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Novel Two-Step Synthesis of Poly(benzothiazoles) via New Precursor Polyamides from 2,5-Bis[(cyanoethyl)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[(cyanoethyl)thio]-1,4-phenylenediamine with aromatic diacid chlorides. The aromatic polyamides with pendant (cyanoethyl)thio groups had inherent viscosities in the range of 0.83–1.97 dL·g^{-1}. The precursor polyamides were subjected to thermal cyclization at 340 °C in an inert atmosphere to convert them to the corresponding poly(benzothiazoles) with high molecular weights. The mechanism of the thermal cyclization is discussed on the pyrolysis GC-MS analyses of the polyamides in detail. The precursor polyamides were also characterized by X-ray diffraction studies. Dynamic mechanical anlaysis showed that the polyamide obtained from the diamine and 4,4′-oxydibenzoyl chloride and the corresponding poly(benzothiazole) had glass transition temperatures of 158 and 350 °C, respectively. The films also had excellent mechanical properties. The poly(benzothiazoles) obtained from the precursor polyamides showed excellent thermal properties which were comparable to those of the poly(benzothiazoles) synthesized by solution polycondensation in poly(phosphoric acid).

Introduction

Aromatic poly(benzothiazoles) were introduced in the field of heteroaromatic thermally stable polymers in 1965[1–3] and have drawn attention to their excellent mechanical properties, which have extended to the research of fibers and films and molecular composites.[4–12] Currently, they are also of special interest as third-order nonlinear optical materials due to their conjugated structure.[13–15] High molecular weight aromatic poly(benzothiazoles), which have been prepared directly by means of the poly(phosphoric acid) method, are insoluble in common organic solvents; hence, the potential utility of poly(benzothiazoles) has been restricted in spite of many potential applications.

Several approaches to the solubilization of aromatic heterocyclic rigid-rod polymers have been reported by means of complex formation with Lewis acids in aprotic organic solvents.[16–18]

We have focused on new soluble precursor polyamides which could be converted to the poly(benzothiazoles) through thermal cyclization to improve the difficulty of processing the poly(benzothiazoles). First of all, we have synthesized and characterized isopropylthio pendant aromatic precursor polyamides which were subjected to thermal conversion to the corresponding poly(benzothiazoles) starting from 2,5-bis(isopropylthio)-1,4-phenylenediamine and various aromatic dicarboxylic acid chlorides.[19] Second, the precursor polyamides having bulky and polar [(methoxycarbonyl)ethyl]thio pendant groups were designed and synthesized to achieve good solubility of the polyamides in organic solvents and to reduce the temperature for the conversion to the poly(benzothiazoles) through the reverse reaction of Michael addition.[20] However, the weight loss of the polyamides having *p*- or *m*-phenylene linkages reached 41% during thermal conversion to the corresponding poly(benzothiazole) due to the elimination of methyl acrylate and water due to the bulky pendant groups: therefore, it might lead to deterioration of the poly(benzothiazoles). Now we have designed a new 2,5-dimercapto-1,4-phenylenediamine derivative for the synthesis of precursor polyamides having pendant (cyanoethyl)thio groups in order to reduce the weight loss during the thermal cyclization rather than the loss for the polyamides synthesized previously and to convert to the corresponding poly(benzothiazoles) at a lower temperature as well.

The present paper deals with a new two-step synthesis and characterization of the soluble precursor polyamides and poly(benzothiazoles) obtained through thermal cyclization of the polyamides. The mechanism of thermal cyclization was also discussed in detail.

Experimental Section

Materials. 2,5-Bis[(cyanoethyl)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 dropwise with vigorous stirring under nitrogen 22.4 mL (0.270 mol) of 3-bromopropionitrile (**II**). Then 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 5 h. The precipitated product was collected by filtration, washed repeatedly with water, and dried under vacuum. Recrystallization from dichloromethane afforded 20.9 g (61.5%) of pure III as pale green needles: mp 129.7–130.5 °C; IR (KBr) 3448 and 3354 (NH), 2930 (CH^2), 2250 cm^{-1} (CN); mS (70 eV) *m/e* 279 $(MH)^+$; ^1H NMR ($CDCl_3$) δ 2.56 (t, 4H, CH_2), 2.99 (t, 4H, CH_2), 6.88 (s, 2H, aromatic); ^{13}C NMR δ 141.0, 122.5, 118.7, 118.1, 29.6, 18.5. Anal. Calcd for $C_{12}H_{14}N_4S_2$: C, 51.77; H, 5.07; N, 20.12; S, 23.04. Found: C, 51.67; H, 5.10; N, 20.12; S, 22.77.

