamide obtained from the diamine and 4,4'-oxydibenzoyl chloride and the corresponding polybenzothiazole had glass transition temperatures of 95 and 340 °C, respectively. The polybenzothiazoles obtained from the precursor polyamides showed excellent thermal properties which were comparable to those of the polybenzothiazoles synthesized by solution polycondensation in polyphosphoric acid.

## Introduction

Aromatic polybenzothiazoles have been known as a class of aromatic heterocyclic polymers that exhibit excellent thermal stability.[1-3] Recently rigid-rod polybenzothiazoles have become of interest because these polymers have a potential for fabrication into high-strength and high-modulus fibers and films.[4-8] High molecular weight aromatic polybenzothiazoles have usually been prepared directly by the high-temperature solution polycondensation of aromatic bis(o-aminothiols) with aromatic dicarboxylic acids by using polyphosphoric acid that acts as both a reaction medium and a condensing agent.[1,2] Since aromatic polybenzothiazoles are insoluble in common organic solvents, the potential utility of polybenzothiazoles has been restricted so far.

Recently, we have synthesized and characterized isopropylthio-pendant aromatic precursor polyamides which were subjected to thermal conversion to the corresponding polybenzothiazoles starting from 2,5-bis(isopropylthio)-1,4-phenylenediamine and various aromatic dicarboxylic acid chlorides.[9] However, the precursor polyamides which had rather rigid structures, such as p-phenylene, naphthalene, and biphenyl linkages, were insoluble in organic solvents, and the complete conversion to the corresponding polybenzothiazoles required temperatures higher than 400 °C.

Now we have designed a new 2,5-dimercapto-1,4-phenylenediamine derivative for the synthesis of precursor polyamides having pendant [(methoxycarbonyl)ethyl]thio groups, which should improve the solubility of the precursor polyamides in organic solvents and reduce the temperature for the conversion to the corresponding polybenzothiazoles lower than that of the polyamides having the isopropylthio pendant groups.

The present paper deals with a new two-step synthesis and characterization of the soluble precursor polyamides and polybenzothiazoles obtained through thermal cyclization of the polyamides.

## Experimental Section

**Materials. 2,5-Bis[[(methoxycarbonyl)ethyl]thio]-1,4-phenylenediamine (III).** 2,5-Diamino-1,4-benzenedithiol dihydrochloride (I) was obtained from Tokyo Kasei Kogyo Co., Ltd., Japan, as a pale yellow powder.

A 30.0-g (0.122-mol) portion of 2,5-diamino-1,4-benzenedithiol dihydrochloride (I) was dissolved in a solution of 21.6 g (0.54 mol) of sodium hydroxide in 300 mL of water under a slow stream of argon. The solution was cooled to 5 °C with an ice-water bath and to this was added 29.4 mL (0.269 mol) of methyl 3-bromopropionate (II) dropwise with vigorous stirring under argon. To the solution was added 1.0 g (3.12 mmol) of cetyltrimethylammonium chloride. Stirring was continued at 5 °C for 1 h and further at room temperature for 3 h. The precipitated product was collected by filtration, washed repeatedly with water, and dried under vacuum. Recrystallization from cyclohexane afforded 21.0 g (50.0%) of pure III as yellow needles: mp 83.5–84.3 °C; IR (KBr) 3454 and 3360 (NH), 2956 and 2992 (CH$_3$ and CH$_2$), 1723 cm$^{-1}$ (ester C=O); MS (70 eV) *m/e* 344 (M$^+$); $^1$H NMR (CDCl$_3$) δ 2.58 (t, 4 H, CH$_2$), 3.01 (t, 4 H, CH$_2$), 3.68 (s, 6 H, CH$_3$), 6.82 (s, 2 H, aromatic); $^{13}$C NMR δ 172.3, 140.4, 121.8, 119.8, 51.8, 34.4, 29.4. Anal. Calcd for C$_{14}$H$_{20}$N$_2$O$_4$S$_2$: C, 48.82; H, 5.85; N, 8.13; S, 18.62. Found: C, 48.96; H, 5.97; N, 7.92; S, 18.54.

