Polymer Journal, Vol. 35, No. 11, pp 859—867 (2003)

Synthesis and Characteristics of Hyperbranched Polybenzoxazoles *via* Poly(*o*-hydroxyamide) Precursors

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(Received February 11, 2003; Accepted August 26, 2003)

ABSTRACT: The novel AB_2 and A_2B type monomers for hyperbranched polybenzoxazoles (HBPBOs) containing one (or two) hydroxy amine and two (or one) carboxylic acid groups in the aromatic backbones were prepared starting from 5-methoxyresorcinol and 4-fluorobenzonitrile for AB_2 and 3,5-dihydroxybenzoic acid and 3-fluoro-6-nitrophenol for A_2B monomer. Hyperbranched poly(*o*-hydroxyamide)s (HBPHAs) as precursors of HBPBOs were synthesized by self-polycondensation of the AB_x type monomers in the presence of (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP) as a condensing agent at room temperature. The terminal groups of free carboxylic acid or amine were chemically modified with 2-amino-4-*tert*-butylphenol or 3,5-dimethylbenzoic acid. End-capped HBPHAs had good solubility in aprotic solvents and tetrahydrofuran (THF) having the weight average molecular weight (M_w) in the range of 27000–131000. The conversion of HBPHA to HBPBO was carried out by thermal and chemical cyclization methods. HBPBOs prepared by chemical cyclization of HBPHAs in polyphosphoric acid (PPA) were soluble in aprotic solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-Dimethylacetamide (DMAc), Dimethyl Formamine (DMF), and THF, whereas thermally cyclized ones were insoluble in any organic solvents. ^{1}H NMR and IR analyses indicated that the chemical cyclization proceeded quantitatively. The weight-average molecular weights (M_w) of soluble HBPBOs were found to be 23000–97000 by gel permeation chromatography (GPC) measurement with standard polystyrene calibration. Both of HBPBOs prepared by thermal and chemical cyclization methods showed excellent thermal stability having the 10 wt% weight loss (T_{10}) in the range of 488–537 °C under nitrogen.

KEY WORDS Polybenzoxazoles / Hyperbranched Polymer / Cyclodehydration / Poly(*o*-hydroxyamide)s / One-pot Polymerization / AB_2 Monomer /

The aliphatic polybenzoxazoles (PBOs) were first synthesized through the melt polycondensation of 3,3′-diaminobenzidine tetrahydrochloride and sebacic acid by Brinker *et al.* in 1959.[1] Six years later, linear aromatic polybenzoxazoles (PBOs) were first reported by Imai *et al.*[2] and have since been under widespread investigation. For a few decades, both of AA–BB and AB type monomer systems have been studied in the synthesis of linear polybenzoxazoles having good thermal and mechanical properties.[3–7] Fibers prepared from this polymer have superior tensile strength and flame retardance. PBO fibers were used in high-performance composites and comfortable protective garments. However, in spite of these attractive properties, their application has been somewhat limited since their poor processability. The processability or solubility of these polymers could be improved by the introduction of the flexible units or bulky pendant groups to the main chain.[8–11]

Nowadays, It is well known that dendritic macromolecules such as dendrimers or hyperbranched polymers have unusual properties compared to their linear analogues like as better solubility, lower solution viscosity and higher functionality.[12–16] Although dendrimers have unique architecture, their preparation involves tedious steps such as repeating protection and deprotection reactions. On the other hand, hyperbranched polymers have some benefits of their simple preparation compared to dendrimers because they can be produced by one step polymerization of AB_x monomers.[17–21] Recently, Gong *et al.* demonstrated the synthesis of hyperbranched poly(aryl ether oxazole)s from an ABB′ monomer containing a pair of phenolic groups and an aryl fluoride *via* nucleophilic substitution reaction.[22] Baek *et al.* reported the synthesis of quinoxaline–benzoxazole hyperbranched polymers from an AB_2 monomer in polyphosphoric acid (PPA).[23] However, their solubilities of the quinoxaline–benzoxazole hyperbranched polymers were not good in common organic solvents except methansulfonic acid. We designed and prepared two types of new monomers which contain ether linkages in the main chain to give the chain flexibility. The hyperbranched polybenzoxazoles were synthesized by two step process. The two step process *via* precursors would result in better applicability than the one step process. For example, the poly(*o*-hydroxyamide) precursors are useful as thermally stable photosensitive polymers because of their appropriate dissolution rate in aqueous alkaline solution.[24,25]

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Previously we reported the synthesis of hyperbranched polybenzoxazoles from an AB_2 monomer as a communication.[26] Herein, we describe details about the synthesis and characterization of soluble hyperbranched polybenzoxazoles having the excellent thermal stability by the one-pot condensation of novel AB_2 and new A_2B type monomers *via* poly(*o*-hydroxyamide) precursors.

EXPERIMENTAL

Materials

N, *N*-Dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and *N*-methyl-2-pyrrolidinone (NMP) were dried with calcium hydride and then distilled under reduced pressure. Acetic anhydride, dichloromethane and acetone were used after distillation with magnesium, calcium chloride, and calcium sulfate, respectively. Lithium chloride (LiCl) was dried at 130 °C *in vacuo* and kept under nitrogen. 3,5-Dihydroxy benzoic acid and (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP) were used after recrystallization with water and *n*-hexane, respectively. Triethylamine (TEA) and 4-methylpyridine were purified by distillation in the presence of potassium hydroxide. Other solvents and reagents were used as received.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 (300 MHz) spectrometer. IR spectra were measured as a KBr pellet with a JASCO FT/IR-460 Plus spectrophotometer. Molecular weights were determined by gel permeation chromatography (GPC) with polystyrene calibration using a JASCO HPLC 880 PU fitted with Shodex KD 806 M and 802.5 columns in DMF containing lithium bromide (0.01 mol L^{-1}) as an eluent or SHODEX GPC-104/101 with Shodex KD 806 M and KD 802 columns in DMF. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Seiko DSC 6200 and TG/DTA 6200, respectively. Inherent viscosity was measured at a concentration of 0.5 g dL^{-1} with a Ostwald type viscometer in DMAc at 30 °C.

