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Synthesis and Properties of Fluorine-Containing Aromatic Polybenzoxazoles from Bis(*o*-aminophenols) and Aromatic Diacid Chlorides by the Silylation Method

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ABSTRACT: A series of poly(*o*-hydroxy amides) of high molecular weights was synthesized by the low-temperature solution polycondensation of *N,N′,O,O′*-tetrakis(trimethylsilyl)-substituted 2,2-bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane with aromatic diacid chlorides. Subsequent thermal cyclodehydration of the poly(*o*-hydroxy amides) at 250 °C in vacuo afforded the polybenzoxazoles with high molecular weights. Most of the poly(*o*-hydroxy amides) dissolved readily in a variety of solvents, whereas the polybenzoxazoles were insoluble with some exceptions. The polybenzoxazoles had high glass transition temperatures of 260–325 °C and were stable up to 450 °C in air.

Introduction

Aromatic polybenzoxazoles have been known since 1964 as a class of aromatic heterocyclic polymers that exhibit excellent thermal stability.[1,2] Recently, rigid-rod polybenzoxazoles have become of interest because these polymers have a potential for fabrication into high-strength and high-modulus fibers.[3,4]

Aromatic polybenzoxazoles were generally synthesized by three methods. The first synthesis was described by Kubota and Nakanishi,[5] who obtained organic-insoluble polybenzoxazoles in two steps by the prior formation of soluble poly(*o*-hydroxy amides) having high molecular weights through the low-temperature solution polycondensation of bis(*o*-aminophenols) with aromatic diacid chlorides, followed by thermal cyclodehydration. A different approach, the one-step synthesis of aromatic polybenzoxazoles, was investigated by Moyer et al.,[6] which involved the high-temperature melt or solid-state polycondensation of bis(*o*-aminophenols) with aromatic diacid diphenyl esters. Iwakura et al.[7] demonstrated a more facile method for the preparation of aromatic polybenzoxazoles by the direct solution polycondensation of bis(*o*-aminophenols) with aromatic diacids using polyphosphoric acid that acts as both reaction medium and condensing agent. Quite recently, Ueda et al.[8] developed a modified method for the synthesis of polybenzoxazoles with the use of a mixture of phosphorus pentoxide and methanesulfonic acid in place of the polyphosphoric acid.

Because fluorine-containing aromatic polybenzoxazoles are expected to have some unique properties, we investigated the synthesis of aromatic polybenzoxazoles from 2,2-bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane and aromatic diacid derivatives. However, the synthesis of high-molecular-weight polybenzoxazoles was difficult because of low nucleophilicity of the fluorine-containing monomer caused by the existence of the electron-withdrawing hexafluoroisopropylidene group.

Recently we reported that *N,N′*-bis(trimethylsilyl)-substituted aromatic diamines were more reactive than the parent diamines toward diacid chlorides, giving high-molecular-weight aromatic polyamides.[9,10] We also found that aromatic diamines with low nucleophilicity could be activated more positively through the conversion to the *N*-silylated diamines.[11-13] These findings have led to the suggestion that nucleophilicity of the fluorine-containing bis(*o*-aminophenol) could be improved by the silylation method sufficiently enough to form high-molecular-weight polybenzoxazoles. The silylation of the bis(*o*-aminophenol) would bring about another advantage of undergoing a selective reaction. For example, *N,O*-bis(trimethylsilyl)-*o*-aminophenol should be attacked by an acid chloride at the *N*-silylated amine site selectively, forming exclusively the corresponding amide product, a precursor of the benzoxazole compound. The reason is that the amino group of *o*-aminophenol is activated through silylation, whereas the hydroxyl group is deactivated, as it is well demonstrated that the silylation of the hydroxyl group is normally a protection against electrophilic attack.[14,15]

The present article deals with the synthesis and characterization of fluorine-containing aromatic polybenzoxazoles from 2,2-bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane and aromatic diacid chlorides

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by the silylation method. Two other polybenzoxazoles having no fluorine atom were also prepared and characterized for comparison.