**Other Materials.** Benzoyl chloride (IV), isophthaloyl chloride (VIIa), and terephthaloyl chloride (VIIb) were obtained commercially and purified by vacuum distillation. 4,4'-Biphenyldicarbonyl chloride (VIIc), 2,6-naphthalenedicarbonyl chloride (VIId), and 4,4'-oxydibenzoyl chloride (VIIe) were prepared by a conventional reaction of the corresponding aromatic dicarboxylic acids with thionyl chloride, followed by vacuum distillation. Solvents such as N-methyl-2-pyrrolidone (NMP) and methanesulfonic acid were purified by distillation. Marlotherm S, which is a high-boiling solvent consisting of a mixture of dibenzylated toluene, was supplied by Impex Chemicals Ltd., Japan.

**Model Reaction. 2,5-Bis[[(methoxycarbonyl)ethyl]thio]-1,4-bis(benzamido)benzene (V).** To a solution of 1.72 g (5.00 mmol) of III in 10.0 mL of NMP was added 1.16 mL (10.00 mmol) of IV with stirring at 0 °C under argon, and the solution was stirred at that temperature for 4 h.

The product was isolated by pouring the solution into 400 mL of water. Recrystallization from a mixture of hexane and dichloromethane (2:1 by volume) afforded 2.66 g (96%) of pure V as colorless needles: mp 158–159 °C; IR (KBr) 3355 (NH), 1731 (ester C=O), 1672 cm$^{-1}$ (amide C=O); $^1$H NMR (CDCl$_3$) δ 2.64 (t, 4 H, CH$_2$), 3.18 (t, 4 H, CH$_2$), 3.59 (s, 6 H, CH$_3$), 7.5–8.9 (m, 12 H, aromatic); $^{13}$C NMR (CDCl$_3$) δ 171.8, 165.1, 135.7, 134.5, 132.1, 128.9, 127.2, 125.8, 124.4, 51.9, 34.0, 31.5. Anal. Calcd for C$_{28}$H$_{28}$N$_2$O$_6$S$_2$: C, 60.85; H, 5.11; N, 5.07; S, 11.60. Found: C, 60.90; H, 5.04; N, 5.05; S, 11.70.

**2,6-Diphenylbenzo[1,2-d:4,5-d']bisthiazole (VI).** A mixture of 0.276 g (0.500 mmol) of V in Marlotherm-S was heated at 350 °C for 5 h under a slow stream of argon. After standing, the product, VI, precipitated from the clear solution at room temperature. This product was washed successively with hexane and acetone, dried, and recrystallized from dichloromethane as pale yellow plates to afford 0.092 g (53%) of VI; mp 304–305 °C (lit.[3] mp 303–304 °C).

**Polymerization. Polymer VIIIa from III and VIIa.** To a solution of 0.861 g (2.50 mmol) of III in 5.0 mL of NMP was added 0.508 g (2.50 mmol) of VIIa in one portion at 0 °C with stirring. The mixture went into solution after 5 min of stirring, and the solution viscosity increased gradually with time. After stirring at 20–25 °C for 6 h, the solution was poured into 300 mL of methanol. The precipitated polymer was collected by filtration, washed repeatedly with methanol, and dried at 80 °C under vacuum. The inherent viscosity of the polyamide was 1.59 dL·g$^{-1}$, measured at a concentration of 0.5 g·dL$^{-1}$ in methanesulfonic acid at 30 °C: IR (film) 3340 (NH), 1737 (ester C=O), 1677 cm$^{-1}$ (amide C=O); $^1$H NMR (DMSO-$d_6$) δ 2.66 (t, 4 H, CH$_2$), 3.14 (t, 4 H, CH$_2$), 3.56 (s, 6 H, CH$_3$) 7.67–8.66 (m, aromatic); $^{13}$C NMR (DMSO-$d_6$) δ 171.5, 164.9, 135.2, 134.3, 131.2, 130.1, 130.5, 128.7, 127.5, 127.2, 51.4, 33.1, 28.3. Anal. Calcd for (C$_{22}$H$_{22}$N$_2$O$_6$S$_2$)$_n$: C, 55.68; H, 4.67; N, 5.90; S, 13.51. Found: C, 55.62; H, 4.57; N, 5.79; S, 13.42.

