NOTES

Thermal Rearrangement of Poly(*o*-hydroxyimide)s Synthesized from 4,6-Diaminoresorcinol Dihydrochloride

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Aromatic polybenzoxazoles (PBOs) are well known as high performance polymeric materials due to their excellent thermal stability, high solvent and chemical resistance, thermo-oxidative stability and outstanding mechanical properties, which make them attractive for many applications such as fabrication of high-strength and high-modulus fibers.^{1–4}

PBOs have been prepared by several methods, *i.e.*, a one-step solution polycondensation of bis(*o*-aminophenol)s with aromatic dicarboxylic acids in polyphosphoric acid, a melt polycondensation of bis(*o*-aminophenol)s with diacid diphenyl esters.⁸ Alternatively, they have been synthesized by two-step methods starting from bis(*o*-aminophenol)s or their trimethylsilylated derivatives^{5–7,9} with aromatic dicarboxylic acid chlorides or tetracarboxylic anhydrides giving precursor poly(*o*-hydroxyamide)s (PAOHs) or poly(*o*-hydroxyimide)s (PIOHs) followed by thermal rearrangement of the hydroxy-containing precursors to the final PBOs. Using the precursor polymers has advantage in processability of precursors even though almost PBOs do not dissolve in organic solvents, and do not melt at elevated temperatures.

There have been many reports for PBOs preparation *via* the PAOHs precursor method,^{5,16–23} whereas not so many papers describe about the thermal conversion of PIOHs to PBOs. After the first synthesis of poly(3,3'-dihydroxy 4,4'-diphenylene) pyromellitimide and thermal conversion to the corresponding PBO was reported by Kardash *et al.* in 1967,²⁴ several studies have been reported.^{10–15} Although PIOHs has been prepared from the smallest diamino-diphenol monomer, 4,6-diaminoresorcinol,²⁵ it is noteworthy that no report was found concerning the thermal rearrangement of PIOHs synthesized from 4,6-diaminoresorcinol to PBOs

that are expected to possess high modulus and high strength because of their compact rigid rod structure.

In this paper, we describe results in synthesis of PIOHs from 4,6-diaminoresorcinol dihydrochloride (DAR), and attempts of thermal conversion to PBOs. Preparation of PBOs *via* the PAOHs route is also described in comparison.

EXPERIMENTAL

Materials

Aromatic tetracarboxylic acid dianhydrides **1**: pyromellitic dianhydride (PMDA) **1a**, 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) **1b**, 3,3',4,4'-oxydiphthalic anhydride (ODPA) **1c**, and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) **1d** were sublimated prior to use. 4,6-Diaminoresorcinol dihydrochloride (DAR) was recrystallized from water with HCl and dried at 80 °C in vacuum. 3,3'-Dihydroxy-4,4'-aminobiphenyl (HAB) was recrystallized from a water/DMAc cosolvent and dried at 60 °C in vacuum.¹² Isophthalic acid **6a**, terephthalic acid **6b**, 4,4'-dicarboxydiphenyl ether **6c**, and 4,4'-biphenyldicarboxylic acid **6d** were used as received. *N*-Methyl-2-pyrrolidinone (NMP) was stirred over calcium hydride overnight and then distilled under reduced pressure.

Measurements

The FT-IR spectra were measured with Jasco Fourier Transform Infrared Spectrometer FT-IR-600 Plus using KBr disc or films. Thermogravimetric analyses were performed on TG/DTA 6200 SII Seiko Instruments Inc EXSTAR 6000 thermal analyzer using a heating rate of 20 °C min^{–1} in nitrogen. Differential

Equation 1.

scanning calorimeter DSC data were obtained on DSC 6200 SII Seiko Instruments Inc. EXSTAR 6000 in nitrogen atmosphere at a heating rate of 10 °C using sealed aluminum pans. Dynamic mechanical analyses (DMA) were made with DVA-200, heating rate 5 °C min⁻¹ from ambient temperature to 350 °C at a frequency of 10 Hz. A sample 30 mm in length, 5 mm in width, and approximately 0.5–0.7 mm. Mechanical properties of solution cast films were determined using TENSILON/UTM-II-20 TOKYO BALDWIN CO. LTD., with a load cell of 5 kg, rate 4 mm min⁻¹. Measurements were performed at room temperature with film specimens (40 mm long, 5 mm wide and about 0.2–0.5 mm thick).

