

Novel Two-Step Synthesis of Polybenzothiazoles *via* Precursor Polyamides Having Reactive Pendant Groups from 2,5-Bis[(carboxyethyl)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 low-temperature solution polycondensation of 2,5-bis[(carboxyethyl)thio]-1,4-phenylenediamine with aromatic dicarboxylic acid chlorides. The aromatic polyamides having reactive pendent (carboxyethyl)thio groups had inherent viscosities in the range of 0.57 and 1.66 dl g⁻¹. The precursor polyamides were subjected to thermal cyclization to the corresponding polybenzothiazoles along with the elimination of acrylic acid and water, which were detected by GC-MS analysis of the polyamides. The resulting polymers were characterized as high temperature aromatic polymers.

KEY WORDS New Synthetic Method / Two-Step Synthesis / Thermal Cyclization / Polyamides with Reactive Pendants / Polybenzothiazoles /

Currently, polybenzothiazoles have drawn attention not only to the research for fibers, films, and molecular composites as their excellent thermal and mechanical properties,¹⁻⁹ but also to that for functional polymers such as third-order nonlinear optical materials due to their conjugated structures.¹⁰⁻¹⁶ Aromatic polybenzothiazoles, which were introduced in the field of heteroaromatic thermally stable polymers in 1965,¹⁷⁻¹⁹ were prepared directly by using polyphosphoric acid, which acts as both reaction medium and condensing agent. Since aromatic polybenzothiazoles are insoluble in common organic solvents, the potential utility of the polybenzothiazoles had been restricted in spite of many potential applications.

We have focused on new soluble precursor polyamides which could be converted to the polybenzothiazoles through thermal cyclization to improve the difficulty of processing of the polybenzothiazoles. A series of precursor

polyamides having pendant groups²⁰⁻²² was synthesized and characterized in order to achieve good solubility of the polyamides in organic solvents and to reduce the temperature for the conversion to the corresponding polybenzothiazoles.

Now, we have designed a new 2,5-dimer-capto-1,4-phenylenediamine derivative, 2,5-bis[(carboxyethyl)thio]-1,4-phenylenediamine, for the synthesis of precursor polyamides having reactive (carboxyethyl)thio groups. The pendant (carboxyethyl)thio groups would be expected to give the precursor polyamides enough flexibility during the thermal cyclizations, and to reduce the temperature for conversion to the corresponding polybenzothiazoles.

The polyamides, which are soluble in organic solvents and readily converted to the corresponding polybenzothiazoles by thermal treatments, should also have a special potential of constructing films with nanometer thickness by

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using Langmuir–Blodgett (LB) technique. The LB films of the polyamides should be obtained from the salts consisting of a long-chain alkyl amine and the precursor polyamides with carboxyl groups; after that, the films are converted to those of polybenzothiazoles by the appropriate thermal treatment. These studies are under investigation.^{23,24}

EXPERIMENTAL

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 (**IIId**), and 4,4'-oxydibenzoyl chloride (**VIIe**) were obtained commercially and purified by distillation under reduced pressure. Solvents such as *N*-methyl-2-pyrrolidone (NMP) were purified by vacuum distillation with calcium hydride. Marlotherm-S, which is a high boiling solvent consisting of a mixture of dibenzylated toluene, was supplied by Impex Chemicals, Ltd., Japan.

Monomer Synthesis

2,5-Bis[(carboxyethyl)thio]-1,4-phenylenediamine (III). 2,5-Bis[[methoxycarbonyl]ethyl]thio]-1,4-phenylenediamine (**II**) was prepared from 2,5-diamino-1,4-benzenedithiol dihydrochloride and methyl 3-bromopropionate according to the method reported previously.²¹ A 10.0 g (0.029 mol) portion of 2,5-bis[[methoxycarbonyl]ethyl]thio]-1,4-phenylenediamine (**II**) was dissolved in 400 ml of concentrated hydrochloric acid in an ice–water bath. The solution was heated at 80°C for 10 h and white salt of the monomer precipitated from the solution. The precipitate was collected by filtration and dissolved in 1000 ml of water. The pH of the solution was adjusted between 3 and 4 with sodium bicarbonate to obtain diamine **III**. The precipitated product was collected by filtration, washed repeatedly with