AB_2 type Monomer Preparation. Synthesis of 3,5-Bis-(4-cyanophenoxy) anisole ***1***

In a 1000 mL round-bottomed three-neck flask equipped with a condenser and a gas inlet were placed 5-methoxyresorcinol (14.0 g, 0.1 mol), 4-fluorobenzonitrile (24.2 g, 0.2 mol), potassium carbonate (55.3 g, 0.4 mol) and DMAc (300 mL). The reaction mixture was stirred at 150 °C for 5 h and then cooled. The resulting mixture was poured into water (6000 mL) and the precipitate was isolated by filtration. The crude product was washed with water and then dried at 60 °C for one day in a vacuum oven (95% yield). The white crystal was obtained by recrystallization in ethanol to give 3,5-bis(4-cyanophenoxy)anisole (30.9 g): 90.3% yield; mp 94–96 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 7.81–7.86 (dd, 4 H, Ar–H), 7.16–7.20 (dd, 4 H, Ar–H), 6.61–6.62 (d, 2 H, Ar–H), 6.46–6.47 (t, 1 H, Ar–H), 3.74(s, 3 H, methoxy); IR (KBr) 2230 cm^{-1} (cyano group).

Synthesis of 3,5-Bis(4-cyanophenoxy)-2-nitroanisole ***2***

To a 1000 mL round-bottomed three-neck flask equipped with a gas inlet were added 3,5-bis(4-cyanophenoxy)anisole **1** (27.4 g, 80 mmol) and 300 mL of acetic anhydride. Cupric nitrate trihydrate (24.2 g, 100 mmol) was added slowly into the same flask at room temperature and stirred for 5 h after the addition. The reaction mixture was poured into cold water and the crude product was isolated by filtration. The crude product was washed with water twice and then dried at room temperature for two days in a vacuum oven. The yellow product was recrystallized from ethanol to give 3,5-bis(4-cyanophenoxy)-2-nitroanisole (13.6 g): 44.0% yield; mp 53–55 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 7.83–7.87 (m, 4 H, Ar–H), 7.24–7.32 (m, 4 H, Ar–H), 7.03–7.04 (d, 1 H, Ar–H), 6.63–6.64 (d, 1 H, Ar–H), 3.91 (s, 3 H, methoxy); IR (KBr) 1536 cm^{-1} (nitro group), 1341 cm^{-1} (nitro group).

Synthesis of 3,5-Bis(4-cyanophenoxy)-2-nitrophenol ***3***

To a 500 mL round-bottomed three-neck flask equipped with a gas inlet were added 3,5-bis(4-cyanophenoxy)-2-nitro anisole **2** (11.62 g, 30 mmol) and 150 mL of anhydrous dichloromethane under nitrogen. Boron tribromide (11.3 mL, 120 mmol) was added slowly *via* syringe to the flask cooled by dry-ice at −50 °C. After the removal of the dry-ice bath, the reaction mixture was stirred for 5–6 h and then for 20 h at room temperature. The resulting mixture was poured into 1000 mL of cold water and then extracted with diethyl ether. The extract was washed with cold water and then dried with anhydrous magnesium sulfate. Yellow crude product was obtained after evaporation and dried at 60 °C for one day in a vacuum oven (99.0% yield). The yellow crude product was purified by column chromatography in ethyl acetate and hexane as eluents and recrystallized from a mixture of ethanol and water to give a light yellow crystal (8.9 g): 79.3% yield; mp 150–151 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 11.72 (s, 1 H Ar–OH), 7.84–7.90 (m, 4 H, Ar–H), 7.24–7.34 (m, 4 H, Ar–H), 6.52–6.53 (d, 1 H, Ar–H), 6.50–6.51

(d, 1 H, Ar–H); IR (KBr) 3500 cm^{-1} (hydroxy group), 1536 cm^{-1} (nitro group), 1341 cm^{-1} (nitro group).

*Synthesis of 3,5-Bis(4-carboxylphenoxy)-2-nitrophenol **4***

To a 200 mL round-bottomed flask equipped with a condenser and a gas inlet were added 3,5-bis(4-cyanophenoxy)-2-nitrophenol **3** (7.47 g, 20 mmol) and 75 mL of phosphoric acid (85%). The reaction mixture was stirred for 4 h under reflux and then cooled to room temperature. The resulting mixture was poured into cold water and then stirred at room temperature for 6 h after adjusting the pH value to 11 in order to remove insoluble particles through filtration. After neutralization with hydrochloric acid to pH 3–4, the precipitate was isolated by filtration and washed with dilute hydrochloric acid and water. The crude product was dried at 80 °C for one day in a vacuum oven (94.0% yield). The yellow crude product was purified by column chromatography in tetrahydrofuran and hexane as eluents to give a light yellow powder (7.1 g): 86.5% yield; mp 267–269 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 12.93 (s, 2H Ar–COOH), 11.59 (s, 1 H Ar–OH), 7.93–7.98 (m, 4 H, Ar–H), 7.15–7.22 (m, 4 H, Ar–H), 6.45–6.46 (d, 1 H, Ar–H), 6.34–6.35 (d, 1 H, Ar–H); IR (KBr) 1692 cm^{-1} (carboxylic group).

*Synthesis of 3,5-Bis(4-carboxylphenoxy)-2-aminophenol Hydrochloride (AB_2 monomer, **5**)*

To a 100 mL of high-pressure reactor, 3,5-bis(4-carboxylphenoxy)-2-nitrophenol **4** (6.17 g, 15 mmol), 10% palladium-charcoal catalyst (0.62 g) and 70 mL of a mixture of methanol and tetrahydrofuran (50:50 (v/v)) were charged. The reaction mixture was stirred under hydrogen of 14 $kg_f\,cm^{-2}$ at room temperature for 48 h. The resulting mixture was filtered with celite to remove the catalyst. The dark purple filtrate was concentrated by evaporation and then hydrochloride was added to the concentrated solution. The mixture was stirred for 6 h at room temperature and then poured into diethyl ether. The precipitate was isolated by filtration. The light brown powder was dried at 40 °C for 2 d in a vacuum oven to give 3,5-bis(4-carboxylphenoxy)-2-aminophenol hydrochloride (5.8 g): 92.5% yield; ^{1}H NMR (DMSO-d_6, ppm) δ 11.16 (brs, 2 H, Ar–COOH), 7.91–7.97 (m, 4 H, Ar–H), 7.05–7.14 (m, 4 H, Ar–H), 6.51–6.52 (d, 1 H, Ar–H), 6.22–6.23 (d, 1 H, Ar–H); ^{13}C NMR (DMSO-d_6, ppm) δ 166.6, 160.2, 159.5, 153.3, 152.2, 149.0, 131.7, 131.6, 126.3, 125.8, 118.1, 117.7, 102.9, 101.5; IR (KBr) 3413 cm^{-1}, 3072 cm^{-1}, 1691 cm^{-1} (carboxylic group). Anal. Calcd for $C_{20}H_{16}ClNO_7$: C, 57.50; H, 3.86; N, 3.35. Found: C, 57.32; H, 4.01; N, 3.14.