Synthesis of Poly(o-hydroxyimide)s (PIOHs) 2

PIOHs **2** were synthesized by the reaction between **1** and DAR using the high temperature polycondensation method.²⁵ Films of **2** were prepared by casting 20% or 15% (w/v) solution of **2** on aluminum foil and removing solvent in a vacuum oven at 25 °C for 24 h. And then, the films were heated *in vacuo* at 100 °C for 1 h, 200 °C for 1 h and 300 °C for 1 h. The aluminum was removed by dipping in 2 M hydrochloric acid aqueous solution.

Synthesis of Poly(o-hydroxyamide)s (PAOHs) 7

Synthesis of PAOHs **7** were carried out according to typical procedure as direct solution polycondensation aromatic diacids **6** with DAR.²⁶

Thermal Treatment

Thermal treatment of **2** was carried out by heating

the films of **2** for 30 min at 350, 400, 450, 500, and 550 °C in nitrogen atmosphere. The conversion of **7** to **3** was carried out by heating the polymer powders at 340 °C and 360 °C for 30 min in nitrogen atmosphere.

RESULT AND DISCUSSION

Eq 1 illustrates preparation of PBOs *via* PIOHs **2** in the present work. PIOHs **2** were synthesized from tetracarboxylic anhydrides **1** and DAR by the high temperature solution method in NMP at 170 °C.²⁵ Yields of **2** were over 93% as shown in Table I.

Although the reaction mixtures after polymerization were homogeneous, polyimides **2** except for **2b** obtained from BPDA were insoluble in organic solvents, whereas this kind of polyimides was described as soluble in amide solvents.²⁵ Therefore, the films of **2** were prepared from the reaction mixture. As they adhered tenaciously to the glass plates, they were cast on aluminum foil, and then the foil was removed by aqueous hydrochloric acid. All polyimides gave flexible films.

In the FT-IR spectra of PIOHs **2**, two absorption bands at 1720 and 1780 cm⁻¹ characteristic for imide carbonyl group and the broad absorption band at 3200 cm⁻¹ corresponding to the hydroxyl group were observed.

Table I shows thermal properties of PIOHs **2**. As glass transition temperatures (*T_g*'s) of **2** were not observed using DSC, they were measured by dynamic mechanical thermal analysis (DMA). The polyimide **2b** from BPDA exhibited the highest *T_g*, while **2c** from ODPA showed the lowest *T_g*. These polymers showed

Table I. Properties of PIOHs **2**

PIOH	Yield %	η_{inh}^a dL g ⁻¹	T_g^b °C	T_{10}^c °C	E' of DMA (GPa)			Mechanical Properties		
					at 70 °C	at 200 °C	at 250 °C	Modulus GPa	Elongation at break %	Strength MPa
2a	93	—	329	520	3.05	2.65	2.33	—	—	—
2b	94	0.55	346	495	3.91	3.14	2.72	2.10	0.5	82
2c	97	—	298	455	2.98	2.39	1.95	2.45	6.4	87
2d	98	—	309	510	3.92	3.19	2.65	1.90	5.2	57

^aMeasured in NMP at 30 °C with concentration of 0.5 g dL⁻¹. ^bDetected by DMA. ^cTemperature of 10% weight loss.

Figure 1. TG curve of PIOH **2b**. (a) before heating, (b) after heating at 550 °C.

10% weight loss at temperatures in the range of 455–520 °C. Residue at 800 °C is in the range from 44 to 48%. Table I also collects the results of thermomechanical and mechanical properties of the films of **2**. It can be seen for PIOHs **2** that the values of the storage modulus E' at 200 °C are lower in the range of 19–20% in comparison to those at 70 °C, except for **2a** (13%). However, even at 250 °C, the films preserve a rather high values of E' , indicating their high thermal stability.