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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.

Model Reaction. 2,5-Bis[(cyanoethyl)thio]-1,4-bis(benzamido)benzene (V). To a solution of 1.39 g (5.00 mmol) of **III** in 10.0 mL of NMP was added with stirring at 0 °C under nitrogen 1.16 mL (10.00 mmol) of **IV**, 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 tetrahydrofuran afforded 2.31 g (95%) of pure **V** as colorless needles: mp 238–239 °C; IR (KBr) 3429 (NH), 2249 (CN), 1669 cm^{-1} (amide C=O); ^{1}H (DMSO-d_6) δ 2.78 (t, 4H, CH$_2$), 3.19 (t, 4H, CH$_2$), 7.5–8.4 (m, 12H, aromatic): ^{13}C NMR (CDCl$_3$) δ 165.5, 135.6, 133.9, 131.8, 129.7, 128.4, 127.9, 127.6, 119.0, 28.7, 17.2. Anal. Calcd for $C_{26}H_{22}N_4O_2S_2$: C, 64.18; H, 4.56; N, 11.51; S, 13.18. Found: C, 64.35; H, 4.52; N, 11.48; S, 12.74.

2,6-Diphenylbenzo[1,2-*d*:4,5-*d′*]bisthiazole (VI). A 0.487-g (1.000-mmol) portion of **V** was heated at 340 °C for 5 h in a glass tube oven under vacuum. The product was sublimated to afford 0.251 g (72.9%) of pure **VI**; mp 301–303 °C (lit.^{3} mp 303–304 °C).

Polymerization. Polymer VIIIa from III and VIIa. To a solution of 0.696 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 0.90 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} in methanesulfonic acid at 30 °C: IR (film) 3352 (NH), 2249 (CN), 1674 cm^{-1} (amide C=O); ^{1}H NMR (DMSO-d_6) δ 2.83 (t, 4H, CH$_2$), 3.24 (t, 4H, CH$_2$), 7.68–8.67 (m, aromatic); ^{13}C NMR (DMSO-d_6) δ 165.0, 135.6, 134.3, 130.8, 130.1, 128.7, 128.1, 127.3, 119.0, 28.6, 17.2. Anal. Calcd for $(C_{20}H_{16}N_4O_2S_2)_n$: C, 58.81; H, 3.95; N, 13.72; S, 15.70. Found: C, 58.89; H, 4.21; N, 13.65; S, 15.38.

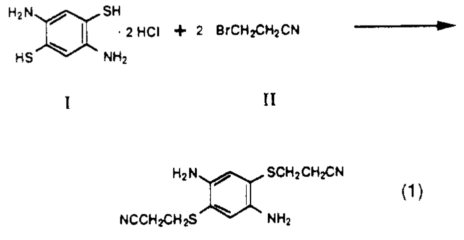
Polymer VIIIb from III and VIIb. To a solution of 0.696 g (2.50 mmol) of **III** in 5.0 mL of NMP containing 5 wt % of lithium chloride was added 0.508 g (2.50 mmol) of **VIIb** in one portion at 0 °C with stirring. The mixture went into solution after 5 min of stirring, and the solution viscosity increased 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 1.53 dL·g^{-1} in methanesulfonic acid; IR (KBr) 3346 (NH), 2249 (CN), 1667 cm^{-1} (amide C=O). Anal. Calcd for $(C_{20}H_{16}N_4O_2S_2)_n$: C, 58.81; H, 3.95; N, 13.72; S, 15.70. Found: C, 59.04; H, 4.06; N, 13.60; S, 15.36.

Polymer IXb from VIIIb. In a test tube, 0.50 g of **VIIIb** was heated at 340 °C for 1 h under vacuum, giving **IXb**. The yield of **IXb** was 0.33 g (66%), and the inherent viscosity was 1.94 dL·g^{-1}, measured at a concentration of 0.5 d·dL^{-1} in methanesulfonic acid: IR (KBr) 1480, 1400, 1308 cm^{-1}. Anal. Calcd for $(C_{14}H_6N_2S_2)_n$: C, 63.13; H, 2.27; N, 10.52. Found: C, 63.55; H, 2.89; N, 10.26.