Experimental Section

Materials. *N,O*-Bis(trimethylsilyl)-*o*-aminophenol (1). The compound was synthesized according to the method of Kricheldorf[16] in a 65% yield by the reaction of *o*-aminophenol with trimethylsilyl chloride in the presence of triethylamine as a hydrogen chloride acceptor; bp 54–56 °C (0.1 Torr) [lit.[16] bp 75–77 °C (0.2 Torr)]; IR (NaCl) 1250, 850, and 750 cm^{-1} ($SiCH_3$); ^1H NMR ($CDCl_3$) δ 0.24 (s, 9 H, $NSiCH_3$), 0.28 (s, 9 H, $OSiCH_3$), and 6.2–6.6 (m, 4 H, aromatic).

3,3′-Bis(trimethylsiloxy)-4,4′-bis((trimethylsilyl)amino)biphenyl (6a). 4,4′-Diamino-3,3′-dihydroxybiphenyl (5a) was prepared by the method of Burkhardt and Wood[17] in a 66% yield by the demethylation of commercial 4,4′-diamino-3,3′-dimethoxybiphenyl with 52% hydrogen iodide; mp 289 °C (by differential thermal analysis; lit.[17] mp 292 °C).

To a solution of 4.32 g (20 mmol) of **5a** and 8.50 g (84 mmol) of triethylamine in 80 mL of dry tetrahydrofuran (THF), 9.12 g (84 mmol) of trimethylsilyl chloride was added dropwise with stirring at 20 °C under nitrogen. The mixture was stirred at that temperature for 1 h and then at 60 °C for 4 h. The precipitated triethylammonium chloride was removed by filtration under nitrogen atmosphere, and the crude product was obtained by distilling out the THF solvent from the filtrate. Vacuum distillation (bp 200–230 °C (0.5 Torr)) and subsequent recrystallization from ligroin afforded 5.45 g (54%) of pure **6a** as colorless prisms: mp 157–159 °C; IR (nujol) 1250, 850, and 750 cm^{-1} ($SiCH_3$); ^1H NMR ($CDCl_3$) δ 0.00 (s, 18 H, $NSiCH_3$), 0.23 (s, 18 H, $OSiCH_3$), and 6.5–7.1 (m, 6 H, aromatic). Anal. Calcd for $C_{24}H_{44}N_2O_2Si_4$: C, 57.09; H, 8.78; N, 5.55. Found: C, 57.09; H, 8.77; N, 5.83.

2,2-Bis(4-(trimethylsiloxy)-3-((trimethylsilyl)amino)phenyl)propane (6b). 2,2-Bis(4-hydroxy-3-nitrophenyl)propane was synthesized according to the method of Buu-Hoi[18] in a 64% yield by the nitration of 2,2-bis(4-hydroxyphenyl)propane with 60% nitric acid in acetic acid; mp 132.5–133 °C (lit.[18] mp 134 °C).

2,2-Bis(3-amino-4-hydroxyphenyl)propane (5b) was prepared by the conventional reduction of the nitro compound with stannous chloride in ethanol; mp 256–258 °C, with decomposition (lit.[18] mp 256 °C, with decomposition).

The tetrasilyl compound **6b** was synthesized as described for **6a** by starting with 5.17 g (20 mmol) of **5b**, 9.12 g (84 mmol) of trimethylsilyl chloride, and 8.50 g (84 mmol) of triethylamine in 80 mL of dry THF. Two repeated fractional distillations afforded 6.45 g (59%) of the product as a colorless viscous liquid: bp 205–210 °C (0.1 Torr); IR (NaCl) 1250, 850, and 750 cm^{-1} ($SiCH_3$); ^1H NMR ($CDCl_3$) δ 0.10 (s, 18 H, $NSiCH_3$), 0.23 (s, 18 H, $OSiCH_3$), and 6.4–6.6 (m, 6 H, aromatic). Anal. Calcd for $C_{27}H_{50}N_2O_2Si_4$: C, 59.28; H, 9.21; N, 5.12. Found: C, 59.17; H, 9.21; N, 5.42.

2,2-Bis(4-(trimethylsiloxy)-3-((trimethylsilyl)amino)phenyl)-1,1,1,3,3,3-hexafluoropropane (6c). 2,2-Bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (5c) was supplied by Central Glass Co., Japan, as a white powder; mp 243–245 °C.