water, and dried under vacuum. It was recrystallized from methanol to give pure 2,5-bis[(carboxyethyl)thio]-1,4-phenylenediamine (**III**) as pale green plates; mp > 170°C (decomp.). The yield was 7.0 g (76.3%). The infrared (IR) spectrum (KBr) exhibited absorptions at 3337 and 3263 cm⁻¹ (N–H), 2917 cm⁻¹ (CH₂), and 1692 cm⁻¹ (C=O). The ¹H nuclear magnetic resonance (NMR) spectrum (dimethyl sulfoxide (DMSO)-*d*₆) showed peaks at 2.43–2.48 (t, 4H, methylene), 2.86–2.91 (t, 4H, methylene), and 6.73 ppm (s, 2H, aromatic). The ¹³C NMR spectrum (DMSO-*d*₆) showed signals at 172.7, 139.8, 119.4, 118.0, 33.8, and 28.3 ppm.

Anal. Calcd for C₁₂H₁₆N₂O₄S₂: C, 45.55%; H, 5.10%; N, 8.85%; S, 20.27%. Found: C, 45.39%; H, 5.22%; N, 8.75%; S, 20.35%.

Model Reaction

2,5-Bis[(carboxyethyl)thio]-1,4-bis(benzamido)benzene (V). To a solution of 0.316 g (1.00 mmol) of 2,5-bis[(carboxyethyl)thio]-1,4-phenylenediamine (**III**) in 2.0 ml of NMP, 0.281 g (2.00 mmol) of benzoyl chloride (**IV**) was added with stirring at 0°C under nitrogen, and the solution was stirred at 20°C for 4 h. The product was isolated by pouring the solution into 200 ml of water and dried under vacuum. The yield of 2,5-bis[(carboxyethyl)thio]-1,4-bis(benzamido)benzene (**V**) was 0.509 g (97%) as colorless powder; mp 304.3–305.3°C. The IR spectrum (KBr) exhibited bands at 3338 cm⁻¹ (N–H), 1728 cm⁻¹ (carboxyl C=O), and 1642 cm⁻¹ (amide C=O). The ¹H NMR spectrum (DMSO-*d*₆) showed peaks at 2.51–2.56 (t, 4H, methylene), 3.04–3.10 (t, 4H, methylene), 7.53–8.02 ppm (m, 12H, aromatic), and 9.95 ppm (s, 2H, amide). The ¹³C NMR spectrum (DMSO-*d*₆) showed signals at 172.5, 165.3, 135.0, 134.0, 131.7, 130.1, 128.4, 127.5, 127.0, 33.4, and 28.5 ppm.

Anal. Calcd for C₂₄H₂₆N₂O₆S₂: C, 59.53%; H, 4.61%; N, 5.34%; S, 12.22%. Found: C, 59.34%; H, 4.65%; N, 5.21%; S, 12.02%.

2,6-Diphenylbenzo[1,2-d':4,5-d'']bisthiazole

(VI). A mixture of 0.200 g (0.381 mmol) of diamide compound V in 5.0 ml of Marlotherm-S was heated at 300°C for 5 h under a slow stream of argon. After standing the clear solution at room temperature, the product of 2,6-diphenylbenzo[1,2-*d*:4,5-*d'*]bisthiazole (VI) precipitated. It was collected, washed successively with hexane and acetone, and dried. The yield was 0.084 g (64%). It was recrystallized from dichloromethane to afford pale yellow plates; mp 304–305°C (lit.¹⁹ mp 303–304°C).

Polymerization

A typical example of the polycondensation is given below.

