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Polymer 47 (2006) 4549–4556

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Synthesis of nitrile and benzoyl substituted poly(biphenylene oxide)s via nitro displacement reaction

Insik In, Sang Youl Kim *

Department of Chemistry, School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-Gu, Daejeon 305-701, South Korea

Received 16 November 2005; received in revised form 18 April 2006; accepted 26 April 2006

Abstract

A series of substituted poly(biphenylene oxide)s (PBPOs) was synthesized via nucleophilic nitro displacement reactions. High molecular weight PBPO's with nitrile groups were effectively synthesized from the polymerization of A-B type monomers with K_2CO_3 as a base in *N*-methyl-2-pyrrolidinone (NMP) at 140 °C. The polymers are completely amorphous, soluble in polar aprotic solvents, and formed flexible films on solution casting. Para-linked PBPO with nitrile groups showed excellent thermal properties such as high 5% weight loss temperature above 530 °C and T_g at 241 °C which is higher than those of commercially available PPO™ ($T_g = 210$ °C). The pendent nitrile groups of PBPO were easily transformed to carboxylic acid groups by acidic hydrolysis.

Keywords: High performance polymers; Poly(aryl ethers); Step-growth polymerization

1. Introduction

Poly(arylene ether)s constitute an important class of high temperature engineering thermoplastics having many excellent characteristics, which include good mechanical property and high chemical/thermal/hydrolytic stability. Due to the above characteristics, poly(arylene ether)s are finding important applications in the aerospace, electronic, automotive, and related areas [1,2].

Poly(arylene ether)s are generally synthesized by the step growth polymerization of activated dihalo monomers with bisphenoxide via nucleophilic aromatic substitution (S_NAr) reaction, where the generation of aryl ether linkages is the polymer-forming reaction [3]. It has been demonstrated that both sulfone and ketone groups are effective in activating aryl halides toward nucleophilic displacement and useful in the preparation of amorphous poly(aryl ether sulfone)s and semi-crystalline poly(aryl ether ketone)s, respectively. Heterocyclic (i.e. imide, quinoxaline, and benzoxazole), perfluoroalkyl, amide, triple bond, nitrile, and imine groups have also been used as activating groups to produce new poly(arylene ether)s [2].

Among various poly(arylene ether)s, poly(phenylene oxide) (PPO) consisting of alternating linkages of 1,4-phenylene and ether groups in the repeating units is the simplest form of poly(arylene ether) [4,5]. Even though the presence of flexible ether linkages, PPO is semi-crystalline and direct synthesis of high molecular weight PPO is difficult [6,7]. Poly(2,6-dimethyl-1,4-oxyphenylene) (PPO™), substituted PPO commercialized by GE, is an amorphous polymer with excellent thermal property, high resistance to aqueous chemicals and steam, good mechanical properties, and excellent dielectric characteristics ($\varepsilon = 2.58$). Many PPO derivatives with various pendent groups instead of methyl groups were prepared, but the structural variation was confined to only side groups because of the limitation of the oxidative coupling reaction. Additionally, incorporation of electron-withdrawing groups as pendent groups of PPO has not been successfully accomplished via oxidative coupling reaction.

Incorporation of one additional phenyl ring into the main chain of PPO results in poly(biphenylene oxide) (PBPO) that is expected to have superior performance than PPO (Fig. 1). However, PBPO without substituents is highly crystalline and direct synthesis of high molecular weight PBPO is nearly impossible. Therefore, researches have been

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* Corresponding author. Tel.: +82 42 869 2834; fax: +82 42 869 2810.
E-mail address: kimsy@kaist.ac.kr (S.Y. Kim).

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doi:10.1016/j.polymer.2006.04.052

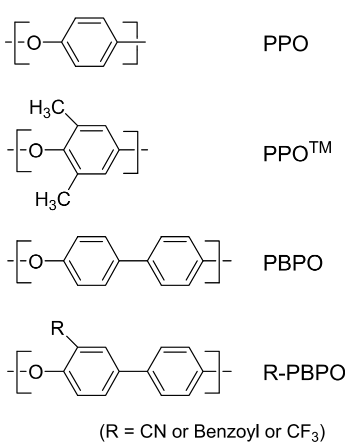


Fig. 1. Repeating unit structures of various PPOs and PBPOs.

concentrated on the facile and efficient synthesis of substituted PBPO with high molecular weight.