*A_2B type Monomer Preparation. Synthesis of 2-Benzyloxy-4-fluoronitro Benzene **6***

To a 500 mL round-bottomed flask equipped with a condenser and a gas inlet were added 3-fluoro-6-nitrophenol (15.71 g, 0.1 mol), benzyl bromide (17.10 g, 0.1 mol), potassium carbonate (27.64 g, 0.2 mol) and 190 mL of acetone under nitrogen. The reaction mixture was refluxed for 7 h and then cooled to room temperature. The resulting mixture was poured into water (1800 mL). The crude product was isolated by filtration and recrystallized from ethanol. Bright yellow needle-like crystal was obtained after dried at room temperature for overnight: 80.9% yield; mp 53–55 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 8.00–8.05 (m, 1 H, Ar–H), 7.31–7.47 (m, 6 H, Ar–H), 6.94–7.01 (m, 1 H, Ar–H), 5.31 (s, 2 H, –CH_2); IR (KBr) 1522 cm^{-1}, 1351 cm^{-1}. Anal. Calcd for $C_{13}H_{10}FNO_3$: C, 63.16; H, 4.08; N, 5.67. Found: C, 63.13; H, 4.12; N, 5.60.

*Synthesis of 3,5-Bis(3-benzyloxy-4-nitrophenoxy)benzoic Acid **7***

In a three-neck flask equipped with a Dean-Stark trap, a condenser and a nitrogen inlet were put 3,5-dihydroxybenzoic acid (3.08 g, 20 mmol), potassium carbonate (16.58 g, 120 mmol), toluene (30 mL) and 60 mL of DMSO. The reaction mixture was heated with stirring at 155 °C for 3 h under nitrogen, and during this period the water formed was collected in the Dean-Stark trap. After cooling the flask to room temperature, 2-benzyloxy-4-fluoronitrobenzene **6** (9.89 g, 40 mmol) was added into the flask. The reaction mixture was heated to 100 °C for 20 h and then allowed to cool to room temperature. The reaction mixture was poured into cold water (1500 mL) and then neutralized with dilute hydrochloride. The white powdery product was isolated by filtration and purified by column chromatography in a mixture of tetrahydrofuran and hexane (50:50 (v/v)) as an eluent to give a light yellow powder. The light yellow crystal was obtained after recrystallization in a mixture of ethyl acetate and hexane (40:60 (v/v)): 52.3% yield; mp 161–163 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 7.98–8.01 (d, 2 H, Ar–H), 7.26–7.43 (m, 12 H, Ar–H), 7.17–7.18 (d, 2 H, Ar–H), 6.72–6.76 (dd, 2 H, Ar–H), 5.28 (s, 4 H, –CH_2); IR (KBr) 1700 cm^{-1}, 1516 cm^{-1}, 1348 cm^{-1}. Anal. Calcd for $C_{33}H_{24}N_2O_{10}$: C, 65.13; H, 3.98; N, 4.60. Found: C, 65.05; H, 4.03; N, 4.47.

*Synthesis of 3,5-Bis(4-amino-3-hydroxyphenoxy)benzoic Acid Dihydrochloride (A_2B monomer, **8**)*

To a 100 mL of high-pressure reactor, 3,5-bis(3-benzyloxy-4-nitro-phenoxy)-benzoic acid (6.09 g, 10 mmol), 10% palladium-charcoal catalyst (0.61 g) and 70 mL of a mixture of methanol and tetrahydrofuran (50:50 (v/v)) were charged. The following procedure was similar to that of preparation of **5**. The light purple powder was dried at 40 °C for 2 d in the vacuum oven to give 3,5-bis(4-amino-3-hydroxyphenoxy)-benzoic acid dihydrochloride (4.21 g): 95.5% yield; ^{1}H NMR (DMSO-d_6, ppm) δ 11.13 (s, 1 H, Ar–COOH), 9.91 (br, 2 H, Ar–OH), 7.37–7.40 (d, 2 H, Ar–H), 7.18–7.19 (m, 2 H, Ar–H), 7.01–7.02 (t, 1 H, Ar–H), 6.78–6.79 (d, 2 H, Ar–H), 6.60–6.64 (m, 2 H, Ar–H); ^{13}C NMR (DMSO-d_6, ppm) δ 165.96, 157.97, 155.70, 152.21, 134.14, 125.27, 115.68, 113.52, 113.41, 109.87, 106.88; IR (KBr) 3372 cm^{-1}, 2955 cm^{-1}, 1701 cm^{-1} (carboxylic group). Anal. Calcd for $C_{19}H_{18}Cl_2N_2O_6$: C, 51.72; H, 4.11; N, 6.35. Found: C, 51.58; H, 4.30; N, 6.21.

