A New Synthetic Route to Benzoxazole Polymer via Tandem Claisen Rearrangement

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Aromatic polybenzoxazoles have excellent mechanical and thermal properties. These polymers can be spun into ultrahigh-strength fibers and are capable of being used in the area of conventional and molecular composites.[1−5] Synthesis of aromatic polybenzoxazoles is generally achieved by two different synthetic methods. One is a one-step method using poly(phosphoric acid) (PPA),[6] phosphorus pentoxide/methanesulfonic acid (PPMA),[7] or trimethylsilyl polyphosphate (PPSE)/*o*-dichlorobenzene[8] as the reaction medium based on bis(*o*-aminophenol)s and aromatic diacids. The other one is a two-step method:[9−12] a poly(*o*-hydroxyamide), which is initially synthesized by condensation of an aromatic diacid chloride with a bis(*o*-aminophenol), then thermally cyclized with loss of water in the bulk state or in solution to the final aromatic benzoxazole polymer. In fact, mononuclear *o*-aminophenols, used as monomers for polybenzoxazoles, are readily oxidized. This determines their use as trimethylsilyl derivatives or hydrochlorides. It is also reported that aramids, containing a cyano, nitro, or halogen group ortho to the amide nitrogen, can be converted thermally at high temperatures to benzoxazole polymers via intramolecular aromatic nucleophilic displacement reaction by the amide oxygen.[13,14] More recently, Mathias demonstrated a successful thermal conversion of hydroxy-containing polyimides to polybenzoxazoles with loss of carbon dioxide.[15] Although aromatic polybenzoxazoles have long been of interest for their excellent properties, low solubility and difficult processability limited these materials as choices for new material development. Efforts in the synthesis of processable polybenzoxazoles led to fluorinated monomers and copolymers via preformed benzoxazole linkages.[16−22]

Phenolic hydroxy groups can be readily formed via tandem Claisen rearrangement of the isobutenyl bis(aryl ether) moiety in a small molecule or a polymer by heating.[23−27] In the present communication, we wish to report a new synthetic route to the soluble aromatic polybenzoxazole **4** by thermal transformation of the precursor aromatic polyamide **2**, as shown in Scheme 1. During the thermal treatment, the thermal tandem Claisen rearrangement of isobutenyl bis(aryl ether) moieties ortho to amide nitrogen in polyamide **2** initially led to the formation of bis(*o*-amidephenol) linkages, followed by the intramolecular cyclization (between the hydroxy and amide groups), with loss of water, to oxazole rings in the resulting polymer **4**.

The diamine monomer **1**, (2-{2-[(2-amino-4-*tert*-butylphenoxy)methyl]allyl}oxy-5-*tert*-butylaniline), was designed and synthesized.[28] This compound has two tertiary butyl groups para to an isobutenyl ether group, as shown in Scheme 1. The isobutenyl bis(aryl ether) moiety capable of the tandem Claisen rearrangement (TCR) was successfully introduced into the molecular structures. Generally speaking, Claisen rearrangement preferentially occurs to the ortho position of the ether group, but rearragement to the para position also takes place if there is no para substituent.[23] For the structure of the diamine **1**, TCR takes place only to the ortho position of the isobutenyl bis(aryl ether) moiety, due to the presence of a para substituent.

A novel polyamide **2**[29] was synthesized by low-temperature solution polycondensation of diamine **1** and terephthaloyl chloride, as shown in Scheme 1. The structure of this polymer was confirmed by IR, ^{1}H NMR, and ^{13}C NMR measurements. In the IR spectrum of the resulting polyamide, carbonyl absorption corresponding to an amide bond was observed at 1672 cm^{-1}. In