Polyamide VIIIa from III and Diacid Chloride VIIa. To a solution of 0.791 g (2.500 mmol) of 2,5-bis[(carboxyethyl)thio]-1,4-phenylenediamine (III) in 5.0 ml of NMP was added 0.508 g (2.500 mmol) of solid isophthaloyl dichloride (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. Polyamide VIIIa was collected by filtration, washed repeatedly with water and methanol, and dried at 80°C under vacuum. The inherent viscosity of the polyamide was 0.57 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ in methanesulfonic acid at 30°C. The IR spectrum (film) showed absorptions at 3329 cm⁻¹ (N–H), 1713 (carboxyl C=O), 1674 cm⁻¹ (amide C=O). The ¹H NMR spectrum (DMSO-*d*₆) showed peaks at 2.56–2.60 (t, 4H, methylene), 3.09–3.13 (t, 4H, methylene), and 7.66–8.25 ppm (m, 6H, aromatic). The ¹³C NMR spectrum (DMSO-*d*₆) showed signals at 175.7, 164.9, 134.9, 134.3, 130.6, 128.8, 127.1, 33.4, and 28.2 ppm.

Anal. Calcd for (C₂₀H₁₈N₂O₆S₂)_n: C, 53.80%; H, 4.06%; N, 6.27%; S, 14.36%. Found: C, 54.00%; H, 4.37%; N, 6.05%; S, 14.36%.

Polyamide VIIIb from III and Diacid Chloride

VIIIb. To a solution of 0.791 g (2.500 mmol) of 2,5-bis[(carboxyethyl)thio]-1,4-phenylenediamine (III) in 5.0 ml of NMP containing 5 wt% of lithium chloride was added 0.508 g (2.500 mmol) of solid terephthaloyl dichloride (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. 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. Polyamide VIIIb was collected by filtration, washed repeatedly with water and methanol, and dried at 80°C under vacuum. The inherent viscosity of the polyamide was 1.01 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ in methanesulfonic acid at 30°C. The IR spectrum (KBr) showed absorptions at 3325 cm⁻¹ (N–H), 1713 cm⁻¹ (carboxyl C=O), and 1674 cm⁻¹ (amide C=O).

Anal. Calcd for (C₂₀H₁₈N₂O₆S₂)_n: C, 53.80%; H, 4.06%; N, 6.27%; S, 14.36%. Found: C, 53.74%; H, 4.20%; N, 6.32%; S, 14.00%.

Polybenzothiazoles IXb from Polyamide VIIIb. In a test tube, 0.5 g of polyamide VIIIb was heated at 350°C for 1 h under argon, giving polybenzothiazole IXb. The IR spectrum (KBr) showed absorptions at 1484, 1402, and 1313 cm⁻¹.

Anal. Calcd for (C₁₄H₆N₂S₂)_n: C, 63.13%; H, 2.27%; N, 10.52%. Found: C, 63.57%; H, 2.68%; N, 9.96%.

Measurements

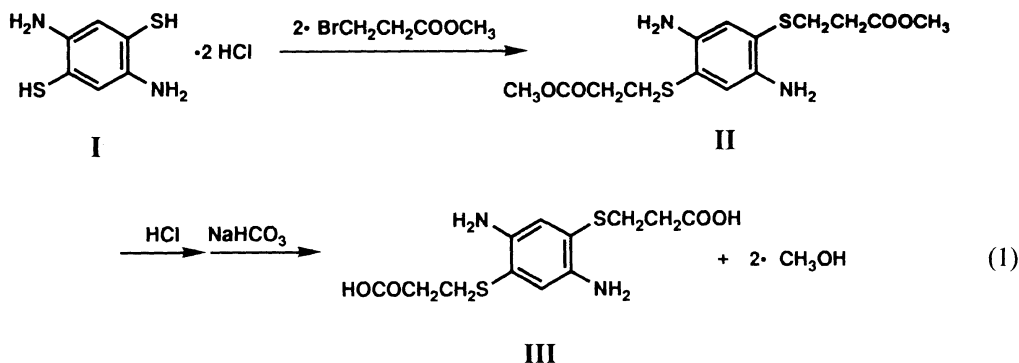
IR spectra were recorded on a Horiba FT-520 spectrophotometer. Both ¹H NMR and ¹³C NMR were recorded on a JEOL JNM-GSX270 spectrometer (270 MHz). Differential thermal analysis (DTA) and thermogravimetry (TG) were performed with a Rigakudenki thermal analyzer TAS-200 at a heating rate of 10°C min⁻¹ in nitrogen. Pyrolysis gas chromatography analysis and mass spectrometry