**Polymer VIIIb from III and VIIb.** To a solution of 0.861 g (2.50 mmol) of III in 5.0 mL of NMP containing 5 wt % of lithium chloride was added 0.508 g (2.50 mmol) of VIIb in one portion at 0 °C with stirring. The mixture went into solution after 5 min of stirring, and the solution viscosity increased gradually with time. A portion of the NMP solution was added as needed during the polymerization to keep the reaction mixture homogeneous. After stirring at 20–25 °C for 6 h, the solution was poured into 300 mL of methanol. The precipitated polymer was collected by filtration, washed repeatedly with methanol, refluxed with methanol for 6 h, and dried at 80 °C under vacuum. The inherent viscosity of the polyamide was 1.36 dL·g$^{-1}$ in methanesulfonic acid: IR (KBr) 3336 (NH), 1737 (ester C=O), 1673 cm$^{-1}$ (amide C=O). Anal. Calcd for (C$_{22}$H$_{22}$N$_2$O$_6$S$_2$)$_n$: C, 55.68; H, 4.67; N, 5.90; S, 13.51. Found: C, 55.64; H, 4.65; N, 5.90; S, 13.51.

**Polymer IXb from VIIIb.** In a test tube, 0.50 g of VIIIb was heated at 400 °C for 1 h under vacuum, giving IXb. The yield of IXb was 0.31 g (63%), and the inherent viscosity was 1.55 dL·g$^{-1}$, measured at a concentration of 0.5 g·dL$^{-1}$ in methanesulfonic acid: IR (KBr) 1480, 1398, 1308 cm$^{-1}$. Anal. Calcd for (C$_{14}$H$_6$N$_2$S$_2$)$_n$: C, 63.13; H, 2.27; N, 10.52. Found: C, 63.25; H, 2.60; N, 10.20.

**Measurements.** IR spectra were recorded on a Nicolet 20DBX FT-IR spectrophotometer. Both $^1$H NMR and $^{13}$C NMR were recorded on a JEOL JNM-GSX270 spectrometer (270 MHz). Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were performed with a Rigakudenki thermal analyzer TAS-200 at a heating rate of 10 °C·min$^{-1}$ in nitrogen. Pyrolysis gas chromatography analysis and mass spectrometry (GC–MS) were carried out using a Shimadzu GCMS-QP1000 (Gaskuropak 54) apparatus equipped with a Shimadzu PYR-1A pyrolyzer. Wide-angle X-ray diffraction patterns were obtained for powder specimens on a Rigakudenki RAD-RB X-ray diffraction apparatus equipped with a monochromator (graphite) using Cu Kα radiation (50 kV, 150 mA). Dynamic mechanical

analysis (DMA) was carried out using a Toyoseiki Rheolograph-Solid in the tensile mode at a frequency of 10 Hz and a heating rate of 3 °C·min$^{-1}$ in air.

## Results and Discussion

**Monomer Synthesis.** 2,5-Bis[[(methoxycarbonyl)ethyl]thio]-1,4-phenylenediamine (III) as a polymer-forming monomer was readily synthesized by the reaction of 2,5-diamino-1,4-benzenedithiol dihydrochloride (I) with methyl 3-bromopropionate (II) under phase-transfer conditions in an aqueous sodium hydroxide solution with use of cetyltrimethylammonium chloride as a phase-transfer catalyst (eq 1). The method employed was virtually the same as



(1)
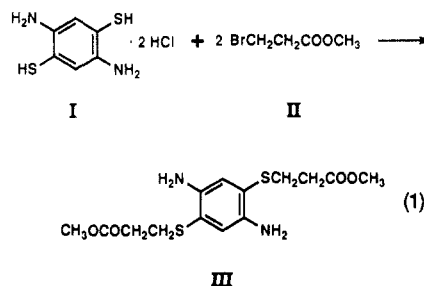
that for the synthesis of 2,5-bis(isopropylthio)-1,4-phenylenediamine reported previously.[9]

**Model Reaction.** Before polymer synthesis, the model reaction of diamine monomer III with benzoyl chloride (IV) was investigated (eq 2).