To a solution of 7.32 g (20 mmol) of **5c** in 50 mL of dry THF, 6.78 g (42 mmol) of hexamethyldisilazane and 1.08 g (10 mmol) of trimethylsilyl chloride were successively added dropwise with stirring at 20 °C under nitrogen. The solution was stirred at that temperature for 5 h and further at 60 °C for 40 h. After removal of the THF solvent from the solution under reduced pressure, the residue was distilled in vacuo yielding the crude product; bp 140–150 °C (0.1 Torr). This was recrystallized from ligroin to afford 10.5 g (80%) of pure **6c** as colorless prisms; mp 117–119 °C.

This compound was also prepared as described for **6a** in a 79% yield by the reaction of **5c** with trimethylsilyl chloride in the presence of triethylamine in dry THF; IR (nujol) 1250, 850, and 750 cm^{-1} ($SiCH_3$); ^1H NMR ($CDCl_3$) δ 0.03 (s, 18 H, $NSiCH_3$), 0.20 (s, 18 H, $OSiCH_3$), and 6.6–6.8 (m, 6 H, aromatic). Anal. Calcd for $C_{27}H_{44}F_6N_2O_2Si_4$: C, 49.51; H, 6.77; N, 4.28. Found: C, 49.39; H, 6.88; N, 4.37.

Other Materials. Benzoyl chloride (**2**), isophthaloyl chloride (**7a**), and terephthaloyl chloride (**7b**) were obtained commercially and purified by vacuum distillation.

2,6-Naphthalenedicarbonyl chloride (**7c**) was prepared by the conventional chlorination of 2,6-naphthalenedicarboxylic acid with thionyl chloride; mp 186–187 °C (lot.[19] mp 186 °C).

4,4′-Oxydibenzoyl chloride (**7d**) was synthesized in a similar manner from 4,4′-oxydibenzoic acid and thionyl chloride; mp 83–84 °C (lit.[20] mp 88 °C).

4,4′-(1,1,1,3,3,3-Hexafluoroisopropylidene)dibenzoyl chloride (**7e**) was prepared as described for **7c** by the chlorination of 4,4′-(1,1,1,3,3,3-hexafluoroisopropylidene)dibenzoic acid (supplied by Central Glass Co.); mp 94–95 °C (lit.[21] mp 94.5–95.5 °C).

Solvents such as dichloromethane, THF, and *N,N*-dimethylacetamide (DMAc) were purified by distillation.

Model Reaction. 2′-Hydroxybenzanilide (3). To a solution of 1.270 g (5.0 mmol) of **1** in 5 mL of DMAc, 0.703 g (5.0 mmol) of **2** was added dropwise with stirring at 0 °C under nitrogen, and the solution was stirred at that temperature for 2 h. The product was isolated by puring the solution into 300 mL of water. Recrystallization from methanol afforded 0.93 g (87%) of pure **3** as colorless plates: mp 168–168.5 °C (lit.[22] mp 169–171 °C); IR (KBr) 3400 (N–H and O–H) and 1635 cm^{-1} (C=O).

2-Phenylbenzoxazole (4). A portion of **3** was heated in a test tube at 190 °C for 4 h under nitrogen. During this time, a pale yellow sublimate of the pure product formed in the upper part of the tube: mp 99–100 °C (lit.[23] mp 102.5–103.9 °C); IR (KBr) 1615 cm^{-1} (C=N).

Polymerization. Polymer 8aa from 6a and 7a. In a flask, 1.263 g (2.5 mmol) of **6a** was dissolved in 5 mL of DMAc under nitrogen. The solution was solidified with a dry ice–acetone bath, and to this was added 0.508 g (2.5 mmol) of **7a** in one portion. The cooling bath was changed to an ice–water bath, and the mixture was stirred at 0–5 °C for 8 h under nitrogen. The viscous solution obtained was poured into 400 mL of methanol. The precipitated polymer was collected, washed thoroughly with methanol, and dried at 20 °C in vacuo. The yield was 0.86 g (99%). The inherent viscosity of the polymer was 0.50 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C; IR (film) 3400 (N–H and O–H) and 1650 cm^{-1} (C=O). Anal. Calcd for $(C_{20}H_{14}N_2O_4)_n$: C, 69.35; H, 4.07; N, 8.09. Found: C, 69.09; H, 4.06; N, 8.19.