The synthesis of substituted PBPO has to be different with the synthesis of 2,6-di-substituted PPO because the oxidative coupling reaction is not successful due to the high oxidative potential of biphenol monomer. Recently, our group reported successful synthesis of trifluoromethyl substituted PBPO with high molecular weight [8–10]. The synthesis was accomplished through nucleophilic aromatic substitution (S_NAr) reaction using a nitro-leaving group activated by trifluoromethyl groups that are stable even at relatively high temperature. This nitro displacement reaction has been successfully extended to the synthesis of poly(phenylene oxide), poly(ether ketone), poly(ether sulfone), poly(ether amide), and poly(ether amine) [11–17]. But in some cases, trifluoromethylated polymers do not show high glass transition temperatures. Even though the rigid biphenylene oxide backbone structure, CF_3–PBPO has rather lower glass transition temperature ($T_g = 201$ °C) having compared with PPO™ ($T_g = 210$ °C) with the phenylene oxide backbone structure. Therefore, its application to high performance polymers is rather limited due to the low glass transition temperature.

In this study, new poly(biphenylene oxide)s with various substituents were synthesized via nitro displacement reaction. The incorporated substituents should be effective for nucleophilic nitro displacement reaction and inert to nitrite ions which can cause side reactions at high temperature above 140 °C [18–22]. Nitrile and benzoyl groups were tested as the substituents for the synthesis of substituted PBPO (Fig. 1). The benzoyl group has similar activating power to the trifluoromethyl group and the nitrile group is known as the strongest activating group in S_NAr reaction. In addition, the nitrile group can be easily transformed to the carboxylic acid groups after hydrolysis. These acid functionalized poly(aryl ethers) are promising candidates for some applications such as fuel cell membranes. And the systematic evaluation of all these polymers will develop the detailed structure–property relationship of poly(biphenylene oxide)s.

2. Experimental

2.1. Materials

All starting reagents were purchased from Aldrich Co. Inorganic reagents such as K_2CO_3 were dried at 120 °C under vacuum for 12 h before use. *N*-Methyl-2-pyrrolidinone (NMP) was stirred in the presence of CaH_2 overnight and then distilled under reduced pressure. Toluene was dried over sodium and distilled before use. Other commercially available reagent grade chemicals were used without further purification. 2-Amimo-5-bromobenzophenone was prepared according to the literature [23].

2.2. Characterization

FT-IR spectra of the compounds were obtained with a Brucker EQUINOX-55 spectrophotometer using KBr pellet or film. NMR spectra of the synthesized compounds were recorded on Brucker Fourier Transform AVANCE 300 spectrometers. High-resolution mass (HR-MS) spectra of the monomers and model compounds were obtained with a Jeol JMS-SX-102 mass spectrometer. Inherent viscosity data were obtained in NMP with a Canon-Ubbelohde type viscometer at a concentration of 0.5 g/dL at 30 °C. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TA 2200 thermal analyzer system at a heating rate of 20 °C/min in nitrogen or air.

2.3. Monomer synthesis

2.3.1. 2-Amino-5-bromobenzonitrile (*1*) [24]

A 500 mL two-neck flask equipped with a dropping funnel and nitrogen inlet was charged with 10.00 g (84.65 mmol) of 2-aminobenzonitrile and 150 mL of carbon tetrachloride. 4.4 mL (85 mmol) of bromine in 50 mL of carbon tetrachloride was dropped into the solution for 2 h and the reaction mixture was warmed to room temperature for 6 h. After additional stirring for 2 h, 50 mL of 1 M NaOH aqueous solution was slowly added into the reaction mixture. The reaction mixture was extracted with ethyl acetate, dried with magnesium sulfate, and evaporated by rotary evaporation. 12.6 g of **1** was obtained as a white crystal after recrystallization from carbon tetrachloride.

Yield: 76%. Mp 98 °C. ^{1}H NMR ($CDCl_3$, ppm): 7.36 (d, $J=3.63$ Hz, 1H), 7.40 (dd, $J=13.1$ and 3.63 Hz, 1H), 6.64 (d, $J=13.1$ Hz, 1H), 4.34 (b, NH_2).