Scheme 1

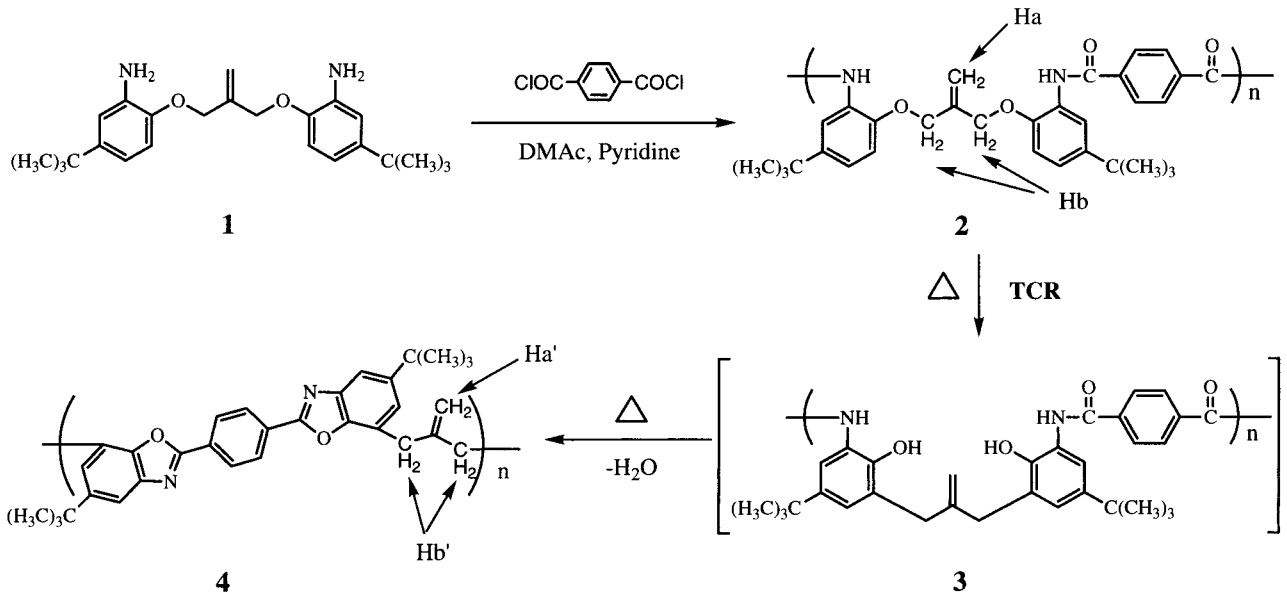

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Table 1. Results of Polymerization and Thermal Conversion to Polybenzoxazole

							solubility[e]			
polymer	yield, %	η_{inh},[a] dL/g	M_w[b]	M_w/M_n	T_g,[c] °C	T_d,[d] °C	amide solvents	DMSO	THF	$CHCl_3$
2	89	0.22	30 000	1.76			+	+	+	+
4	80	0.22	19 000	1.97	208	426 (355)	±	±	+	+

[a] Inherent viscosity measured in chloroform at a concentration of 0.5 g/dL at 30 °C. [b] Measured by gel permeation chromatography (GPC) in $CHCl_3$ as an eluent with polystyrene as a standard. [c] Measured by DSC using a heating rate of 20 K min^{-1} under a nitrogen atmosphere. [d] Measured by TGA using a heating rate of 10 K min^{-1} under nitrogen atmosphere (426 °C) and air (355 °C). [e] Amide solvents: dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP); DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

addition, a broad absorption at 3428 cm^{-1} assigned to the amide bond was also observed. In the ^1H NMR spectrum, the peak attributed to the amide proton was observed at 8.52 ppm. Furthermore, two peaks for the protons Ha and Hb (see Scheme 1) in the polymer were observed at 5.41 and 4.73 ppm, respectively. This indicates that the isobutenyl bis(aryl ether) moiety capable of TCR was successfully incorporated into the structure of polyamide **2**.