Polymer 8ba from 6b and 7a. The reaction of 1.368 g (2.5 mmol) of **6b** with 0.508 g (2.5 mmol) of **7a** in 5 mL of DMAc was carried out with stirring at 0–5 °C for 8 h under nitrogen. The polymer was isolated by pouring the reaction solution into methanol. The polymer weighed 0.96 g (99%) and had an inherent viscosity of 0.55 dL·g^{-1} in DMAc; IR (film) 3400 (N–H and O–H) and 1640 cm^{-1} (C=O). Anal. Calcd for $(C_{23}H_{20}N_2O_4)_n$: C, 71.12; H, 5.19; N, 7.21. Found: C, 71.34; H, 5.42; N, 7.55.

Polymer 8ca from 6c and 7a. A mixture of 1.638 g (2.5 mmol) of **6c** and 0.508 g (2.5 mmol) of **7a** in 5 mL of DMAc was reacted with stirring at 0–5 °C for 8 h under nitrogen. The yield of the isolated polymer was 1.23 g (99%), and the inherent viscosity was 0.64 dL·g^{-1} in DMAc; IR (film) 3400 (N–H and O–H) and 1650 cm^{-1} (C=O). Anal. Calcd for $(C_{23}H_{14}F_6N_2O_4)_n$: C, 55.65; H, 2.84; N, 5.65. Found: C, 55.44; H, 2.68; N, 5.88.

Polymer 9aa from 8aa. The thermal cyclodehydration of polymer film **8aa** was carried out by heating at 250–260 °C for 30 h in vacuo; IR (film) 1620 cm^{-1} (C=N). Anal. Calcd for $(C_{20}H_{10}N_2O_2)_n$: C, 77.41; H, 3.25; N, 9.03. Found: C, 77.20; H, 3.57; N, 9.19.

Polymer 9ba from 8ba. The heat treatment of polymer film **8ba** was conducted under the same conditions as above: IR (film) 1620 cm^{-1} (C=N). Anal. Calcd for $(C_{23}H_{16}N_2O_2)_n$: C, 78.39; H, 4.58; N, 7.95. Found: C, 78.62; H, 4.73; N, 7.92.

Polymer 9ca from 8ca. Polymer film **8ca** was heated under the same conditions as above; IR (film) 1620 cm^{-1} (C=N). Anal. Calcd for $(C_{23}H_{10}F_6N_2O_2)_n$: C, 60.01; H, 2.19; N, 6.08. Found, C, 59.94; H, 2.03; N, 6.17.

Measurements. IR and ^1H NMR spectra were recorded on a Hitachi EP-G3 spectrophotometer and a Varian EM-390 spectrometer (90 MHz), respectively. Differential thermal analysis (DTA), thermogravimetry (TG), and thermomechanical analysis (TMA, penetration method) were performed with Shimadzu thermal analyzers DTA-30M, TGA-30M, and TMA-30M, respectively. Wide-angle X-ray diffraction patterns were obtained for polymer films at room temperature on a Rigakudenki XG X-ray diffraction apparatus with nickel-filtered Cu Kα radiation

Table I
Synthesis of Aromatic Poly(*o*-hydroxy amides)[a]

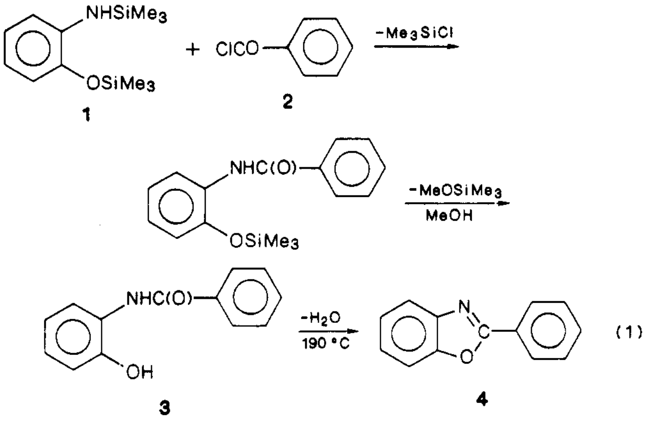
bis(*o*-aminophenol) component	polymer[b] code	polymer[b] η_{inh},[c] $dL \cdot g^{-1}$
5a	**8aa**	0.33
5b	**8ba**	0.16
5c	**8ca**	0.08
6a	**8aa**	0.50
6b	**8ba**	0.55
6c	**8ca**	0.64

[a] Polymerization was carried out with 2.5 mmol of the bis(*o*-aminophenol) component and 2.5 mmol of **7a** in 5 mL of DMAc at 0–5 °C for 8 h under nitrogen. [b] All polymers were obtained in a quantitative yield. [c] Measured at a concentration of 0.5 $g \cdot dL^{-1}$ in DMAc at 30 °C.