2.3.2. 5-Bromo-2-nitrobenzonitrile (**2**) [25]

A 100 mL two-neck flask equipped with a dropping funnel and nitrogen inlet was charged with 4.89 g of sodium perborate hydrates and 20 mL of acetic acid. The mixture was stirred at 55 °C and 1.00 g (5.08 mmol) of **1** in 60 mL of acetic acid was added via dropping funnel for 6 h. Perborate solid dissolves into the solution slowly and the reaction mixture changed to clear orange color. After observing white precipitation near the surface of flask, the reaction mixture was cooled and precipitated into 300 mL of distilled water. The dark brown solid was filtered and dried under vacuum. The crude product sublimed under vacuum (0.1 mmHg) at 80 °C to give yellow brown crystal.

Yield: 45%. Mp 115 °C. FT-IR (KBr, cm^{-1}): 2236, 1530, 1341. ^{1}H NMR ($CDCl_3$, ppm): 8.2 (d, $J=13.1$ Hz, 1H), 8.0 (d, $J=2.91$ Hz, 1H), 7.97 (dd, $J=13.1$ and 2.9 Hz, 1H).

2.3.3. 4-Methoxy-3′-cyano-4′-nitrobiphenyl (*3a*)

4-Methoxyphenylboronic acid was prepared by the previous reported method [26]. A 100 mL three-neck flask was charged with 2.00 g (8.81 mmol) of **2**, 1.74 g (8.81 mmol) of 3-methoxyphenylboronic acid, and 0.305 g (0.264 mmol) of tetrakis(triphenyl phosphine) palladium. Nine milliliter of 2 M aqueous Na_2CO_3 solution, 4.5 mL of ethanol, 18 mL of toluene were added to the reaction mixture. After overnight stirring at 100 °C, the mixture was cooled and the resulting solid was filtered and dried under vacuum. A yellow crystal of **3a** was obtained after recrystallization from ethanol.

Yield: 90%. ^{1}H NMR ($CDCl_3$, ppm): 8.37 (d, $J=13.1$ Hz, 1H), 8.03 (d, $J=3.6$ Hz, 1H), 7.93 (dd, $J=13.1$ and 2.9 Hz, 1H), 7.59 (d, $J=13.8$ Hz, 2H), 7.05 (d, $J=13.8$ Hz, 2H), 3.87 (s, 3H). HR-MS (*m*/*e*) 254.0685, Calcd 254.0693 for $C_{14}H_{10}N_2O_3$.

2.3.4. 3-Methoxy-3′-cyano-4′-nitrobiphenyl (*3b*)

3-Methoxyphenylboronic acid was prepared by the previous reported method [26]. The above procedure was repeated with 2.00 g (8.81 mmol) of **2**, 1.74 g (8.81 mmol) of 4-methoxyphenylboronic acid, and 0.293 g (0.254 mmol) of tetrakis (triphenyl phosphine) palladium. A yellow crystal of **3b** was obtained after recrystallization from toluene.

Yield: 74%. ^{1}H NMR ($CDCl_3$, ppm): 8.40 (d, $J=13.1$ Hz, 1H), 8.07 (d, $J=2.91$ Hz, 1H), 7.98 (dd, $J=13.1$ and 2.91 Hz, 1H), 7.47 (t, $J=11.6$ Hz, 1H), 7.19 (m, 1H), 7.10 (m, 1H), 7.04 (m, 1H), 3.88 (s, 3H). HR-MS (*m*/*e*) 254.0692, Calcd 254.0691 for $C_{14}H_{10}N_2O_3$.

2.3.5. 4-Hydroxy-3′-cyano-4′-nitrobiphenyl (*4a*)

A 50 mL one-neck flask was charged with 0.725 g (2.85 mmol) of **3a** and 13 mL of methylene chloride. 1.2 mL (13 mmol) of BBr_3 was dropped into the reaction mixture via syringe at −78 °C. After 6 h, the flask was warmed to room temperature and stirring was continued for 4 h. The reaction mixture was poured into the ice-cold water and the resulting yellow solid was filtered and dried under reduced pressure. After recrystallization from acetone, yellow crystal (0.66 g) of **4a** was produced.