*Preparation of Polymer **P4***

Polymer **P4** was prepared by polycondensation of A_2B type monomer (**8**, 0.41 g, 1.0 mmol) with DBOP (0.38 g, 1.0 mmol), dried LiCl (0.09 g, 2.0 mmol) and 4-methyl pyridine (0.29 mL, 3.0 mmol) in 3 mL of NMP under nitrogen. The reaction mixture was stirred at room temperature for 5 h. The end-capping solution composed of 3,5-dimethylbenzoic acid (2.0 mmol), DBOP (0.77 g, 2.0 mmol), 4-methylpyridine (0.20 mL, 2.0 mmol) and 4 mL of NMP was added slowly to the reaction mixture and stirred for additional 4 h. The reaction mixture was poured into 600 mL of methanol containing 0.1 wt% lithium chloride. The precipitated polymer was isolated by filtration, and dissolved in Dimethyl Formamide (DMF). After reprecipitation in methanol, the product was filtered, and dried at room temperature for two days in a vacuum oven: 67.4% yield; ^{1}H NMR (DMSO-d_6, ppm) δ 9.38–9.61 (d, 2 H), 7.46–7.64 (m, 4 H, Ar–H), 7.33 (s, 2 H, Ar–H), 7.17 (s, 1 H, Ar–H), 6.82 (s, 1 H, Ar–H), 6.55–6.62 (m, 4 H, Ar–H), 2.30 (s, 6 H, methyl); ^{13}C NMR (DMSO-d_6, ppm) δ 165.55, 163.91, 158.25, 158.03, 154.05, 153.40, 151.91, 150.98, 137.65, 137.49, 134.32, 132.94, 127.30, 127.00, 125.65, 125.37, 125.24, 122.36, 121.53, 112.16, 111.50, 109.52, 109.27, 109.24, 106.83, 106.60, 20.85; IR (KBr) 1655 cm^{-1} (amide).

Thermal Cyclodehydration

Polymer **P5** was prepared as follows. Poly(*o*-hydroxyamide) (**P4**) (0.5 g) was dissolved in 2.0 mL of NMP for overnight. The solution was cast on a glass plate and cured in a vacuum oven for 1 h at room temperature, 100 °C, 200 °C, and 300 °C, respectively and finally cooled to room temperature slowly: IR (KBr) 1623 cm^{-1} (–C=N), 1593 cm^{-1} (C=C), 1474 cm^{-1}, 1079 cm^{-1} (C–O–C).

Chemical Cyclodehydration

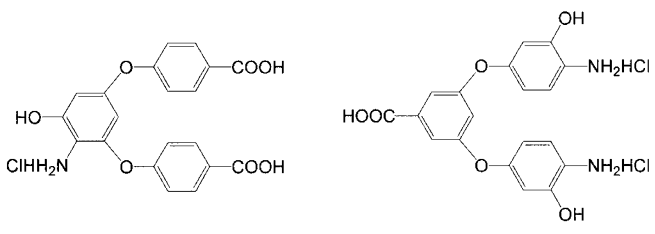
Polymer **P6** was prepared as follows. To a 100 mL round-bottomed flask equipped with a gas inlet were added 0.5 g of poly(*o*-hydroxyamide) (**P4**) and 20 g of polyphosphoric acid (PPA). The reaction mixture was heated slowly to 160 °C and stirred for 24 h. The resulting mixture was poured into cold water (400 mL) and isolated by filtration. The precipitate was washed with diluted sodium bicarbonate and then dried at 30 °C for 1 d in a vacuum oven: 85% yield; ^{1}H NMR (DMSO-d_6, ppm) δ 7.75 (br, 4 H, Ar–H), 7.16 (br, 3 H, Ar–H), 6.60 (br, 5 H, Ar–H), 2.29 (s, 6 H, methyl); IR (KBr) 1622 cm^{-1} (–C=N), 1593 cm^{-1} (C=C), 1475 cm^{-1}, 1079 cm^{-1} (C–O–C).

RESULTS AND DISCUSSION

Monomer Synthesis

We prepared two types of new monomers for HBPBO (Scheme 1). The monomers were designed to enhance the solubility of corresponding polymers by introduction of flexible ether units in the backbone. An AB_2 type monomer, 3,5-bis(4-carboxylphenoxy)-2-aminophenol hydrochloride **5**, was prepared starting from 5-methoxyresorcinol and 4-fluorobenzonitrile as described in previous report.[26]

On the other hand, an A_2B type monomer, 3,5-bis(4-amino-3-hydroxy-phenoxy) benzoic acid dihydrochloride **8**, was prepared starting from 3-fluoro-6-nitrophenol and 3,5-dihydroxybenzoic acid as shown in Scheme 2. The hydroxy group of the 3-fluoro-6-nitrophenol was protected with benzyl bromide in the presence of potassium carbonate to afford 2-benzyloxy-4-fluoronitrobenzene **6**, which was subsequently reacted with 3,5-dihydroxybenzoic acid in *N*,*N*-dimethylacetamide (DMAc), yielding 3,5-bis(3-benzyloxy-4-nitrophenoxy)benzoic acid **7**. Finally



AB_2 type monomer A_2B type monomer

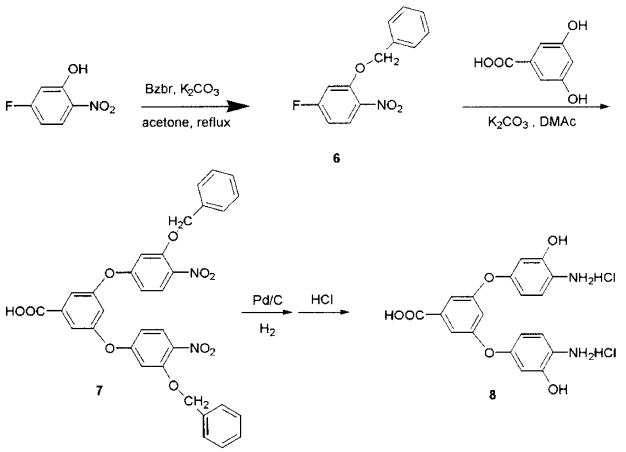
Scheme 1. Two types of monomers.

monomer **8** was prepared by reduction of compound **7** in the presence of 10% palladium-charcoal catalyst and following acidification by hydrochloric acid. Total yield of the monomer **8** from 3-fluoro-6-nitrophenol was 40%. The structure of monomer **8** was characterized by ^{1}H, ^{13}C NMR, IR, and elementary analysis. The IR spectra of monomer **8** showed characteristic N–H (3372 cm^{-1}), O–H (2955 cm^{-1}) and C=O (1701 cm^{-1}) peaks. All of the peaks in the ^{1}H NMR spectrum were well assigned to estimated structure (Figure 1).