Tandem Claisen rearrangement for polyamide **2** was carried out in *N*,*N*-di-*n*-butylaniline at 240 °C for 20 h under nitrogen.[30] A white powdery polybenzoxazole **4** instead of the polymer **3** was obtained by precipitation of the reaction mixture into methanol. The structure of the polybenzoxazole **4** was confirmed by IR, ^1H NMR, and ^{13}C NMR spectra. In the IR spectra, the carbonyl absorption for an amide bond at 1672 cm^{-1} observed in the precursor polyamide **2** disappeared after the thermal treatment, while a new peak corresponding to the C═N bond of oxazole rings was observed at 1626 cm^{-1} for the resulting benzoxazole polymer **4**. In addition, the peak at 8.52 ppm of the amide proton in the ^1H NMR spectrum of polyamide **2** also disappeared after the thermal treatment. Furthermore, the chemical shifts of protons Ha and Hb in the polymamide **2** changed to 5.12 and 3.71 ppm assigned to the respective protons Ha′ and Hb′ in the resulting polybenzoxazole **4** (see Scheme 1). Hence, it is clear that, during the thermal treatment, the tandem Claisen rearrangement (formation of hydroxy groups) followed by in-situ intramolecular cyclization between the hydroxy groups and ortho amides, with loss of water, led to the polybenzoxazole **4**.

The results of the polymerization and subsequent thermal conversion are summarized in Table 1. After the thermal conversion, a loss in molecular weight to some 63% of the prior polymer **2** was observed by gel permeation chromatography (GPC). However, the inherent viscosity of the resulting benzoxazole polymer **4** was found to be the same as that of the parent polyamide **2**. Surprisingly, the polybenzoxazole **4** has low solubility in amide solvents and DMSO compared to its precursor polyamide **2** but is easily soluble in THF and chloroform. A colorless and transparent film was obtained by casting THF or $CHCl_3$ solution of the resulting polybenzoxazole **4** on a glass plate. This implies that almost no oxidization took place during the thermal conversion procedure. The resulting polybenzoxazole **4** is promising in application to film products. The thermogravimetric analysis (TGA) reveals the excellent thermal stability of this novel benzoxazole polymer **4**: decomposition temperatures were observed at 426 °C in nitrogen and 355 °C in air. The glass transition temperature was observed at 208 °C by the differential scanning calorimetry (DSC), and no melting point was found by the DSC technique. The amorphous characteristic was also confirmed by wide-angle X-ray diffraction. By comparison with the TGA stability of some whole aromatic polybenzoxazoles,[16,19] the benzoxazole polymer **4** prepared in this work has relatively low thermal stability, which is caused by the aliphatic units in the polymer backbone.

In summary, a new synthetic route to a novel aromatic polybenzoxazole **4** has been successfully achieved by thermal conversion of the precursor polyamide **2** containing isobutenyl bis(aryl ether) moieties in the polymer main chain. During the thermal conversion, the tandem Claisen rearrangement gave hydroxy groups ortho to the amide groups; sequential intramolecular cyclization, with loss of water, led to the resulting aromatic benzoxazole polymer **4**. This polymer has excellent thermal stability, relatively high glass transition temperature, and good solubility.