Yield: 96%. FT-IR (KBr, cm^{-1}): 3316, 2244, 1588, 1517, 1337, 1266, 836. ^{1}H NMR (DMSO-d_6, ppm): 10.0 (s, OH), 8.41 (m, 2H), 8.19 (dd, $J=13.1$ and 2.91 Hz, 1H), 7.79 (d, $J=13.1$ Hz, 2H), 6.93 (d, $J=13.1$ Hz, 2H). ^{13}C NMR (DMSO-d_6, ppm): 159.4, 146.2, 145.7, 132.4, 130.4, 129.0, 126.4, 126.3, 116.2, 115.7, 107.7. HR-MS (*m*/*e*) 240.0537, Calcd 240.0535 for $C_{13}H_8N_2O_3$.

2.3.6. 3-Hydroxy-3′-cyano-4′-nitrobiphenyl (*4b*)

The above procedure was repeated with 2.00 g (7.87 mmol) of **3b**, 42 mL of methylene chloride, and 3.4 mL (35 mmol) of BBr_3. After recrystallization from ethyl acetate, yellow crystal (1.07 g) of **4b** was produced.

Yield: 96%. FT-IR (KBr, cm^{-1}): 3336, 2240, 1589, 1522, 1472, 1339, 855, 788. ^{1}H NMR (DMSO-d_6, ppm): 9.75 (s, OH), 8.42 (m, 2H), 8.18 (dd, $J=8.74$ and 2.14 Hz, 1H), 7.35 (m, 1H), 7.27 (m, 1H), 7.18 (t, $J=2.07$ Hz, 1H), 6.92 (m, 1H). ^{13}C NMR (DMSO-d_6, ppm): 158.1, 146.8, 146.3, 137.3, 133.5, 131.8, 130.4, 126.3, 118.2, 116.8, 115.5, 114.1, 107.6. HR-MS (*m*/*e*) 240.0536, Calcd 240.0535 for $C_{13}H_8N_2O_3$.

2.3.7. 5-Bromo-2-nitrobenzophenoene (*5*) [23]

A 100 mL two-neck flask equipped with a dropping funnel and nitrogen inlet was charged with 2.79 g of sodium perborate hydrates and 10 mL of acetic acid. The flask was kept at 60 °C and 1.00 g (3.62 mmol) of 5-bromo-2-aminobenzophenone in 10 mL of acetic acid was added via dropping funnel for 6 h. After dropping, heating was continued for additional 6 h. The reaction mixture was cooled and poured into 300 mL of distilled water. The oily product was filtered and dried under vacuum. Flash column chromatography (ethyl acetate/hexane = 1:1) yielded a yellow solid (0.66 g) of **5**.

Yield: 60%. Mp 128 °C. ^{1}H NMR ($CDCl_3$, ppm): 8.10 (d, $J=8.76$ Hz, 1H), 7.80 (dd, $J=8.77$ and 2.12 Hz, 1H), 7.74 (d, $J=7.35$ Hz, 2H), 7.60 (m, 2H), 7.47 (t, $J=7.37$ Hz, 2H). ^{13}C NMR ($CDCl_3$, ppm): 191.6, 145.3, 137.6, 135.3, 134.1, 133.6, 131.7, 129.5, 129.2, 128.9, 125.9.

2.3.8. 4-Methoxy-3′-benzoyl-4′-nitrobiphenyl (*6a*)

The above procedure of **3a** was repeated with 4-methylphenyl boronic acid and **5**.

Yield: 92%. ^{1}H NMR ($CDCl_3$, ppm): 8.30 (d, $J=8.72$ Hz, 1H), 7.83 (m, 3H), 7.60 (m, 4H), 7.48 (t, $J=6.78$ Hz, 2H), 7.0 (d, $J=8.72$ Hz, 2H), 3.85 (s, $-OCH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): 193.8, 160.8, 147.0, 144.6, 136.9, 135.9, 133.7, 130.0, 129.2, 128.7, 128.6, 127.8, 126.3, 125.1, 114.7, 55.4. HR-MS (*m*/*e*) 333.1003, Calcd 333.1001 for $C_{20}H_{15}NO_4$.

2.3.9. 3-Methoxy-3′-benzoyl-4′-nitrobiphenyl (*6b*)

The above procedure of **3a** was repeated with 3-methylphenyl boronic acid and **5**.