(GC-MS) were carried out using a Hitachi M-80A apparatus (PEG-20M 20% for heating at 350°C and OV-1 2% for raising the temperature to 800°C) equipped with a Shimadzu pyrolyzer PYR-2A. The wide angle X-ray diffraction patterns were obtained for powder specimens on a Rigaku Denki RAD-RB X-ray diffraction apparatus equipped with monochromator (graphite) using Cu- K_{α} radiation (50 kV, 150 mA). Dynamic mechanical analysis (DMA) was carried out using a Toyoseiki Rheograph Solid in the tensile mode at a frequency of 10 Hz and a heating rate of 3°C min⁻¹ in air.

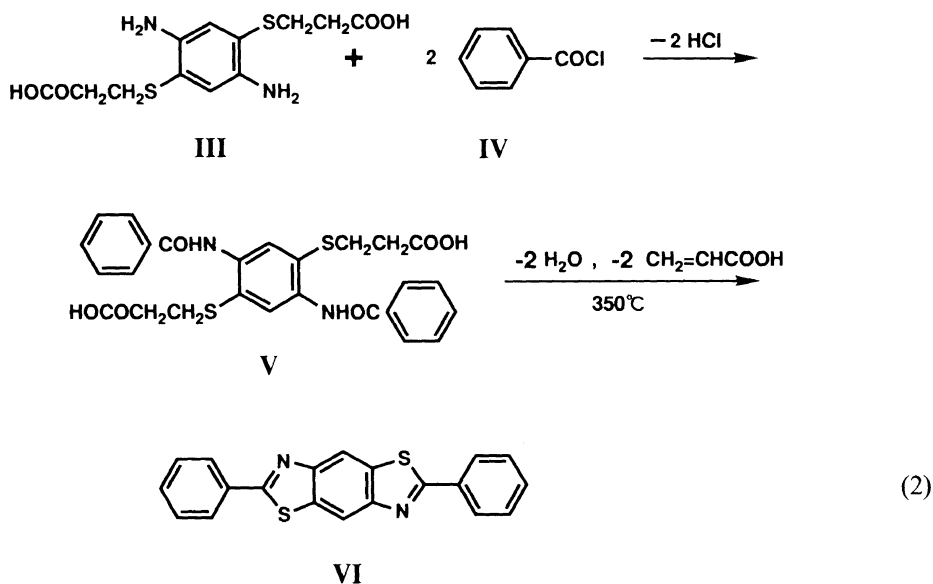
RESULTS AND DISCUSSION

Monomer Synthesis and Model Reaction

2,5-Bis[(carboxyethyl)thio]-1,4-phenylenediamine (**III**) as a polymer-forming monomer was readily synthesized by acid hydrolysis reaction of 2,5-bis[[[(methoxycarbonyl)ethyl]thio]-1,4-phenylenediamine with hydrochloric acid [eq 1]. The synthetic method for diamine **II** as the starting compound has been reported previously,²¹ where the diamine was obtained from 2,5-diamino-1,4-benzenedithiol hydrochloride and methyl-3-bromopropionate.