Synthesis of End-capped Poly(o-hydroxyamide)s

Ueda *et al.* demonstrated the effect of DBOP as a condensing agent for the chemoselective polycondensation of polyamides.[27,28] They revealed that polyamides could be prepared readily by the chemoselective polyamidation of dicarboxylic acids with diamines containing various functional groups *via* DBOP at room temperature. We previously reported the synthesis of HBPBO from an AB_2 monomer (Scheme 3). The free carboxylic end-groups were chemically modified with 2-amino-4-*tert*-butyl phenol as an end-capping agent without isolation of poly(*o*-hydroxyamide), since isolated HBPHA was insoluble in aprotic solvents. The conversion of the end-capping reaction calculated from the integration ratios between the characteristic *tert*-butyl peaks at 1.21 ppm and aromatics at 6.45 ppm by ^{1}H NMR analysis was 85% (spectrum **P1** in Figure 2). The conversion was not influenced by the quantity of end-capping agent in the range of 5–10 times excess. The degree of branching (DB) of hyperbranched polymers was defined as the ratio of the sum of dendritic and terminal units versus total units (dendritic, terminal and linear units). Unfortunately, the DB values of **P1** could not be calculated by ^{1}H and ^{13}C NMR analyses since the each peaks of dendritic, linear, and terminal units were not distinguishable.

Polymer **P4** was prepared by polycondensation of the A_2B monomer **8** in the presence of DBOP and 4-methylpyridine in NMP as shown in Scheme 3.



Scheme 2. Synthesis of A_2B type monomer **8**.

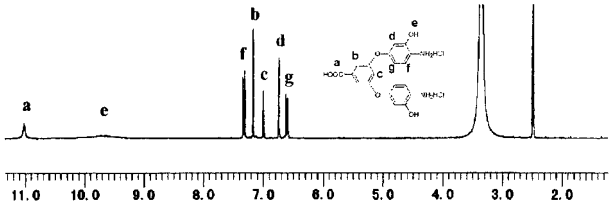
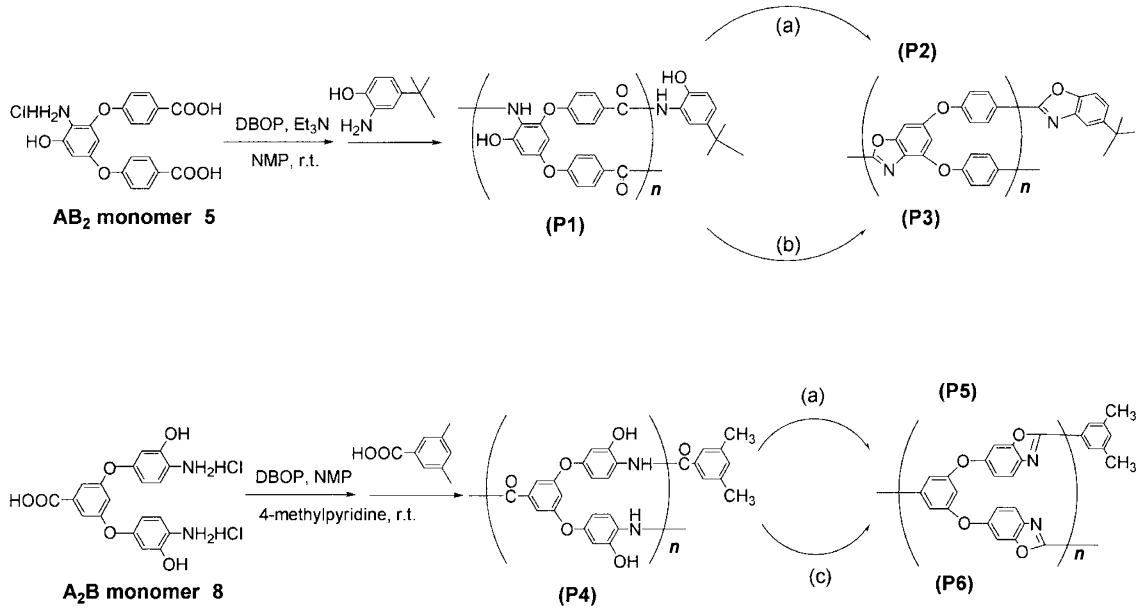


Figure 1. ^{1}H NMR spectrum of A_2B type monomer.



Scheme 3. Synthesis of polymers from the two types of monomers. (a): Thermal cyclization at room temperature, 100 °C, 200 °C, and 300 °C for 1 h *in vacuo*; (b): Chemical cyclization in polyphosphoric acid at 130 °C for 36 h; (c): Chemical cyclization in polyphosphoric acid at 160 °C for 24 h.

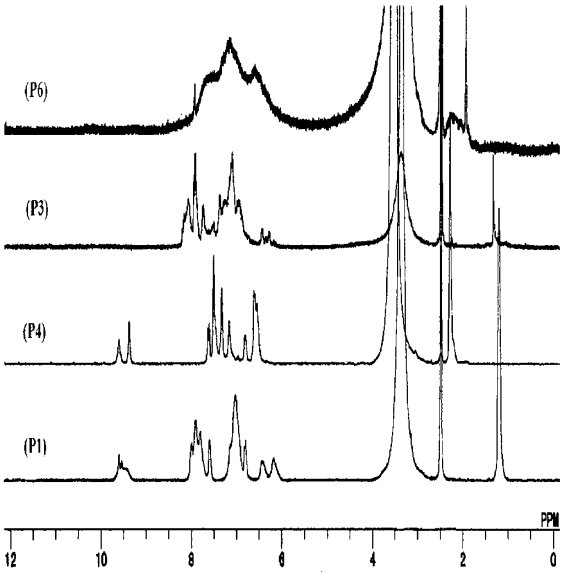


Figure 2. ^{1}H NMR spectra of HBPHA precursors (**P1**, **P4**), and chemically cyclized HBPBOs (**P3**, **P6**).