Yield: 82%. ^{1}H NMR ($CDCl_3$, ppm): 8.31 (d, $J=8.62$ Hz, 1H), 7.85 (dd, $J=8.61$ and 2.03 Hz, 1H), 7.80 (m, 2H), 7.70 (m, 1H), 7.64 (m, 1H), 7.58 (m, 1H), 7.45 (m, 2H), 7.19 (m, 1H), 7.12 (m, 1H), 6.96 (m, 1H) 3.85 (s, $-OCH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): 193.2, 160.0, 147.1, 145.2, 139.0, 135.7, 133.6, 130.1, 129.1, 128.6, 128.5, 127.0, 124.9, 119.6, 114.5, 113.0, 55.2. HR-MS (*m*/*e*) 333.1002, Calcd 333.1001 for $C_{20}H_{15}NO_4$.

2.3.10. 4-Hydroxy-3′-benzoyl-4′-nitrobiphenyl (*7a*)

A 100 mL one-neck flask was charged with 0.73 g (2.2 mmol) of **6a** and 28 g of pyridine hydrochloride. After stirring at 200 °C for 3 h, the reaction mixture was cooled to 80 °C and poured into ice-cold water. The crude product was extracted with ethyl acetate and flash column chromatography (ethyl acetate/hexane = 1:2) yielded yellow solid. After recrystallization from methylene chloride and hexane, 0.45 g of yellow crystal was obtained.

Yield: 77%. ^{1}H NMR (DMSO-d_6, ppm): 9.93 (s, –OH, 1H), 8.31 (d, J = 8.73 Hz, 1H), 8.04 (dd, J = 8.75 and 2.01 Hz, 1H), 7.86 (d, J = 1.97 Hz, 1H), 7.74 (m, 5H), 7.54 (m, 2H), 6.88 (d, J = 8.66 Hz, 2H). ^{13}C NMR (DMSO-d_6, ppm): 193.1, 159.0, 146.4, 143.8, 136.3, 135.6, 133.9, 129.0, 128.9, 127.5, 127.3, 125.5, 125.3, 116.1. HR-MS (*m/e*) 319.0848, Calcd 319.0845 for $C_{19}H_{13}NO_4$.

2.3.11. 3-Hydroxy-3′-benzoyl-4′-nitrobiphenyl (**7b**)

The above procedure was repeated with **6b**.

Yield: 72.4%. FT-IR (KBr, cm^{-1}): 3433, 1667, 1515, 1346. ^{1}H NMR (DMSO-d_6, ppm): 9.70 (s, –OH, 1H), 8.36 (d, J = 8.66 Hz, 1H), 8.07 (dd, J = 8.66 and 2.06 Hz, 1H), 7.88 (m, 4H), 7.54 (t, J = 7.77 Hz, 2H), 7.28 (m, 3H), 6.89 (m, 1H). ^{13}C NMR ($CDCl_3$, ppm): 193.7, 156.3, 146.8, 145.0, 138.9, 136.3, 135.5, 133.7, 130.1, 129.0, 128.5, 128.4, 126.7, 124.8, 119.3, 116.1, 114.0. HR-MS (*m/e*) 319.0847, Calcd 319.0845 for $C_{19}H_{13}NO_4$.

2.3.12. 3-Benzoyl-4-nitrobiphenyl (**8**)

A 50 mL one-neck flask was charged with 1.9375 g (6.3337 mmol) of **4**, 0.8495 g (6.967 mmol) of phenylboronic acid, and 0.22 g (0.19 mmol) of tetrakis(triphenyl phosphine)-palladium. Seven milliliters of 2 M aqueous Na_2CO_3 solution, 3.25 mL of ethyl alcohol, and 14 mL of toluene were added to the reaction flask. After overnight stirring at 90 °C, the mixture was cooled. After extraction with diethyl ether, the crude product was purified by column chromatography (ethyl acetate/hexane = 1:6). The resulting bright yellow solid was dried under vacuum.

Yield: 92%. FT-IR (KBr, cm^{-1}): 1676, 1521, 1350. ^{1}H NMR (DMSO-d_6, ppm): 8.39 (d, J = 13.1 Hz, 1H), 8.11 (dd, J = 13.1 and 3.63 Hz, 1H), 7.97 (d, J = 2.88 Hz, 1H), 7.80 (m, 5H), 7.49 (m, 5H). ^{13}C NMR (DMSO-d_6, ppm): 192.9, 146.3, 145.0, 136.9, 136.2, 135.5, 134.0, 129.4, 129.2, 129.1, 129.0, 128.9, 127.5, 126.6, 125.5. HR-MS (*m/e*) 303.0896, Calcd 303.0895 for $C_{19}H_{13}NO_3$.