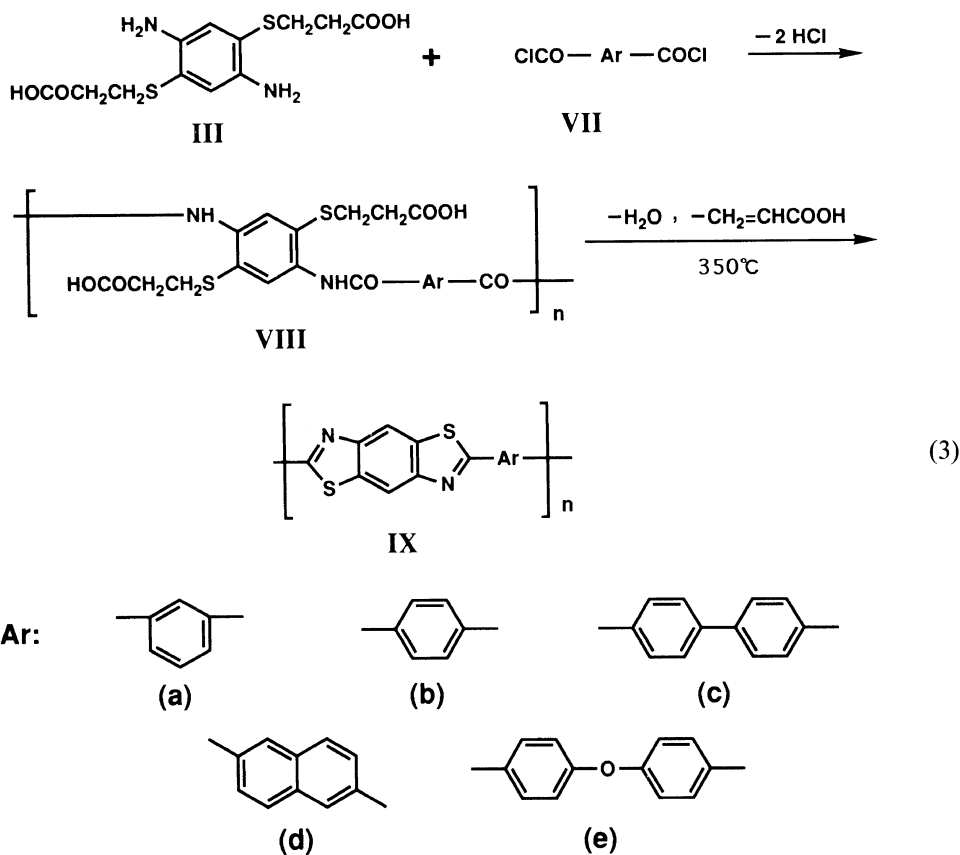
Before polymer synthesis, the model reaction (**IV**) was investigated [eq 2].



The reaction was carried out in NMP at 0°C, and afforded diamide compound **V** in an excellent yield. Then compound **V** was heated at 300°C in a high boiling and inert reaction medium (Marlotherm-S),²⁰ giving readily benzothiazole compound **VI** with the elimination of acrylic acid and water.

Polymer Synthesis

The synthesis of polybenzothiazoles **IX** via precursor 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.



The results are summarized in Table I. The polycondensations of diacid chlorides **VIIa** and **VIIe** in NMP proceeded homogeneously, the those of **VIIb**, **VIIc**, and **VII d** progressed also in homogeneous solution with the use of NMP solution containing lithium chloride as a reaction medium. Thus, various aromatic polyamides **VIII** having pendant (carboxyethyl)thio groups were obtained in inherent viscosities of 0.57–1.66 dl g⁻¹.

The formation of polyamides **VIII** was

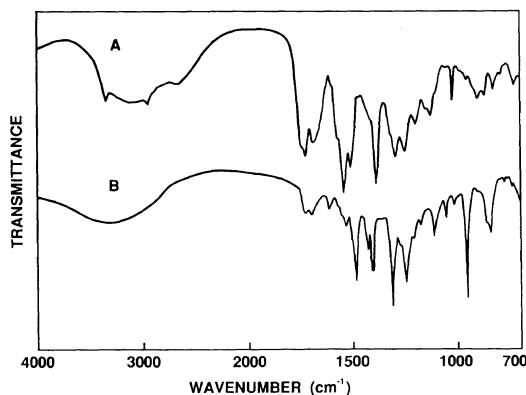
confirmed by means of IR, ¹H and ¹³C NMR spectroscopy, and elemental analysis. The IR spectrum of polyamide **VIIIb** [Figure 1(A)] exhibited absorption bands due to N–H bond, carboxyl group, and amide carbonyl at 3325, 1713, and 1674 cm⁻¹, respectively. Since the ¹H and ¹³C NMR spectra of polyamide **VIIIb** showed peaks due to pendant (carboxyethyl) thio group, amide group, and aromatic definitely, any side reaction on the pendant groups have not occurred during the polym-