The free amino end groups were chemically modified with 3,5-dimethylbenzoic acid. The end-capping solution was prepared by mixing 3,5-dimethylbenzoic acid, DBOP and 4-methyl pyridine in NMP to form the active amide, which is the profer intermediate for chermoselective amidation.[27,28] An excess usage of end-capping solution raised the formation of not only amidation, but undesirable esterification. The desirable poly(*o*-hydroxyamide) could be prepared by using an equimolar amount of the end-capping agents. The conversion of the end-capping reaction was 95%, which was calculated from the comparison of methyl peaks at 2.3 ppm and aromatics at 6.6 ppm by ^{1}H NMR analysis (spectrum **P4** in Figure 2). The DB values of **P4** could not be calculated by ^{1}H and ^{13}C NMR analyses because of the same reasons as **P1**. Polymer **P4** showed good solubility in common organic solvents, similar to **P1** (Table I). The effect of the monomer concentration on η_{inh} was investigated as shown in Figure 3. η_{inh} increased with increasing the concentration of monomer up to 13.5 g dL^{-1}, but the gelation was occurred when the concentration of monomer was 27 g dL^{-1}.

Conversion of HBPHA to HBPBO by Thermal and Chemical Cyclodehydration

The conversion of HBPHA to HBPBO was carried out by two ways, thermal and chemical cyclodehydration. We have monitored the thermal conversion of HBPHA to HBPBO with temperature variation by IR as shown in Figure 4. The characteristic amide peaks of **P1** were observed at 1654 cm^{-1}. The peak intensity was decreased gradually with temperature and disappeared completely above 300 °C. Whereas, two new characteristic peaks for benzoxazole at 1618 cm^{-1} and

Table I. Solubility of Hyperbranched Poly(*o*-hydroxyamide)s and Polybenzoxazoles

Polymer	NMP	DMAc	DMF	DMSO	THF	GBL[a]	$CHCl_3$	1N NaOH
P1	++	++	++	++	++	++	–	++
P2	–	–	–	–	–	–	–	–
P3	++	++	++	++	+–	–	–	–
P4	++	++	++	++	++	++	–	+
P5	–	–	–	–	–	–	–	–
P6	+	+	+	+	–	–	–	–

[a] γ-butyrolactone; ++, soluble at room temperature; +, soluble on heating; +–, partially soluble; –, insoluble.

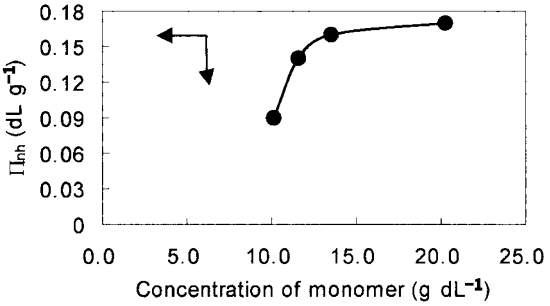


Figure 3. Inherent viscosity of polymer **P4** with concentration of monomer **8**.

1477 cm^{-1} were clearly observed above 250 °C. The spectral change indicated that the thermal conversion of **P1** to **P2** was completed above 300 °C for 1 h *in vacuo*. The small peak at 1700 cm^{-1} was observed in Figure 4a, which results from the unreacted free carboxylic end-groups. Polymer **P4** was also showed the similar results of **P1**. **P5** prepared from **P4** by thermal treatment at 300 °C for 1 h under vacuum was insoluble in organic solvents used in this work, similar to **P2**. This insolubility of thermally cyclized HBPBOs was anticipated to be caused by inter- or intra-molecular cross-linking during the thermal cyclization.

The DSC thermograms in Figure 5 showed that the maximum temperature (T_{max}) for thermal cyclodehydration of **P4** (288 °C) was slightly higher than that of **P1** (274 °C). The TGA thermograms also showed that the weight loss caused by elimination of water in the cyclization step of **P4** took place in the range of 255–318 °C, whereas that of **P1** was observed around 241–312 °C (thermogram (a) in Figure 6). DSC and TGA results explain that **P4** requires a slightly higher cyclizing temperature to convert PBO compared to **P1**.

Polymer **P6** was prepared by chemical cyclization of **P4** in polyphosphoric acid (PPA) at 160 °C for 24 h, which is slightly severe condition compared to those of **P3**. Under the same condition of **P1** (130 °C, 36 h), the precursor **P4** was not completely converted to HBPBO. The difference between the two chemical cyclization conditions was probably due to the gap of cyclized temperature between **P1** and **P4** as shown in Figures 5

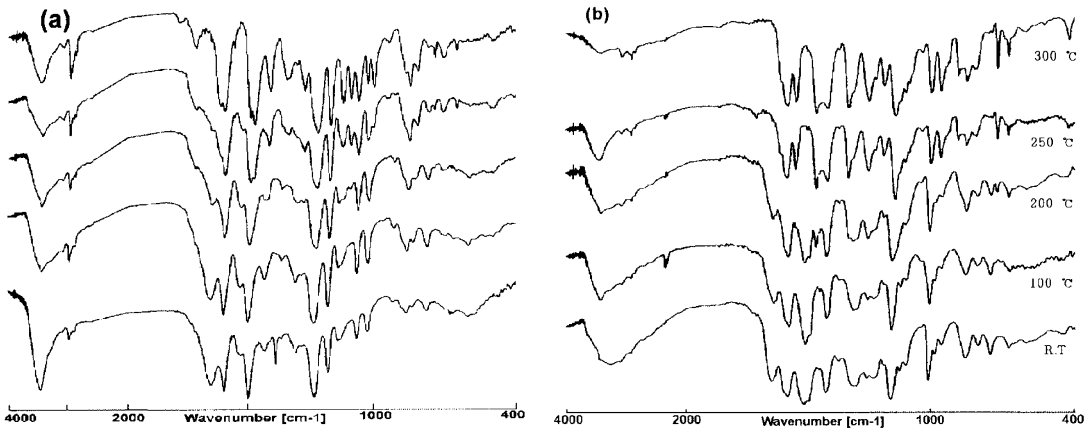


Figure 4. IR spectra of HBPHAs with heat treatment at r.t., 100 °C, 200 °C, 250 °C, and 300 °C for 1 h *in vacuo*. (a) **P1** and (b) **P4**.