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 Rigaku Denki 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 Hitachi M-80A (Gaskuropak 54 for heating at 350 °C and OV-1 2% for raising the temperature to 800 °C) apparatus equipped with a Shimadzu PYR-2A pyrolyzer. Wide-angle X-ray diffraction patterns were obtained for powder specimens on a Rigaku Denki 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

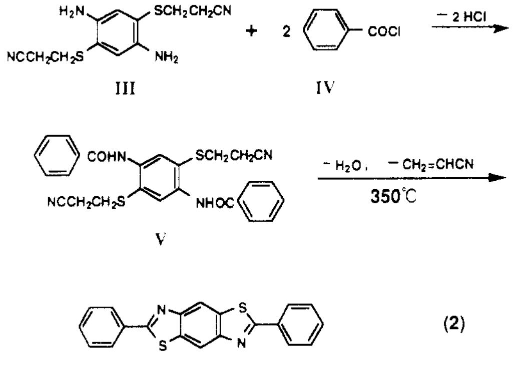
Monomer Synthesis. 2,5-Bis[(cyanoethyl)thio]-1,4-phenylenediamine (**III**) as a polymer-forming monomer was readily synthesized by the reaction of 2,5-diamino-1,4-benzenedithiol dihydrochloride (**I**) with 3-bromopropionitrile (**II**) under phase-transfer conditions in an aqueous sodium hydroxide solution with use of cetyltrimethylammonium chloride as a phase-transfer catalyst (eq 1). The method employed was virtually the same as that for the synthesis of the 2,5-dimercapto-1,4-phenylenediamine derivatives reported previously.[19,20]



III

(1)

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



(2)

VI

The reaction was carried out in NMP at 0 °C and afforded the diamide compound **V** in an excellent yield. Then compound **V** was heated at 350 °C under vacuum in a glass tube oven, giving readily bis(benzothiazole) compound **VI** with the elimination of acrylonitrile and water.

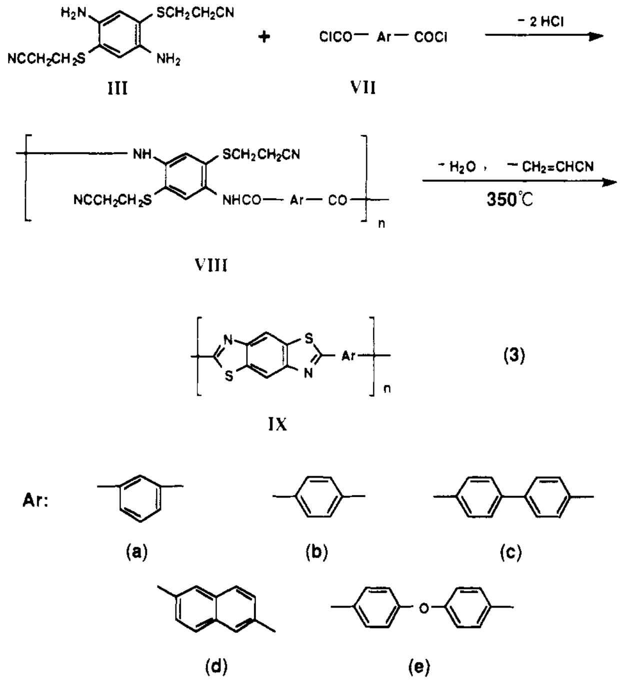
Polymer Synthesis. The synthesis of poly(benzothiazoles) **IX** via intermediate polyamides **VIII** was carried out in two successive steps starting from diamine monomer **III** and aromatic dicarboxylic acid chlorides **VII** as shown in eq 3.

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 homogeneous solution with the use of NMP solution containing lithium chloride as a reaction medium. Thus, various aromatic polyamides

Table I. Synthesis of Aromatic Polyamides

monomer	reaction medium[a]	polymer code	polymer yield (%)	polymer η_{inh}[b] ($dL \cdot g^{-1}$)
VIIa	A	**VIIIa**	98	0.90
VIIb	B	**VIIIb**	95	1.53
VIIc	B	**VIIIc**	97	0.89
VIId	B	**VIIId**	98	1.97
VIIe	A	**VIIIe**	99	0.83

[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 $g \cdot dL^{-1}$ in methanesulfonic acid at 30 °C.