(2)
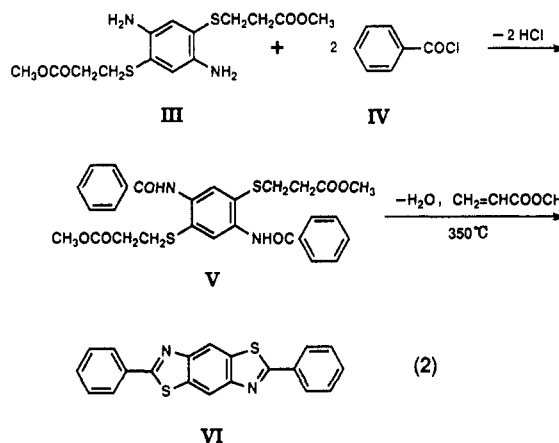
The reaction was carried out in NMP at 0 °C and afforded the diamide compound V in excellent yield. Then compound V was heated at 350 °C in a high-boiling, inert reaction medium (Marlotherm-S),[9-11] giving readily bisbenzothiazole compound VI with the elimination of methyl acrylate and water.
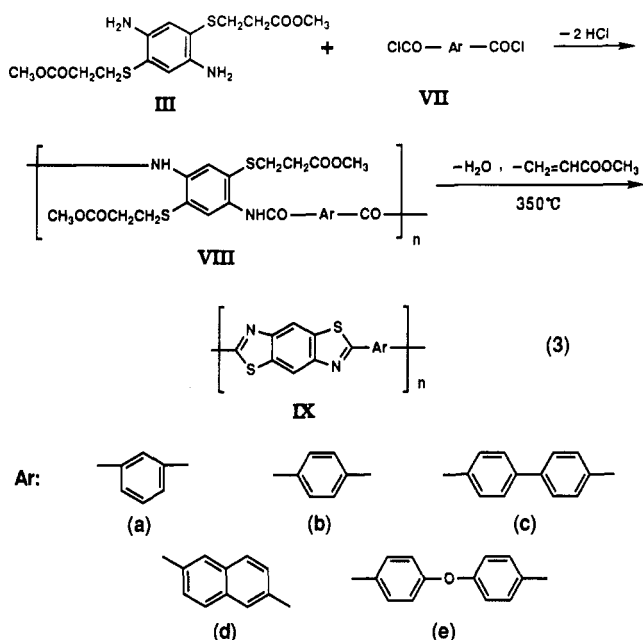
**Polymer Synthesis.** The synthesis of polybenzothiazoles IX via intermediate polyamides VIII was carried out in two successive steps starting from diamine monomer III and aromatic dicarboxylic acid chlorides VII as shown in eq 3.

In the first step, the polyamides were prepared by the low-temperature solution polycondensation method using NMP or NMP solution containing lithium chloride as a reaction medium. The results are summarized in Table I. The polycondensations of diacid chlorides VIIa and VIIe in NMP proceeded homogeneously, and those of VIIb, VIIc, and VIId progressed in a homogeneous solution with use of an NMP solution containing lithium chloride as a reaction medium. Thus, various aromatic polyamides VIII having pendant [(methoxycarbonyl)ethyl]thio groups were obtained in inherent viscosities of 1.32–2.24 dL·g$^{-1}$.

**Table I**
**Synthesis of Aromatic Polyamides**

| monomer | reaction medium[a] | polymer | | |
|---------|-----------|------|-----------|---------------------|
| | | code | yield (%) | $\eta_{inh}$[b] (dL·g$^{-1}$) |
| VIIa | A | VIIIa | 98 | 1.59 |
| VIIb | B | VIIIb | 98 | 1.36 |
| VIIc | B | VIIIc | 99 | 1.32 |
| VIId | B | VIIId | 98 | 2.24 |
| VIIe | A | VIIIe | 98 | 1.59 |

[a] Polymerization was carried out using 2.5 mmol of the diamine and 2.5 mmol of the diacid chlorides in 5.0 mL of (A) NMP or (B) NMP containing lithium chloride at 0 °C for 6 h. [b] Measured at a concentration of 0.5 g·dL$^{-1}$ in methanesulfonic acid at 30 °C.

**Figure 1.** IR spectra (KBr) of (A) polyamide VIIIb and (B) polybenzothiazole IXb.

**Figure 2.** DTA and TGA curves of (A) polyamide VIIIb and (B) polybenzothiazole IXb at a heating rate of 10 K·min$^{-1}$ in nitrogen.

The formation of polyamides VIII was confirmed by means of IR spectroscopy, $^1$H NMR, $^{13}$C NMR, and elemental analysis. The IR spectrum of polyamide VIIIb (Figure 1A) exhibited absorption bands due to a N–H bond and an amide carbonyl group at 3336 and 1673 cm$^{-1}$, respectively, and an ester carbonyl group at 1737 cm$^{-1}$. The $^1$H NMR and $^{13}$C NMR spectra of polyamide VIIIb showed the peaks due to a pendant [(methoxycarbonyl)-ethyl]thio group, amide group, and aromatic group. These peaks corresponded well to that of model compound V. The results of elemental analysis were in good agreement with the calculated values of the proposed structures of polyamides VIII.