(30 kV, 20 mA). Weight- and number-average molecular weights were determined by gel permeation chromatography (GPC) on the basis of polystyrene calibration on a Toyosoda UV-8000 apparatus, tetrahydrofuran being used as an eluent. Tensile properties of polymer films were determined from stress–strain curves obtained with a Shimadzu Autograph IS-5000. Measurements were performed at room temperature by using film specimens (3.0 cm long, 1.0 cm wide, and 0.1 mm thick) at an elongation rate of 33%·min^{-1}.

Results and Discussion

Model Reaction. To determine the reactivity of *N*,*O*-bis(trimethylsilyl)-*o*-aminophenol (**1**), we investigated the reaction with benzoyl chloride (**2**) was investigated (eq 1).



The reaction was carried out in DMAc at 0 °C and found to afford exclusively 2′-hydroxybenzanilide (**3**) in an excellent yield. As expected, the (trimethylsilyl)amino group was more reactive than the (trimethylsilyl)oxy group toward the acid chloride, forming selectively 2′-((trimethylsilyl)oxy)benzanilide. The siloxyamide was desilylated with methanol to give amide compound **3**, which in turn was converted readily to 2-phenylbenzoxazole (**4**) by thermal cyclodehydration.

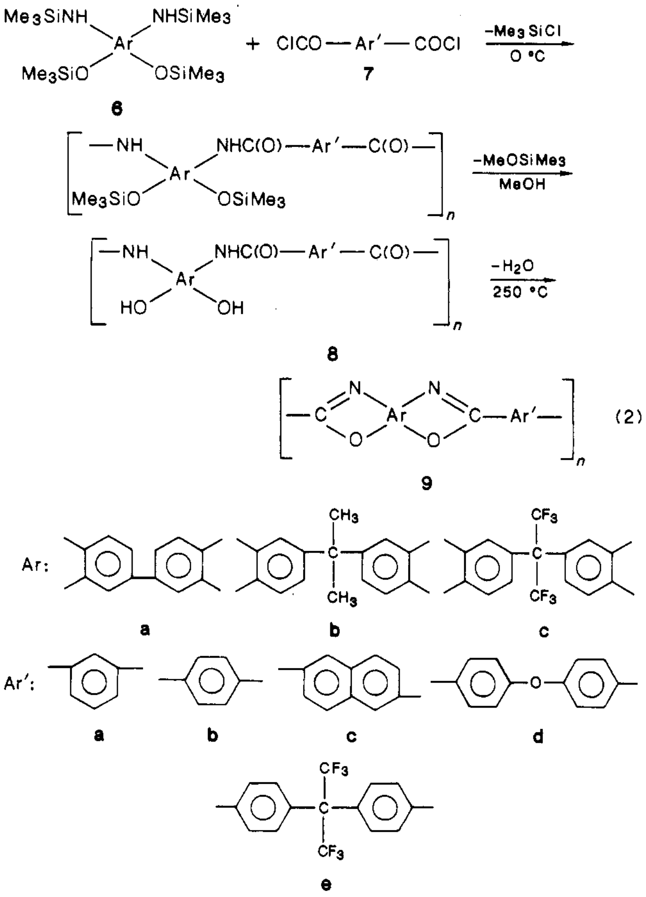
Polymer Synthesis. The direct solution polycondensation of 2,2-bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**5c**) with isophthalic acid was first attempted in polyphosphoric acid. However, polybenzoxazole **9ca** with an inherent viscosity of only 0.06 $dL \cdot g^{-1}$ was obtained by the reaction at 200 °C for 8 h. The low-temperature solution polycondensation of the fluorine-containing bis(*o*-aminophenol) **5c** with isophthaloyl chloride (**7a**) was then tried in DMAc at 0–5 °C for 8 h, and this also yielded poly(*o*-hydroxy amide) **8ca** with a low inherent viscosity of 0.08 $dL \cdot g^{-1}$. Thus, attempts to prepare poly(*o*-hydroxy amide) **8ca** or polybenzoxazole **9ca** of sufficiently high molecular weight were unsuccessful from **5c** by these two methods.