Table I. Synthesis of aromatic polyamides **VIII**

Monomer Reaction medium ^a	Code	Polymer		
		Yield %	η_{inh}^b dl g ⁻¹	
VIIa	A	VIIIa	100	0.57
VIIb	B	VIIIb	100	1.01
VIIc	B	VIIIc	99	1.29
VIIId	B	VIIIId	98	1.66
VIIe	A	VIIIe	100	0.70

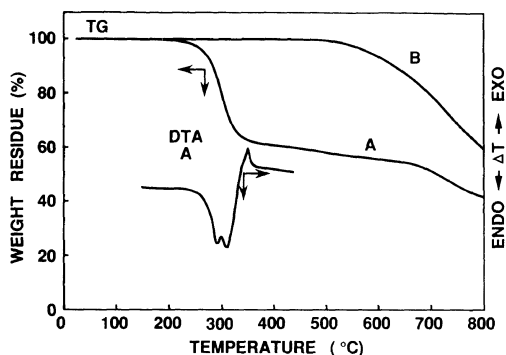
^a Polymerization was carried out using 2.5 mmol of the diamine and 2.5 mmol of the diacid chlorides in 5.0 ml of (A) NMP or (B) NMP containing 5wt% of lithium chloride at 0°C for 6 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in methanesulfonic acid at 30°C.

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

erization. The results of elemental analysis were in good agreement with the calculated values of the proposed structures of polyamides **VIII**.

The thermal conversion of polyamide **VIIIb** was followed by means of DTA, TG, and IR spectroscopy. The DTA curve of polyamide **VIIIb** exhibited an endothermic peak at around 280°C, which corresponded well with the initial weight loss temperature in the TG curve [Figure 2(A)]. The temperature of the initial weight loss was about 200°C, which was the lowest temperature compared with that of the

**Figure 2.** DTA and TG curves of (A) polyamide **VIIIb** and (B) polybenzothiazole **IXb**, at a heating rate of 10°C min⁻¹ in nitrogen.

precursor polyamides having pendant isopropylthio, [(methoxycarbonyl)ethyl]thio, and (cyanoethyl)thio groups.²⁰⁻²² The weight loss observed up to 350°C in the TG curve was 42% for polyamide **VIIIb**, and this value agreed well with the calculated weight loss of 40% based on the elimination of acrylic acid and water to convert to polybenzothiazole **IXb**.

These results suggested that the perfect cyclization of the intermediate polyamides into the polybenzothiazoles required a reaction temperature of 350°C. Thus, the thermal conversion was carried out by heating polyamides **VIII** at 350°C under vacuum. The conversion of **VIIIb** to **IXb** was supported by IR spectroscopy, with entire disappearance of absorption bands due to the both amide and carboxyl groups [Figure 1(B)]. 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 polybenzothiazole prepared by the polyphosphoric acid method.¹⁹ The elemental analysis values were in good agreement with the calculated values of the corresponding polybenzothiazole. Polybenzothiazole **IXb** formed had an inherent viscosity of 1.33 dl g⁻¹ in methanesulfonic acid, indicating that little or no thermal degradation leading to molecular chain scission occurred during the conversion process.

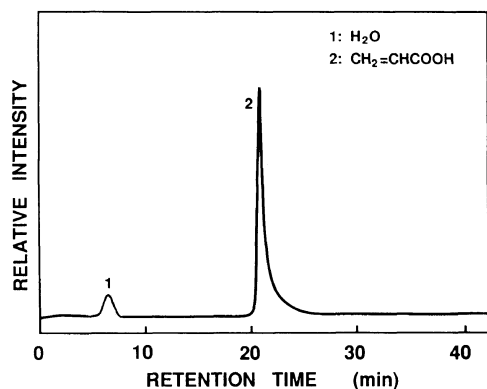


Figure 3. Pyrolysis GC-MS analysis of polyamide **VIIIb** after heating at 350°C for 10 min.