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(28) 2-{2-[(2-Amino-4-*tert*-butylphenoxy)methyl]allyl}oxy-5-*tert*-butylaniline **(**diamine **1)** was synthesized as follows. To a mixture of 2-amino-4-*tert*-butylphenol (8.0 g, 0.048 mol) in 100 mL of tetrahydrofuran (THF) was added acetic anhydride (4.94 g, 0.048 mol). After stirring the reaction mixture overnight at room temperature, THF was removed under reduced pressure. The residue was then washed with water and dried to give 2-acetamido-4-*tert*-butylphenol (9.65 g, 97%). A mixture of 2-acetamido-4-*tert*-butylphenol (4.0 g, 0.019 mol), potassium hydroxide (2.10 g, 0.038 mol), and 3-chloro-2-chloromethyl-1-propene (1.19 g, 9.5 mmol) in ethanol (80 mL) was stirred at 70 °C under argon for 16 h. After ethanol was removed under reduced pressure, the solid residue was washed with water and recrystallized from an ethyl acetate and hexane mixture to give 2-{2-[(2-acetamido-4-*tert*-butylphenoxy)methyl]allyl}oxy-5-*tert*-butylacetamilide (3.73 g, 83%). This compound (3.0 g, 6.43 mmol) was then dissolved in 80 mL of ethanol containing 32 mL of water and 10.32 g of potassium hydroxide. After reflux under nitrogen for 24 h, white crystals were obtained on cooling. The product was collected by filter, washed with water, and dried to give diamine **1** (2.09 g, 85%); mp: 109.5−110.5 °C. IR (KBr): 3435, 3354 (N−H), 1218, 1027 (C−O−C) cm^{-1}. ^1H NMR (DMSO-d_6): δ 1.20 (s, 18 H, $-C(CH_3)_3$), 4.61 (s, 4 H, $-CH_2-$), 5.36 (s, 2 H, $=CH_2$), 6.47 (dd, $J = 6.1$ and 2.3 Hz, 2 H, Ar), 6.70 (d, $J = 3.70$ Hz, 2 H, Ar), 6.71 (d, $J = 2.3$ Hz, 2 H, Ar). ^{13}C NMR (DMSO-d_6): δ 143.25, 142.96, 141.33, 137.02, 114.02, 112.54, 111.62, 111.54, 68.26, 33.59, 31.34. Anal. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.04; H, 8.80; N, 7.12.
(29) In a three-necked flask, 1.88 g (4.93 mmol) of the diamine **1** was dissolved in 10 mL of DMAc. The solution was frozen with a liquid nitrogen bath, and 1.0 g (4.93 mmol) of terephthaloyl chloride was added into the flask. The reaction mixture then was stirred at 0 °C for 1 h under nitrogen and continued for another 3 h at room temperature. The resulting polyamide **2** was precipitated by pouring the reaction mixture into methanol, isolated by filter, and purified by reflux with methanol to give 2.53 g (89.0%). IR (KBr): 3428, 1672, 1201, 1015 cm^{-1}. ^1H NMR (CD_3Cl): δ 1.28 (s, 18H, $-C(CH_3)_3$), 4.73 (s, 4H, $-CH_2-$), 5.41 (s, 2H, $=CH_2$) 6.81 (d, $J = 8.55$ Hz, 2H, Ar), 7.02 (dd, $J = 6.4$ and 2.15 Hz, 2H, Ar), 7.25 (s, 2H, Ar), 7.84 (s, 4H, Ar), 8.52 (s, 3H, 2Ar and 1CONH). ^{13}C NMR (CD_3Cl): δ 164.10, 145.04, 139.78, 137.90, 127.37, 127.24, 121.06, 118.19, 116.78, 111.33, 69.74, 34.78, 31.42. Anal. Calcd for $C_{32}H_{36}N_2O_4$: C, 74.97; H, 7.08; N, 5.46. Found: C, 74.47; H, 7.04; N, 5.32.
(30) Into a flask was added 0.5 g of the precursor polyamide **2** and 5 mL of *N*,*N*-di-*n*-butylaniline. After the flask was flushed with nitrogen and evacuated three times, the temperature was increased up to 240 °C, and the reaction proceeded under stirring at this temperature for 20 h in nitrogen. Then the reaction mixture was poured into methanol to precipitate the crude product. The purification was achieved by reprecipitation from the chloroform solvent into hexane three times and dried at 60 °C in a vacuum overnight to give the resulting polybenzoxazole, 0.40 g (80%). IR (KBr): 1626, 1193, 1015 cm^{-1}. ^1H NMR (CD_3Cl): δ 1.35 (s, 18H, $-C(CH_3)_3$), 3.71 (s, 4H, $-CH_2-$), 5.12 (s, 2H, $=CH_2$), 7.22 (s, 2H, Ar), 7.65 (s, 2H, Ar), 8.13 (4H Ar). ^{13}C NMR (CD_3Cl): δ 162.32, 148.88, 148.38, 145.00, 142.26, 129.91, 128.07, 124.43, 122.14, 115.16, 36.88, 35.34, 32.18. Anal. Calcd for $C_{32}H_{32}N_2O_2(1/4\ H_2O)$: C, 79.89; H, 6.81; N 5.82, Found: C, 79.97; H, 6.75; N 5.67.

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