The thermal conversion of PIOHs **2** to PBOs **3** was investigated by FT-IR spectroscopy. Each film has been heated for 30 min at 350, 400, 450, and 500 °C in nitrogen atmosphere. Polyimides **2c** and **2d** obtained from ODPA and BPDA were also heated at 550 °C for 30 min under nitrogen as comparison. Polyimides **2** were stable up to 400 °C and remarkable sign of the benzoxazole ring could not be found. For instance, when the film of **2c** was heated at 500 °C and 550 °C, no significant decreasing of the absorption bands characteristic for imide carbonyl and appearing of a small new absorption band at about 1556 cm⁻¹ (typical band for benzoxazoles^{13,14}) was observed. The results of IR spectra indicate that part of the imide ring converted to PBO, while the rearrangement was not completed, and imide structure still existed even after heating at 550 °C.

Figure 1 presents thermogravimetric (TG) analysis curves of **2b** before and after treatment at 550 °C. In the case of the before heat treatment, weight decrease is observed at 390 °C, whereas the sample after heat treatment did not show any change at this tempera-

Figure 2. TG curve of PIOHs. (a) BPDA **1b** and HAB, (b) **1b** and DAR.

ture. Although it was reported that the weight loss of **2** occurs in two well-distinct stages,^{10–15} the TG curves in the present study showed only one stage of weight loss. For comparison, polyimide from 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) and BPDA¹³ was prepared, and Figure 2 represents TG curves of PIOHs prepared from BPDA and HAB as well as BPDA and DAR. In this case, double stage decomposition is clearly observed. The first weight loss taking place from 400 to 500 °C corresponds to formation of PBO with decarboxylation reaction and the second one indicates decomposition of PBO. Thus, PIOH from HAB was clearly converted to PBO compared with the case of **2**. This phenomenon can be explained by more flexible nature of HAB, while the thermal rearrangement from **2** to PBO **3** was restricted by the rigid nature of DAR. The results of IR spectra and TG analysis indicate that, in the films of **2**, the unknown thermal reactions that kept polyimide structure occurred at 390 °C.

Decreasing of conversion temperature of PIOHs to PBOs about 50–70 °C was reported after introduction of acetyl group into phenolic group.¹⁴ In the next step, hydroxyl group of **2** was chemically modified by acetylation with acetic anhydride and silylation with *tert*-butyldimethylsilyl chloride. It was expected that such chemical modification of the polymers **2** decreased the temperature of their rearrangement to PBOs **3** and improved solubility of **2**.¹⁴ Acetylation of **2** was carried out according to the method described in literature²⁷ as shown in eq 1. In FT-IR spectrum, a new absorption band appeared at 1147 cm⁻¹ characteristic for the

ester functionality. Acetate polymers **4** except for **4a** from PMDA were soluble in NMP at room temperature and in DMSO on heating. Films of **4** were brittle except for **4c** from ODPA. Introduction of silyl group into polyimides **2** was also carried out according to literature.²⁷ Polymers **5** after silylation were soluble in NMP at room temperature and in DMSO on heating. Films of **5** were flexible (except for **5a** from PMDA).

Table II shows properties of polyimides with functional groups. All polymers after chemical modifications exhibited better solubility. Inherent viscosity was in the range of 0.29–0.48. It has been observed that introduction of acetyl groups into polymer chain decreases their temperature of 10% weight loss. Introduction of *tert*-butyldimethylsilyl group also reduced the temperature of 10% weight loss in the smaller range compared with acetylation. TG curves of polyimides **4** and **5** did not show the characteristic double stage decrease.