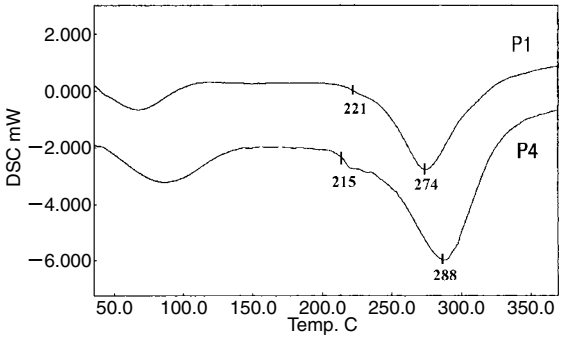


Figure 5. DSC thermogram of poly(*o*-hydroxyamide)s **P1** and **P4**.

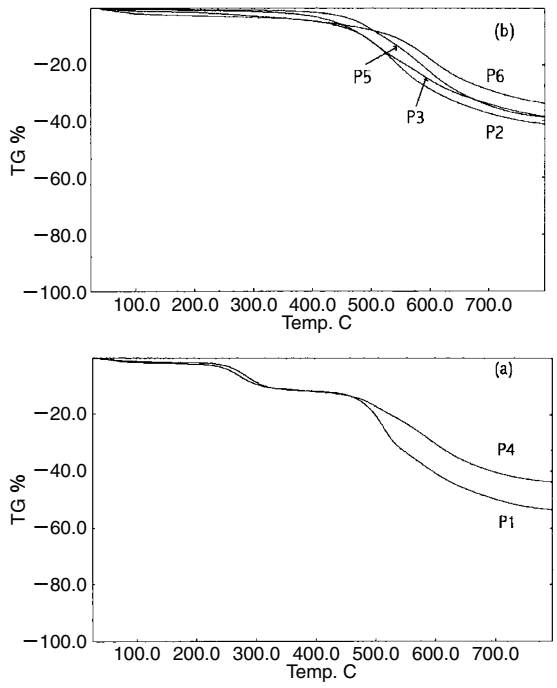


Figure 6. TGA thermogram of (a) HBPHAs and (b) HBPBOs.

and 6. Chemically cyclized polymer **P6** was soluble in aprotic solvents such as NMP, DMAc, DMF, and DMSO when heating up to 100 °C (Table I). This enhanced solubility of chemically cyclized HBPBO is a characteristic properties of hyperbranched polymers.

Table II. Solution and thermal properties of hyperbranched polymers

Polymer	η_{inh}[a] (dL g^{-1})	M_w[b] ($\times 10^4$)	M_w/M_n[b]	T_g[c] (°C)	T_5[d] (°C)	T_{10}[d] (°C)
P1	0.23	2.7[e]	1.6[e]	221	260	301
P2	–	–	–	ND[g]	442	488
P3	0.21	2.3[e]	1.5[e]	ND	425	489
P4	0.17	13.1[f]	1.7[f]	215	274	318
P5	–	–	–	217 (225)[h]	480	520
P6	0.16	9.7[f]	2.1[f]	ND	424	537

[a]Measured at a concentration of 0.5 g dL^{-1} in DMAc at 30 °C. [b]Determined by GPC measurement in DMF containing lithium bromide (0.01 mol L^{-1}) as an eluent with standard polystyrene calibration. [c]Determined by DSC at a heating rate of 10 °C min^{-1} in nitrogen. [d]The temperature at which 5 wt% (T_5) and 10 wt% of weight loss (T_{10}) were determined by TGA at a heating rate of 10 °C min^{-1} in nitrogen. [e]Performed on JASCO HPLC 880 PU fitted Shodex KD 806 M and 802.5 columns. [f]Performed on SHODEX GPC-104/101 with Shodex KD 806 M and 802 columns. [g]Not detectable up to 380 °C by DSC. [h]Glass transition temperature on second heating scan.

The solution properties of **P6** were comparable to those of **P4** (Table II). The η_{inh} and M_w of **P6** were 0.16 (dL g^{-1}) and 97000, which were slightly smaller than those of **P4**. These decrease of η_{inh} and M_w for **P6** compared to **P4** might be caused by the elimination of water during the cyclodehydration. The chemical conversions of precursors to PBOs were confirmed by ^{1}H NMR and IR spectrophotometer as shown in Figures 2 and 7. In the ^{1}H NMR spectra (Figure 2), **P1** showed the characteristic amide peaks at 9.5 ppm and *tert*-butyl peaks at 1.21 ppm, which came from the chemically modified end groups. The amide peaks of **P1** disappeared clearly in **P3**. The amide peaks of **P4** at 9.6 ppm were also disappeared in **P6**. In the IR spectra shown in Figure 7, characteristic amide peaks of **P1** and **P4** observed at 1654 cm^{-1} disappeared completely in **P3** and **P6** and new characteristic peaks for benzoxazoles appeared at 1623 cm^{-1}. These results supported the complete con-

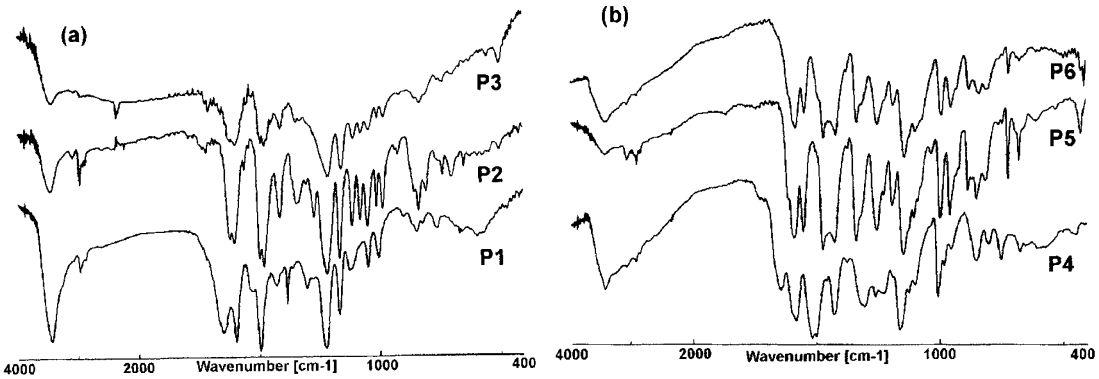


Figure 7. IR spectra of thermally (**P2**, **P5**) and chemically cyclized HBPBOs (**P3**, **P6**) and their precursors (**P1**, **P4**). Polymers prepared from (a) AB_2 monomer and (b) A_2B monomer.

version of HBPHAs to HBPBOs was achieved by the chemical cyclization.