Thermal conversion of polyamide VIIIb was followed by means of DTA, TGA, and IR spectroscopy. The DTA curve of polyamide VIIIb exhibited an endothermic peak at around 320 °C, which corresponded well with the temperature of initial weight loss in the TGA curve (Figure 2A). The weight loss observed up to 360 °C in the TGA curve was 41% for polyamide VIIIb, and this value agreed well with the calculated weight loss of 44% based on the elimination of methyl acrylate and water to convert to polybenzothiazole IXb.

These results suggested that perfect cyclization of the intermediate polyamides into polybenzothiazoles requires a reaction temperature of 360 °C. The temperature of the cyclization is about 100 °C lower than that of the poly-amides synthesized from 2,5-bis(isopropylthio)-1,4-phe-nylenediamine and aromatic dicarboxylic acid chlorides.[9] Thus, the thermal conversion was carried out by heating polyamide VIIIb at 400 °C under vacuum. The conversion of VIIIb to IXb was supported by IR spectroscopy, with
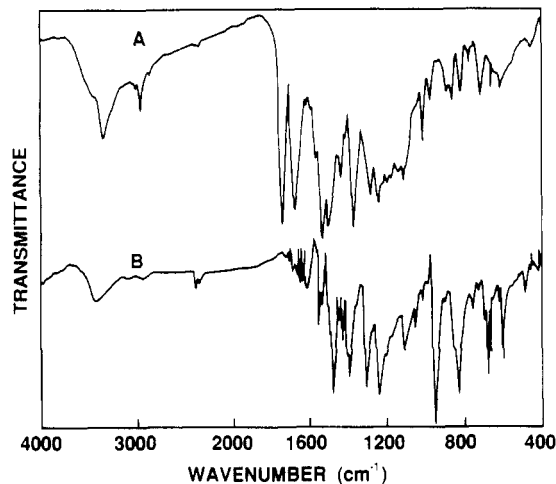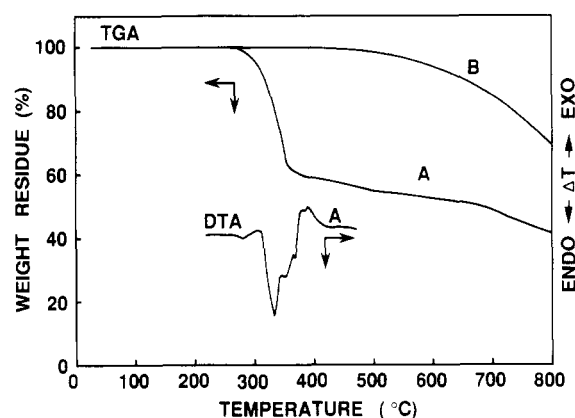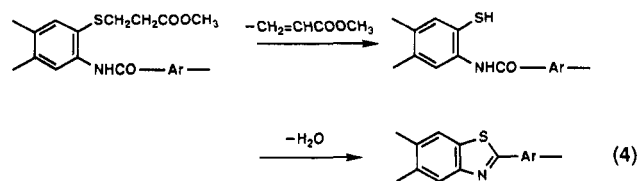
an entire disappearance of absorption bands due to both amide and ester groups (Figure 1B). The IR spectrum of polybenzothiazole IXb was very similar in pattern to that of model compound VI. In addition, the spectrum was consistent with that of the polybenzothiazole prepared by the polyphosphoric acid method.[3] The results of elemental analysis were in good agreement with the calculated values of the corresponding polybenzothiazole. Polybenzothiazole IXb formed had an inherent viscosity of 1.55 dL·g$^{-1}$ in methanesulfonic acid, indicating that little or no thermal degradation leading to molecular chain scission occurred during the conversion process.

In order to prove the mechanism of the thermal cyclization, a pyrolysis GC–MS analysis of polyamide VIIIb was performed. Methyl acrylate and water were detected after heating polyamide VIIIb at 350 °C for 10 min (Figure 3). The generation of the acrylic acid and methanol can be explained in terms of hydrolysis of the methyl acrylate.