As films of **4c** and **5c** prepared from ODPA and **5d** prepared from BTDA were flexible, they were heated at 300, 350, 400, and 450 °C during 30 min under nitrogen in order to change the structure to PBO **3**. After heating at 450 °C, all films became brittle. FT-IR spectra showed small changes of the absorption bands after heating at 450 °C in comparison with polymers before

thermal treatment. The absorption bands characteristic for imide ring are still present. A new small absorption band at 1557 cm⁻¹ (typical for PBOs^{13,14}) appeared after heating at 400 °C. The results of IR investigation indicated that functionalized PIOHs were not converted to PBOs by heating up to 450 °C.

As it was found that thermal conversion from PIOHs **2** to PBOs **3** seemed to be difficult because of rigid structure of DAR, preparation of PBO by thermal conversion of poly(*o*-hydroxyamide)s (PAOHs)^{16–22} that were prepared from DAR was investigated as comparison. Such rearrangement to PBOs has been described to occur at lower temperatures. Preparation of a series of PAOHs **7** from diacids **6** and DAR is shown on eq 2. Synthesis of **7** was carried out according to the typical procedure as the direct polycondensation method for aromatic diacids **6** with DAR using triphenylphosphite and pyridine.^{26,28} The formation of **7** was confirmed by FT-IR spectroscopy. The polymers exhibited the broad absorption band in the region of 2500–3500 cm⁻¹ (O–H and N–H str.) and the absorption band characteristic for amid carbonyl group at about 1658 cm⁻¹ (amide C=O str.).

PAOHs **7** were soluble in NMP at room temperature. As show in Figure 3, two stage decrease was clearly observed in TG curves of **7** contrary to TG curves of **2**. The TG curves of PIOHs synthesized from DAR show only one stage of weight loss. The first one is connected with the weight loss due to the thermal cyclodehydration of **7** to PBO **3**. The TG trace reveals that the weight loss started around 240 °C and came to an

Table II. Properties of functionalized PIOH

PIOH	η_{inh}^a	Solubility ^b		T_{10}^c °C	Film
		DMSO	NMP		
2a	—	—	—	521	flexible
4a	—	—	—	200	—
5a	0.47	+	Gel	413	brittle
2b	0.55	—	++	495	flexible
4b	0.29	++	++	259	brittle
5b	0.39	++	++	454	brittle
2c	—	—	—	456	flexible
4c	0.34	+	++	312	flexible
5c	0.34	+	++	472	flexible
2d	—	—	—	512	flexible
4d	0.40	+	++	249	brittle
5d	0.48	+	++	478	flexible

^aMeasured in NMP at 30 °C with concentration of 0.5 g dL⁻¹. ^b—: insoluble, +: soluble after heating, ++: soluble. ^cTemperature of 10% weight loss.

Figure 3. TG curve of (a) PIOH **2b** and (b) PAOH **7d**.

Equation 2.

end at about 360 °C. In this range of temperature, about 11% of weight loss took place, which is corresponding to dehydration by cyclization reaction between amide and *ortho* OH group (relevant to the theoretical value 10.4%). The appearance of new absorption band at 1624 cm⁻¹ (–C=N str.)^{17–20,22} proves the formation of PBO **3**. Obtained **3** were insoluble in NMP. The results of TG measurement support that conversion from **7** to **3** occurred easily even though DAR was used as a monomer.

CONCLUSIONS

Taking into account results of the investigations, it was found that rearrangement of PIOHs **2** synthesized from DAR to PBOs was not completed even after applying a very high temperature. On the other hands, the TG analysis suggested that unknown thermal reactions occurred at 390 °C giving thermally stable product. It was assumed that conversion from **2** to PBOs can be restricted by insufficient mobility of the polymer chain to restructure the cycles, because PIOHs derived from HAB and PAOHs with DAR could be easily converted to PBOs by heat treatment. Chemical modifications of **2** through replacement of hydrogen of phenolic group with acetyl and *tert*-butyldimethylsilyl did not remarkably influence the temperature and degree of conversion to PBOs. Important properties of such polyhydroxyimides are their strong adhesion to glass, high thermal stability and good mechanical properties.

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