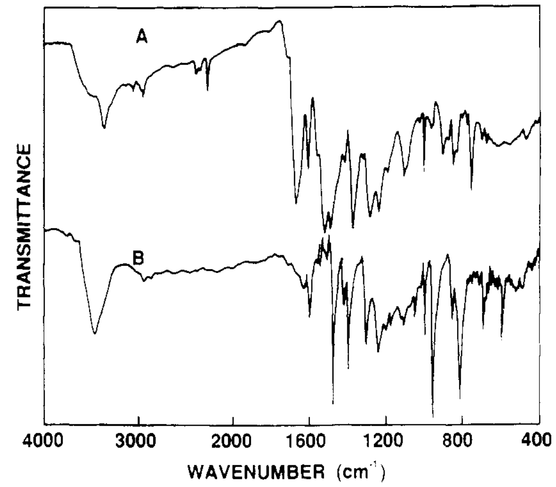


Figure 1. IR spectra (KBr) of (A) polyamide **VIIIb** and (B) poly(benzothiazole) **IXb**.

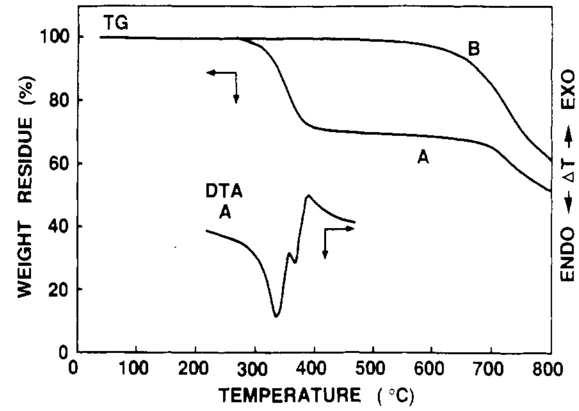


Figure 2. DTA and TGA curves of (A) polyamide **VIIIb** and (B) poly(benzothiazole) **IXb** at a heating rate of 10 $°C \cdot min^{-1}$ in nitrogen.

VIII having pendant (cyanoethyl)thio groups were obtained in inherent viscosities of 0.83–1.97 $dL \cdot g^{-1}$.

The formation of polyamides **VIII** was confirmed by means of IR spectroscopy, ^1H and ^{13}C NMR, and elemental analysis. The IR spectrum of polyamide **VIIIb** (Figure 1A) exhibited absorption bands due to the N–H bond and the amide carbonyl group at 3346 and 1667 cm^{-1}, respectively, and the cyano group at 2249 cm^{-1}. The ^1H and ^{13}C NMR spectra of polyamide **VIIIb** showed the peaks due to pendant (cyanoethyl)thio group, amide group, and aromatic. 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 temperature of polyamide **VIIIb** at the initial weight loss shifted to about 20 °C lower temperature compared with that of the polyamides having pendant [(methoxycarbonyl)ethyl]thio groups.[20]

The weight loss observed up to 360 °C in the TGA curve was 30% for polyamide **VIIIb**, and this value agreed well with the calculated weight loss of 35% based on the elimination of acrylonitrile and water to convert to poly(benzothiazole) **IXb**. These results suggested that perfect cyclization of the intermediate polyamides into poly(benzothiazoles) required a reaction temperature of 360 °C. 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 the entire disappearance of absorption bands due to both amide and cyano groups (Figure 1B). The IR spectrum of poly(benzothiazole) **IXb** was very similar in pattern to that of model compound **VI**. In addition, the spectrum was consistent with that of the poly(benzothiazole) prepared by the poly(phosphoric acid) method.[3] The results of elemental analysis were in good agreement with the calculated values of the corresponding poly(benzothiazole). Poly(benzothiazole) **IXb** formed had an inherent viscosity of 1.94 $dL \cdot g^{-1}$ in methanesulfonic acid, indicating that little or no thermal degradation leading to molecular chain scission occurred during the conversion process. These results showed that the pendant (cyanoethyl)thio groups reduced the weight loss more than that for the polyamides having pendant [(methoxycarbonyl)ethyl]thio groups during the thermal cyclization at a lower temperature to convert to the poly(benzothiazoles).[20]

In order to prove the mechanism of the thermal cyclization, a pyrolysis GC-MS analysis of polyamide **VIIIb** was performed. Acrylonitrile and water were detected after heating polyamide **VIIIb** at 350 °C for 10 min (Figure 3).