Table II
Synthesis of Fluorine-Containing Poly(*o*-hydroxy amides)[a]

diacid chloride	solvent	polymer[b] code	polymer[b] η_{inh},[c] $dL \cdot g^{-1}$
7a	DMAc	**8ca**	0.64
7b	DMAc	**8cb**	0.64
7c	DMAc	**8cc**	0.60
7d	DMAc	**8cd**	0.47
7e	DMAc	**8ce**	0.40
7a/**7b** (50/50)	DMAc	**8cf**	0.86
7a/**7b** (50/50)	tetrahydrofuran	**8cf**	0.83
7a/**7b** (50/50)	dichloromethane	**8cf**	0.63

[a] Polymerization was carried out with 2.5 mmol of **6c** and 2.5 mmol of the diacid chloride in 5 mL of the solvent at 0–5 °C for 8 h under nitrogen. [b] See footnote *b* of Table I. [c] See footnote *c* of Table I.

Next, we applied the silylation method, which is useful for the activation of diamines having low reactivity, to the fluorine-containing bis(*o*-aminophenol) **5c** (eq 2). Taking into account of the results of the model reaction, we investigated the low-temperature solution polycondensation of the silylated bis(*o*-aminophenols) **6a**, **6b**, and **6c** with isophthaloyl chloride (**7a**). The polymerization was carried out in DMAc at 0–5 °C for 8 h, and the results are summarized in Table I. The table also includes the results of the polymerization using the parent bis(*o*-aminophenols) **5a**, **5b**, and **5c** for comparison. Poly(*o*-hydroxy amides) **8aa**, **8ba**, and **8ca** with high inherent viscosities of above 0.5 $dL \cdot g^{-1}$ were readily obtained, and the versatility of the silylation method was once again demonstrated.



Adopting the above method, we successfully synthesized a variety of fluorine-containing poly(*o*-hydroxy amides) having inherent viscosities of 0.4–0.8 $dL \cdot g^{-1}$ by the low-temperature solution polycondensation of bis(*o*-aminophenol) **6c** with various aromatic diacid chlorides **7a**–**7e** (Table II). Since some poly(*o*-hydroxy amides) having

Table III
Synthesis of Fluorine-Containing Polybenzoxazoles[a]

	polybenzoxazole	
poly(*o*-hydroxy amide)	code	η_{inh},[b] dL·g^{-1}
8cd	**9cd**	0.76
8ce	**9ce**	0.49
8cf	**9cf**	0.46

[a] The conversion of the poly(*o*-hydroxy amide) to the polybenzoxazole was carried out by heating at 250–260 °C for 30 h in vacuo. [b] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C.

Table IV
Solubility of Aromatic Poly(*o*-hydroxy amides)[a]

	polymer							
solvent	**8aa**	**8ba**	**8ca**	**8cb**	**8cc**	**8cd**	**8ce**	**8cf**
N-methyl-2-pyrrolidone	++	++	++	++	++	++	++	++
dimethyl sulfoxide	++	++	++	++	++	++	++	++
dimethylformamide	–	+	++	++	++	++	++	++
pyridine	–	++	++	+	++	++	++	++
tetrahydrofuran	–	+	++	–	++	–	++	++
acetone	–	+	++	–	+	–	++	++
methanol	–	–	+	–	++	–	+	+
chloroform	–	–	–	–	–	–	–	–

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

Table V
Solubility of Aromatic Polybenzoxazoles[a]

	polymer							
solvent	**9aa**	**9ba**	**9ca**	**9cb**	**9cc**	**9cd**	**9ce**	**9cf**
conc sulfuric acid	+	+	+	+	+	++	++	++
o-chlorophenol	–	–	+	–	–	–	++	++
N-methyl-2-pyrrolidone	–	–	–	–	–	–	+	++
pyridine	–	–	–	–	–	–	+	++
tetrahydrofuran	–	–	–	–	–	–	–	–
acetone	–	–	–	–	–	–	–	–
methanol	–	–	–	–	–	–	–	–
chloroform	–	–	–	–	–	–	–	–

[a] See footnote *a* of Table IV.