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

Further, the analysis of the eliminated gases was carried out in detail. The characteristic mass numbers of acrylic acid and water, which were 72 (m/z) for acrylic acid and 18 (m/z) for water, were followed by means of mass spectroscopy by heating of polyamide **VIIIb** with raising temperature at a heating rate of 10°C min⁻¹ to 800°C in helium gas (Figure 4).

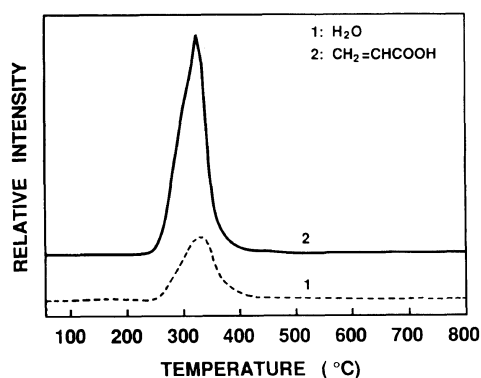
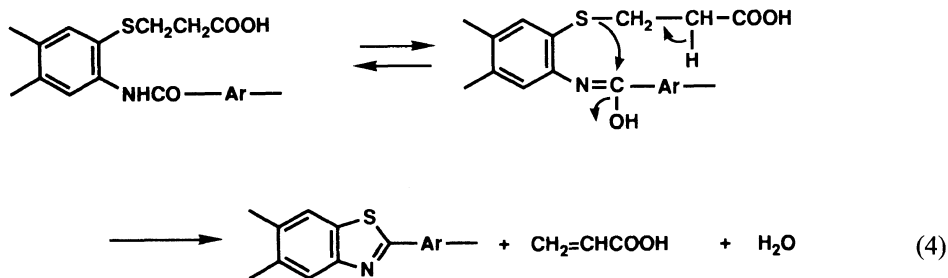


Figure 4. GC-MS analysis of polyamide **VIIIb** at a heating rate of 10°C min⁻¹ in helium.

The generation of acrylic acid and water was detected simultaneously at temperatures between 250 and 400°C. These results suggested that the weight loss of the polyamide during the thermal cyclization occurred together with the generation of the two gases.

Since the acrylic acid and water were detected at the same range of temperature, the thermal cyclization of the polyamides having (carboxyethyl)thio groups is more likely governed by the reaction mechanism of eq 4 which is substantially the same as those of polyamides having pendent groups reported previously.²⁰⁻²²



The lowest temperature of the cyclization in the polyamides having the pendant groups would be explained by the effect of the pendant carboxyl groups, which could give the precursor polyamide enough flexibility to progress the cyclization smoothly; the results of the dynamic mechanical properties will be

shown as the evidence later.

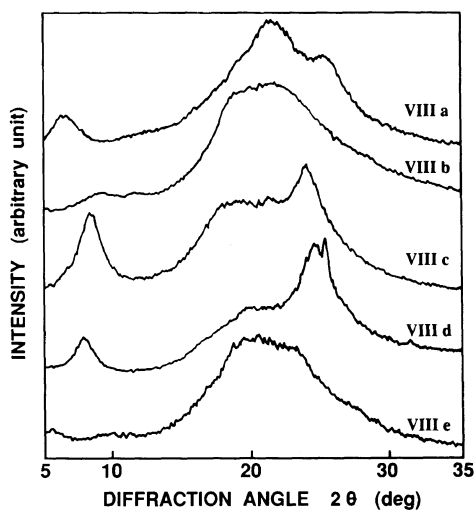
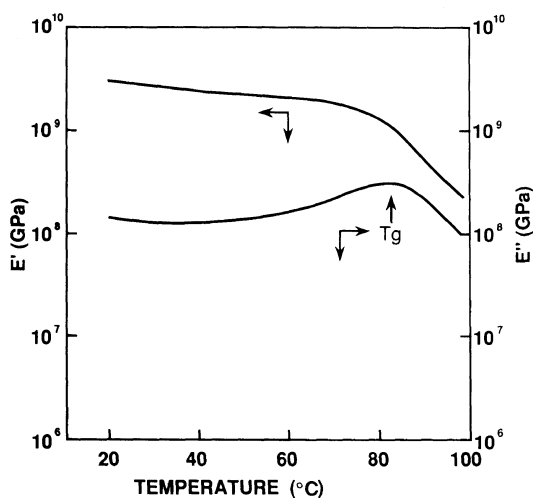
Polymer Characterization