Further, an analysis of eliminated gases was performed in detail; characteristic mass numbers of detected acrylonitrile and water, which were 53 (*m/z*) for acrylonitrile and 18 (*m/z*) for water, were followed by mass spectroscopy with raising the temperature of the polyamide **VIIIb** at

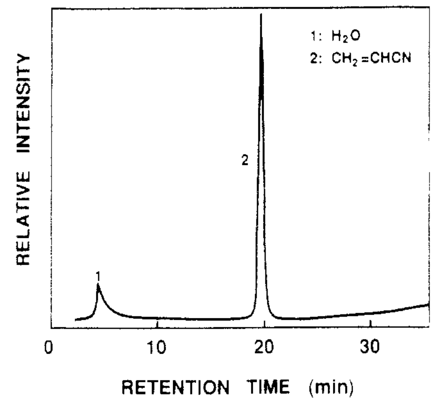


Figure 3. Pyrolysis GC-MS analysis of polyamide **VIIIb** after heating at 350 °C for 10 min.

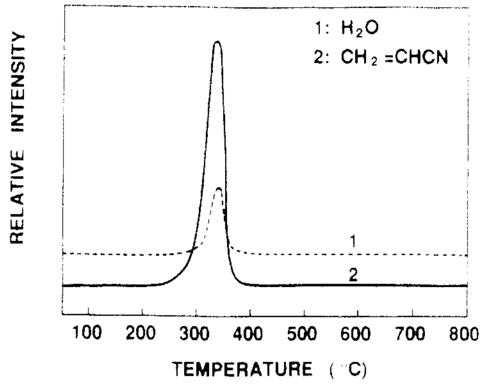
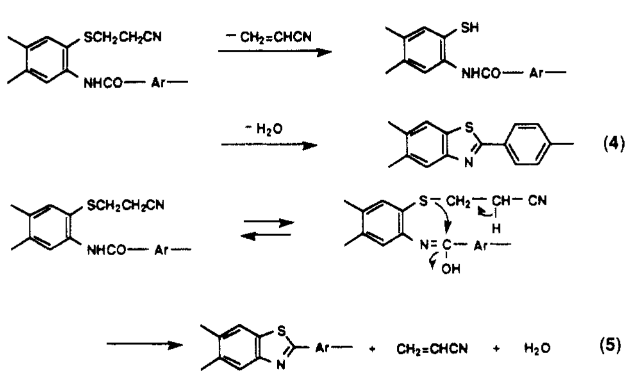


Figure 4. GC-MS analysis of polyamide **VIIIb** at a heating rate of 10 °C·min^{-1} in helium.

a heating rate of 10 °C·min^{-1} to 800 °C in an inert atmosphere (Figure 4). The generation of acrylonitrile and water was detected from 230 to 380 °C and from 250 to 380 °C, respectively. These results suggested that the weight loss of polyamide during the thermal cyclization occurred together with the generation of the two gases. The following two mechanisms of thermal cyclization with the elimination of acrylonitrile and water were proposed from the results of the GC-MS analyses; eqs 4 and 5 show a successive two-step mechanism and a concerted one-step mechanism, respectively.



Both of the mechanisms including reverse reaction of Michael addition, which lead to reducing the temperature of the cyclization, are substantially the same as that of the polyamides having pendant [(methoxycarbonyl)ethyl]thio groups.[20] The temperature at which the generation of the acrylonitrile first occurred was about 20 °C lower than that of water; however, two successive reactions in eq 4 could not be distinguished in the TGA and DTA curves. These results suggested that both equations were equally suitable for the mechanism of thermal cyclization; the thermal cyclization at an initial stage is governed by the reaction of eq 4, followed by the reaction of both eqs 4 and 5 simultaneously.

Table II. Solubility of Aromatic Polyamides[a]

solvent	polymer VIIIa	VIIIb	VIIIc	VIIId	VIIIe
concentrated 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.

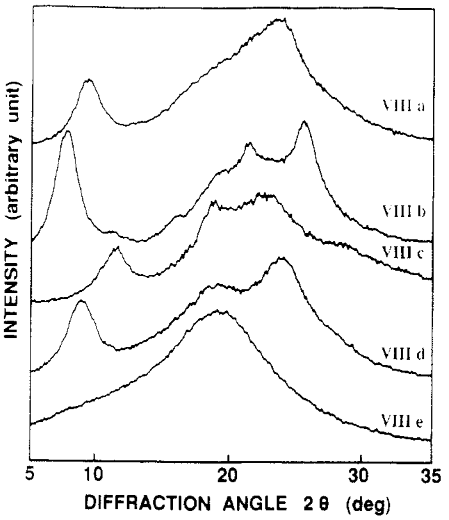


Figure 5. X-ray diffractograms of polyamides **VIII**.