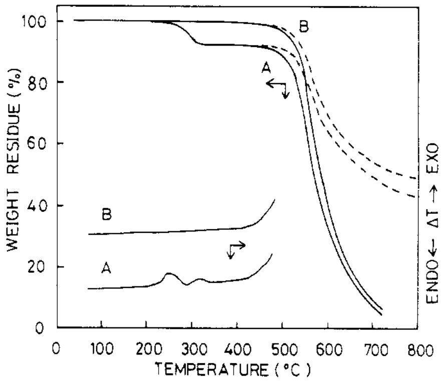


Figure 1. DTA and TG curves for (A) poly(*o*-hydroxy amide) **8ca** and (B) polybenzoxazole **9ca** at a heating rate of 10 K·min^{-1} in air (—) and in nitrogen (···).

trimethylsiloxy groups are more readily soluble in a wide range of solvents than the desilylated poly(*o*-hydroxy amides), the polymerization with a mixture of two phthaloyl chlorides (**7a** and **7b**) in THF or dichloromethane as well as in DMAc proceeded in a homogeneous solution giving poly(*o*-hydroxy amide) **8cf** with enough high inherent viscosity. The weight-average molecular weight ($\bar{M}_w$) and number-average molecular weight ($\bar{M}_n$) of polymer **8cf** having the inherent viscosity of 0.86 dL·g^{-1}, determined by means of GPC, were 31 000 and 21 000, respectively, for standard polystyrene.

The formation of poly(*o*-hydroxy amides) was confirmed by means of IR spectroscopy and elemental analysis. The polymers exhibited an absorption at 3400 cm^{-1} due to amide N–H and hydroxyl O–H groups and a strong carbonyl absorption at 1640–1650 cm^{-1}. The elemental analysis values were in good agreement with the calculated values of the proposed structures of the polymers.

In the second stage, the poly(*o*-hydroxy amides) thus obtained were subjected to thermal cyclodehydration. The conversion to polybenzoxazoles was carried out in the form of films at 250 °C in vacuo, and the conversion process was monitored as a function of time from the change in the IR spectra of the films. The conversion was found to require 15–20 h for its completion. The complete disappearance of the absorption bands at 3400 and 1650 cm^{-1} indicated the completion of the cyclization process, together with the appearance of an absorption at 1620 cm^{-1} characteristic of benzoxazole ring. The elemental analysis values of the converted polymers agreed well with the values calculated for the polymers with benzoxazole structures. The polybenzoxazoles formed had inherent viscosities of 0.4–0.8 dL·g^{-1} (Table III), indicating that no thermal degradation leading to molecular chain scission occurred during the conversion process.

Polymer Characterization. Tables IV and V summarize qualitative evaluations of the solubility of the poly(*o*-hydroxy amides) and polybenzoxazoles, respectively. Most of the poly(*o*-hydroxy amides) were amorphous and readily soluble in dimethylformamide, *N*-methyl-2-pyrrolidone, dimethyl sulfoxide, and pyridine. In general, the introduction of a hexafluoroisopropylidene unit into the poly(*o*-hydroxy amides) improved the solubility of such polymers. Transparent, flexible, and tough films of the poly(*o*-hydroxy amides) could be cast from the DMAc solutions.

The polybenzoxazoles, on the other hand, dissolved only in concentrated sulfuric acid. Despite the fact that most of the polybenzoxazoles were amorphous, they were quite insoluble in organic solvents, with the exception of polymers **9cd** and **9ce**, which contain flexible linking groups in the polymer backbones.

The thermal behavior of the poly(*o*-hydroxy amides) and polybenzoxazoles was studied by using DTA, TG, and TMA techniques. Figure 1 shows typical DTA and TG curves for polymers **8ca** and **9ca** in air and nitrogen atmosphere. The TG curve of poly(*o*-hydroxy amide) **8ca** revealed that the weight loss started at around 230 °C and came to an end at about 330 °C. The weight loss was due to the thermal cyclodehydration of the poly(*o*-hydroxy amide), which was also evidenced from the DTA curve, and the amount of weight loss (8%) agreed quite well with that of the calculated value of 7%. All the polybenzoxazoles did not lose weight up to 450 °C in air or nitrogen, and the temperatures at which 10% weight loss was recorded were 500–570 °C in air and 530–620 °C in nitrogen.