The qualitative solubility behavior of precursor polyamides **VIII** is summarized in Table II. The introduction of bulky pendant (carboxyethyl)thio groups into the polyamide

Table II. Solubility of aromatic polyamides VIII^a

Solvent	Polymer				
	VIIIa	VIIIb	VIIIc	VIII d	VIIIe
Concentrated sulfuric acid	++	++	++	++	++
Methanesulfonic acid	++	++	++	++	++
<i>N</i> -Methyl-2-pyrrolidone + LiCl	++	++	++	++	++
<i>N</i> -Methyl-2-pyrrolidone	++	+	++	+	++
<i>N,N</i> -Dimethylacetamide	++	-	-	-	++
Dimethyl sulfoxide	++	+	+	-	++
<i>m</i> -Cresol	++	-	-	-	-
<i>o</i> -Chlorophenol	++	-	-	-	-
Pyridine	+	-	-	-	+
Chloroform	-	-	-	-	-

^a Solubility: (++) soluble at room temperature; (+) partially soluble; (-) insoluble.

**Figure 5.** X-Ray diffractograms of polyamides VIII.**Figure 6.** Dynamic mechanical properties of film of polyamide VIIIe.

backbone was expected to be effective to the solubility of such polymers. Indeed, polyamides VIIIa and VIIIe having *m*-phenylene linkage and flexible ether connecting group, respectively, were soluble in organic solvents such as NMP, *N,N*-dimethylacetamide, and dimethyl sulfoxide. Polyamides VIIIb, VIIIc, and VIII d having more rigid and symmetrical structures were only soluble in NMP containing lithium chloride. A film of polyamide VIIIe could be obtained from its solution by casting method.

The tensile strength, elongation at break, and tensile modulus of the film of polyamide VIIIe were 55 MPa, 28%, and 1.9 GPa, respectively.

The X-ray diffraction studies for the polyamides revealed that most of the polyamides had fair degree of crystallinity, especially polyamide VIIIc and VIII d had higher crystallinity (Figure 5).

The dynamic mechanical properties of the film of polyamide VIIIe are shown in Figure 6. The polyamide showed a glass transition

temperature (T_g) at 83°C, which was 12°C lower than the T_g of the precursor polyamide having [(methoxycarbonyl)ethyl]thio groups as the most bulky pendant groups reported previously²¹; the results showed that the (carboxyethyl)thio group gave the polyamide enough flexibility, which promote the thermal cyclization and reduce the initial temperature of the reaction. The free-standing film of polybenzothiazole **IXe** could not be obtained due to melting of precursor polyamide **VIIIe** during thermal treatment at 350°C.

Polybenzothiazole **IXb** did not lose weight up to 450°C in nitrogen, and the temperature of 10% weight loss was 650°C in that atmosphere [Figure 2(B)]. 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.

CONCLUSIONS

2,5-Bis[(carboxyethyl)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 (carboxyethyl)thio groups. The soluble precursor polyamides were then converted by thermal treatment to the corresponding poly(benzothiazoles) at 350°C with the elimination of acrylic acid and water. The introduction of pendant (carboxyethyl)thio group reduced the initial temperature of the thermal cyclization of the precursor polyamides. The precursor polyamides having (carboxyethyl)thio groups had a special potential for constructing films with nanometer thickness by using Langmuir–Blodgett (LB) technique.^{23,24}

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