Polymer Characterization. The qualitative solubility behavior of intermediate polyamide **VIII** is summarized in Table II. The introduction of bulky and polar pendant (cyanoethyl)thio groups into the polyamide backbone was expected to be effective 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, *m*-cresol, and *o*-chlorophenol. Polyamides **VIIIb, VIIIc,** and **VIIId** having more rigid and symmetrical structures were only soluble in NMP containing lithium chloride. Generally polyamides **VIII** were less soluble in organic solvents than the polyamides having pendant [(methoxycarbonyl)ethyl]thio groups.[20] All the poly(benzothiazoles) prepared by thermal cyclization lost their solubility in organic solvents.

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 5).

A film of poly(benzothiazole) **IXe** obtained by the thermal conversion of the corresponding precursor polyamide **VIIIe** was smooth, tough, transparent, and dark brown in color. The mechanical properties of the films of polyamide **VIIIe** and polybenzothiazole **IXe** are summarized in Table III. Both the values of the tensile modulus and the tensile strength of poly(benzothiazole) **IXe** were higher than those of polyamides **VIIIe** due to its rigid structure.

Table III. Tensile Properties of Polyamide VIIIe and Poly(benzothiazole) IXe

polymer	tensile strength (MPa)	tensile modulus (GPa)	elongation at break (%)
VIIIe	73	2.4	20.3
IXe	98	2.5	7.9

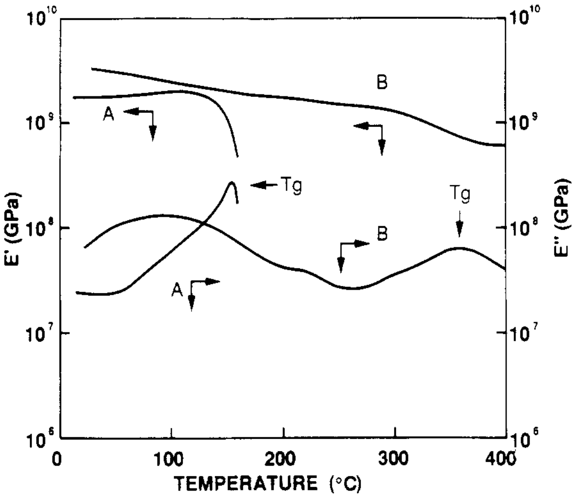


Figure 6. Dynamic mechanical properties of films of (A) polyamide **VIIIe** and (B) poly(benzothiazole) **IXe**.

The dynamic mechanical properties of films of polyamide **VIIIe** and poly(benzothiazole) **IXe** are shown in Figure 6. Although the polyamide showed a glass transition temperature (T_g) at 158 °C, the poly(benzothiazole) obtained from the polyamide had a T_g of 350 °C, maintaining a high dynamic storage modulus (E') even at 300 °C. The E' values of the polyamide and the poly(benzothiazole) at room temperature were 2.2 and 3.3 GPa, respectively. These results led to the conclusion that the poly(benzothiazole) obtained through the thermal cyclization had a more rigid structure than the polyamide.

Poly(benzothiazole) **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 poly(benzothiazole) obtained from precursor polyamide **VIIIb** was comparable to that of the poly(benzothiazole) synthesized by the poly(phosphoric acid) method.

Conclusion

2,5-Bis[(cyanoethyl)thio]-1,4-phenylenediamine was designed and synthesized as a new poly(benzothiazole)-forming monomer. The low-temperature solution polycondensation of this diamine with aromatic dicarboxylic acid chlorides in NMP or a NMP solution containing lithium chloride yielded a new series of aromatic polyamides having pendant (cyanoethyl)thio groups. The soluble precursor polyamides were then converted by thermal treatment to the corresponding poly(benzothiazoles) at 340 °C with the elimination of arylonitrile and water, which were studied by GC-MS analysis in detail. The introduction of pendant (cyanoethyl)thio groups reduced the weight loss more than that for the polyamide which have the pendant [(methoxycarbonyl)ethyl]thio groups at a lower temperature during the thermal cyclization to convert to the poly(benzothiazoles). The films of polyamide **VIIIe** and poly(benzothiazole) **IXe** were flexible and tough and had excellent mechanical properties. The dynamic mechanical analysis showed that polyamide **VIIIe** and poly(benzothiazole) **IXe** had glass transition temperatures of 158 and 350 °C, respectively. The poly(benzothiazoles) 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 poly(benzothiazoles).

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