The result suggested the following successive two-step mechanism for the conversion of the polyamide to the polybenzothiazole (eq 4). The mechanism of the conver-

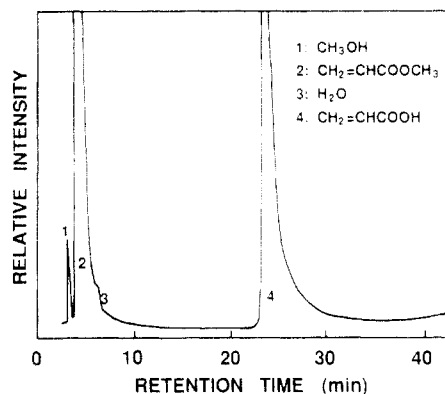sion was substantially the same as that of the polyamides having pendant isopropylthio groups.[9]

**Figure 3.** Pyrolysis GC–MS analysis of polyamide VIIIa after heating at 350 °C for 10 min.

**Table II**
**Solubility of Aromatic Polyamides[a]**

| solvent | polymer | | | | |
|---|---|---|---|---|---|
| | VIIIa | VIIIb | VIIIc | VIIId | VIIIe |
| conc sulfuric acid | ++ | ++ | ++ | ++ | ++ |
| methanesulfonic acid | ++ | ++ | ++ | ++ | ++ |
| N-methyl-2-pyrrolidone + LiCl | ++ | ++ | + | ++ | ++ |
| N-methyl-2-pyrrolidone | ++ | + | – | – | ++ |
| N,N-dimethylacetamide | ++ | + | – | – | ++ |
| dimethyl sulfoxide | ++ | + | – | – | ++ |
| m-cresol | ++ | ++ | – | – | ++ |
| o-chlorophenol | ++ | ++ | – | – | ++ |
| pyridine | + | – | – | – | ++ |
| chloroform | – | – | – | – | + |

[a] Solubility: ++, soluble at room temperature; +, partially soluble or swelling; –, insoluble.

The initial step is cleavage of the carbon–sulfur bond in the pendant [(methoxycarbonyl)ethyl]thio groups of the precursor polyamide with the elimination of methyl acrylate gas and generation of the thiol group. The second step is intramolecular cyclodehydration; the thiol group attacks the amide carbonyl of the intermediate polymer, with the elimination of water giving a benzothiazole ring.

Taking into account the fact that these two successive reactions could not be distinguished in the TGA and DTA studies, an alternative route of a concerted one-step mechanism is also proposed (eq 5). The cyclization proceeds directly to the polybenzothiazole with simultaneous elimination of methyl acrylate and water.



(5)
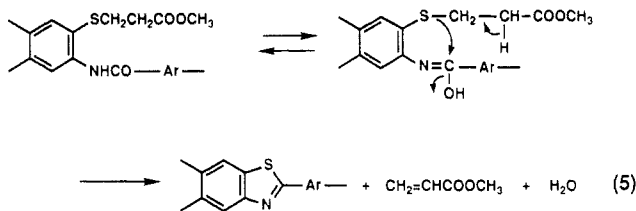
Since the cyclization in both cases includes the reverse reaction of Michael addition, which promotes the cleavage of carbon–sulfur bonds, the temperature of the thermal cyclization is about 100 °C lower than that of the polyamides having isopropylthio pendant groups.

**Polymer Characterization.** The qualitative solubility behavior of intermediate polyamide VIII is summarized in Table II. The introduction of bulky and polar pendant [(methoxycarbonyl)ethyl]thio groups into the polyamide backbone was expected to improve the solubility of such polymers. Indeed, polyamides VIIIa and VIIIe having m-phenylene linkages and flexible ether connecting groups, respectively, were soluble in organic solvents such as NMP,
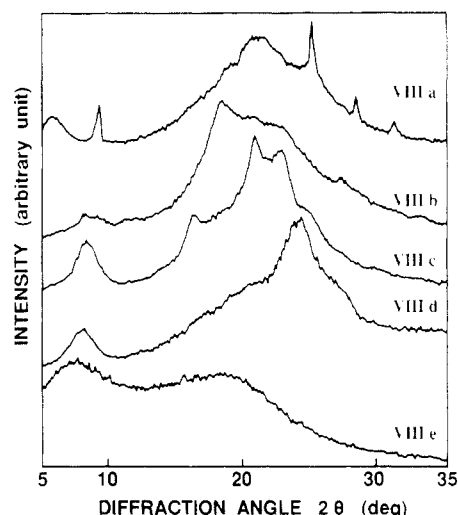