Table VI summarizes the thermal behavior data of the polybenzoxazoles. The polymers had glass transition temperatures (T_g) between 240 and 325 °C. Among the polybenzoxazoles having a *m*-phenylene linkage, the T_g decreased in the order of **9aa**, **9ca**, and **9ba**, which corresponded well to the decreasing order of rigidity of the polymer backbones. The fluorine-containing polybenzoxazoles **9cb**–**9ce**, having linkages other than *m*-phenylene, also had high T_g values of 295–325 °C.

Table VII lists the mechanical properties of the transparent polybenzoxazole films. The tensile strength, elongation at break, and tensile modulus of the films were

Table VI
Thermal Properties of Aromatic Polybenzoxazoles

polymer	T_g,[a] °C	decomposition temp,[b] °C	
		in air	in nitrogen
9aa	290	570	620
9ba	240	500	530
9ca	260	530	545
9cb	310	545	555
9cc	325	540	560
9cd	300	545	560
9ce	295	525	530
9cf	280	545	555

[a] Determined by TMA at a heating rate of 10 K·min^{-1} in air. [b] The temperature at which 10% weight loss was recorded by TG at a heating rate of 10 K·min^{-1}.

Table VII
Mechanical Properties of Aromatic Polybenzoxazole Films

polymer	tensile strength, MPa	elongation at break, %	tensile modulus, GPa
9aa	198	7	4.5
9ba	53	2	2.9
9cc	93	6	2.4
9cd	96	6	2.4
9ce	43	2	2.1
9cf	68	3	2.6

43–198 MPa, 2–7%, and 2.1–4.5 GPa, respectively.

Thus, the fluorine-containing polybenzoxazoles had high glass transition temperatures and excellent mechanical properties and are promising candidates for new high-temperature materials.

Registry No. 3, 3743-70-2; 4, 833-50-1; **8ca** (copolymer), 113753-62-1; **8ca** (SRU), 114533-35-6; **8cb** (copolymer), 113753-63-2; **8cb** (SRU), 114533-36-7; **8cc** (copolymer), 113753-67-6; **8cc** (SRU), 114533-37-8; **8cd** (copolymer), 113753-61-0; **8cd** (SRU), 114533-38-9; **8ce** (copolymer), 113753-66-5; **8ce** (SRU), 114533-39-0; **8cf**, 113753-68-7; **9ca**, 112480-78-1; **9cd**, 112480-83-8; **9ce**, 112480-81-6; benzoxazole, 273-53-0.

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Characteristics of Ethylene–Propylene and Propylene–1-Butene Copolymerization over $TiCl_3 \cdot {}^1/_3AlCl_3–Al(C_2H_5)_2Cl$

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ABSTRACT: An ethylene–propylene (^{13}EP) copolymer containing 0.41 mol % ^{13}C-enriched ethylene has been fractionated on an isotactic basis by a temperature-programmed elution column technique. The ^{13}C NMR analysis of the fractions indicates that the ethylene content decreases as the isotacticity increases. The atactic fraction eluted at 20 °C is about 6 times as high in ethylene content as the isotactic fractions eluted over 110 °C. This fact well accounts for a wide copolymer composition distribution generally found in ethylene–propylene copolymerization prepared with heterogeneous catalysts. A 1-butene–propylene (^{13}BP) copolymer containing 0.20 mol % ^{13}C-enriched 1-butene has been examined similarly. In this case, the 1-butene content of the fractions is almost uniform.

Introduction

In recent years there has been great interest in the control of a composition distribution in the Ziegler–Natta copolymerization. In a previous paper, we determined the triad sequence distributions and monomer reactivity ratio products (r_1r_2) for some ethylene–propylene (EP) copolymers prepared with the $TiCl_3 \cdot {}^1/_3AlCl_3–Al(C_2H_5)_2Cl$ catalyst system by ^{13}C NMR spectroscopy.[1] As a result, it was found that the values of the r_1r_2 products were much greater than unity, and the isolated ethylene unit and three ethylene units were strangely more than predicted by a first-order Markovian scheme. This result strongly suggests that multiple active centers, one center producing an alternating copolymer and the other a block copolymer, may reside in this catalyst system. A similar tendency was found by Soga et al. for EP copolymerizations with $MgCl_2/TiCl_4$-supported catalyst systems.[2,3] On the other hand, Ross suggested that these data may arise from a variation in monomer diffusion within polymer particles to active centers.[4] It is known that the heterogeneous

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