Thermal Properties of Polymers

Polymer **P4** showed two step weight loss in the TGA thermogram (thermogram (a) in Figure 6). It is clear that the first step weight loss (7.2 wt%) at 255–318°C is due to the elimination of water during the cyclodehydration of HBPHA precursor to form the HBPBO. It is well corresponding to the calculated weight loss (7.5 wt%). Thermally or chemically cyclized polymers, **P5** or **P6**, showed only one step weight loss having the 10 wt% weight loss (T_{10}) at 520 °C and 537 °C in nitrogen (Table II) which was a little bit higher than those of **P2** and **P3** (488 °C, 489 °C). This gap seemed to be caused by the difference of molecular weight between the two polymers. TGA results indicated that these polymers were thermally stable which was not inferior compared to their linear analogues.[29,30] Thermally cyclized polymers, **P2** and **P5**, showed similar TGA patterns to chemically cyclized ones (**P3** and **P6**). Glass transition temperatures (T_g) of **P1**, **P4**, and **P5** were 221 °C, 215 °C, and 217 °C respectively, but the T_g values of the other polymers were not detected up to 380 °C by DSC.

CONCLUSION

We prepared the two types of new monomers for hyperbranched polybenzoxazoles. The hyperbranched poly(*o*-hydroxyamide)s as precursors of polybenzoxazole were synthesized successfully by self-polycondensation of AB_2 and A_2B type monomers in the presence of DBOP as a condensing agent. HBPHA precursors have excellent solubility in aprotic solvents having the moderate molecular weight. Although in this study, the molecular weights were determined by GPC with polystyrene calibration, we are trying the alternative measurement of the absolute molecular weights using the GPC with a laser light scattering detector. The conversion of poly(*o*-hydroxyamide) to polybenzoxazole was carried out by thermal or chemical cyclodehydration. The polymers, which were chemically cyclodehydrated in polyphosphoric acid (PPA) have also good solubility in aprotic solvents as well as excellent thermal stability having the T_{10} at 489–537 °C, whereas thermally cyclodehydrated polymers were insoluble in the same solvents.

Acknowledgment. We thank Prof. Mitsuru Ueda of Tokyo Institute of Technology for his helpful discussion.

REFERENCES

1. K. C. Brinker, D. D. Cameron, and I. M. Robinson, U.S. Patent 2 904 537 (Sep. 15, 1959).
2. Y. Imai, I. Taoka, K. Uno, and Y. Iwakura, *Makromol. Chem.*, **83**, 167 (1965).
3. C. Jr. Arnold, *J. Polym. Sci., Macromol. Rev.,* **14**, 265 (1979).
4. P. E. Cassidy, "Thermal stable polymers", Mercel Dekker, New York, N.Y., 1980, p 154.
5. J. F. Wolfe and F. E. Arnold, *Macromolecules,* **14**, 909 (1981).
6. J. F. Wolfe, *Encycl. Polym. Sci. Tech.*, **11**, 601 (1988).
7. A. Kraft, A. C. Grimsdale, and A. B. Holmes, *Angew. Chem. Int. Ed.,* **37**, 402 (1998).
8. Y. Maruyama, Y. Oishi, M. Kakimoto, and Y. Imai, *Macromolecules,* **21**, 2305 (1988).
9. P. E. Cassidy, T. M. Aminabhavi, and J. M. Farley, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **c29**, 365 (1989).
10. W. J. Joseph, J. C. Abed, R. Mercier, and J. E. Mcgrath, *Polymer,* **35**, 5046 (1994).
11. K. H. Park, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 1987 (1998).
12. D. A. Tomalia, A. M. Naylor, and W. A. Goddard III, *Angew. Chem. Int. Ed.*, **29**, 138 (1990).
13. J. M. J. Fréchet, C. J. Hawker, I. Gitsov, and J. W. Leon, *J. Macromol. Sci., Pure Appl. Chem.*, **A33**, 1399 (1996).
14. B. I. Voit and D. Wolf, *Tetrahedron,* **53**, 15535 (1997).
15. H. R. Kricheldorf, O. Bolender, and T. Wollheim, *Macromolecules,* **32**, 3878 (1999).

16. M. Jikei and M. Kakimoto, *Prog. Polym. Sci*., **26**, 1233 (2001).
17. S. Srinivasan, R. Twieg, J. L. Hedrick, and C. J. Hawker, *Macromolecules,* **29**, 8543 (1996).
18. Y. H. Kim, *J. Polym. Sci., Part A: Polym. Chem*., **36**, 1685 (1998).
19. G. Yang, M. Jikei, and M. Kakimoto, *Macromolecules,* **32**, 2215 (1999).
20. D. S. Thompson, L. J. Markoski, J. S. Moore, I. Sendijarevic, A. Lee, and A. J. McHugh, *Macromolecules,* **33**, 6412 (2000).
21. B. Voit, *J. Polym. Sci., Part A: Polym. Chem*., **38**, 2505 (2000).
22. Z. H. Gong, M. Leu, F. I. Wu, and C. F. Shu, *Macromolecules,* **33**, 8527 (2000).
23. J. B. Baek, S. R. Simko, and L. S. Tan, *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)*, **42(2)**, 502 (2001).
24. H. Ahne, R. Rubner, and E. Kuehn, Euro. Patent 23 662 A1 (Feb. 11, 1981).
25. T. K. Kim, K. Y. Choi, K. S. Lee, D. W. Park, and M. Y. Jin, *Polym. Bull.*, **44**, 55 (2000).
26. C. S. Hong, M. Jikei, and M. Kakimoto, *J. Photopolym. Sci. Technol.,* **15**, 219 (2002).
27. M. Ueda, T. Morosumi, M. Kakuta, and R. Sato, *Polym. J.*, **22**, 733 (1990).
28. T. Hayakawa, T. Morishita, M. Okazaki, M. Ueda, K. Takeuchi, and M. Asai, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 3875 (2000).
29. M. Ueda, H. Sugita, and M. Sato, *J. Polym. Sci., Part A: Polym. Chem.*, **24**, 1019 (1986).
30. B. A. Reinhardt, *Polym. Commum.*, **31**, 453 (1990).