**Figure 4.** X-ray diffractograms of polyamides VIII.
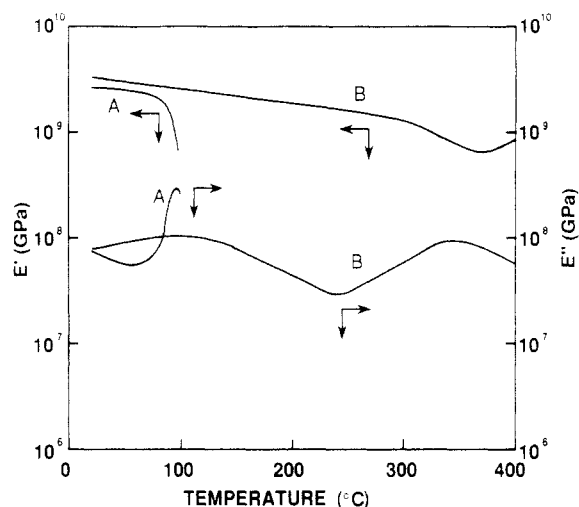


**Figure 5.** Dynamic mechanical properties of films of (A) polyamide VIIIe and (B) polybenzothiazole IXe.

N,N-dimethylacetamide, dimethyl sulfoxide, m-cresol, and o-chlorophenol. Also polyamide VIIIb having a more rigid and symmetrical structure was soluble in m-cresol and o-chlorophenol. The results showed that the introduction of [(methoxycarbonyl)ethyl]thio groups was more effective in enhancing solubility than that of isopropylthio groups.

The X-ray diffraction studies for the polyamides revealed that most of the polyamides had a fair degree of crystallinity, except polyamide VIIIe which was amorphous (Figure 4).

A film of polybenzothiazole IXe obtained by the thermal conversion of the corresponding precursor polyamide VIIIe was dark brown. All the polybenzothiazoles prepared by thermal cyclization lost their solubility in organic solvents.

Dynamic mechanical properties of films of polyamide VIIIe and polybenzothiazole IXe are shown in Figure 5. Although the polyamide showed a glass transition temperature ($T_g$) at 95 °C, the polybenzothiazole obtained from the polyamide had a $T_g$ of 340 °C, maintaining a high dynamic storage modulus ($E'$) even at 300 °C. The $E'$ values of the polyamide and the polybenzothiazole at room temperature were 2.8 and 3.5 GPa, respectively. These results supported the conclusion that the polybenzothiazole obtained through the thermal cyclization had a more rigid structure than the polyamide, showing the excellent thermal stability of the polybenzothiazole.

Polybenzothiazole IXb thus obtained did not lose weight up to 450 °C in nitrogen, and the temperature of 10%

weight loss was 650 °C in that atmosphere. Therefore, the thermal stability of the polybenzothiazole obtained from precursor polyamide VIIIb was comparable to that of the polybenzothiazole synthesized by the polyphosphoric acid method.

## Conclusion

2,5-Bis[[(methoxycarbonyl)ethyl]thio]-1,4-phenylenediamine was designed and synthesized as a new polybenzothiazole-forming monomer. The low-temperature solution polycondensation of this diamine with aromatic dicarboxylic acid chlorides in NMP or NMP solution containing lithium chloride yielded a new series of aromatic polyamides having pendant [(methoxycarbonyl)ethyl]thio groups. The soluble precursor polyamides were then converted by thermal treatment to the corresponding polybenzothiazoles at 360 °C with the elimination of methyl acrylate and water. The introduction of bulky and polar pendant [(methoxycarbonyl)ethyl]thio groups into the polyamides improved the solubility in organic solvents. Dynamic mechanical analysis showed that polyamide VIIe and polybenzothiazole IXe had glass transition temperatures of 95 and 340 °C, respectively. The polybenzothiazoles obtained from the precursor polyamides through thermal treatment showed excellent thermal

stability as determined by TGA and DTA analysis. Thus, the precursor method developed here provides a new potential way for processing intractable polybenzothiazoles.

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