2.3.13. 4-Benzoyl-4-(3′-methylphenoxy)biphenyl (**9**)

A 50 mL three-neck flask was charged with 0.5000 g (1.649 mmol) of **8**, 0.1783 g (1.649 mmol) of *m*-cresol, 0.4557 g (3.297 mmol) of potassium carbonate, 2 mL of toluene, and 3 mL of NMP. The mixture was stirred mechanically and heated to 130 °C. After 6 h, the temperature was increased to 140 °C and maintained for 12 h. The solution was cooled to room temperature. After precipitation into 100 mL of distilled water with 1 mL of acetic acid, the brown solid was filtered and dried under vacuum at 30 °C. The crude product was purified by column chromatography (ethyl acetate/hexane = 1:6).

Yield: 80%, FT-IR (KBr, cm^{-1}): 1660, 1477, 1252. ^{1}H NMR (DMSO-d_6, 100 °C, ppm): 7.97 (m, 2H), 7.80 (d, J = 3.63 Hz, 1H), 7.74–7.43 (m, 9H), 7.18 (m, 2H), 6.91 (d, J = 11.6 Hz, 1H), 6.78 (m, 2H), 2.30 (s, –CH_3). ^{13}C NMR (DMSO-d_6, 100 °C, ppm): 195.4, 156.4, 154.3, 139.7, 139.5, 137.4, 136.2, 133.0, 131.1, 130.3, 129.7, 129.3, 128.8, 128.4, 128.1, 127.3, 126.8, 124.3, 119.5, 119.0, 115.7, 21.2. HR-MS (*m/e*) 364.1462, Calcd 364.1463 for $C_{26}H_{20}O_2C_{26}$.

2.4. Polymerization

2.4.1. CN–PBPO-*p*

A 50 mL three-neck flask was charged with 0.7300 g (3.384 mmol) of **4a**, 0.8398 g (6.080 mmol) of potassium carbonate, 2 mL of toluene, and 3 mL of NMP. The mixture was stirred mechanically and heated to 130 °C. After 6 h, the temperature was increased to 140 °C and maintained for 12 h. The viscous polymer solution was diluted with 3 mL of NMP and cooled to room temperature. After precipitation into 500 mL of distilled water with 1 mL of acetic acid, the white fibrous polymer was filtered and dried under vacuum at 100 °C. The crude polymer was reprecipitated from the NMP solution into methanol.

Yield: 98%. η_{inh}: 0.93 dL/g (NMP, 30 °C). T_g: 241 °C. FT-IR (KBr, cm^{-1}): 2229, 1478, 1240. ^{1}H NMR (DMSO-d_6, 100 °C, ppm): 8.14 (s, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.8 (d, J = 8.33 Hz, 2H), 7.26 (d, J = 8.32 Hz, 2H), 7.20 (d, J = 8.72 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 °C, ppm): 156.9, 155.1, 135.0, 133.7, 132.5, 131.3, 128.1, 118.9, 118.6, 114.8, 103.9.

2.4.2. CN–PBPO-*m*

The above procedure was repeated with 0.7300 g (3.038 mmol) of **4b** and 0.840 g (6.08 mmol) of potassium carbonate.

Yield: 97%. η_{inh}: 0.45 dL/g (NMP, 30 °C). T_g: 200 °C. FT-IR (KBr, cm^{-1}): 2232, 1481, 1239. ^{1}H NMR (DMSO-d_6, ppm): 8.28 (s, 1H), 7.98 (b, 1H), 7.60 (b and m, 3H), 7.18 (b, 1H), 7.02 (b, 1H), ^{13}C NMR (DMSO-d_6, ppm): 158.5, 155.3, 139.8, 134.2, 133.4, 132.2, 131.1, 123.4, 119.1, 118.0, 117.7, 115.7, 103.3.

2.4.3. Bz–PBPO-*p* and Bz–PBPO-*m*

The same experimental conditions as CN–PBPO-*p* and CN–PBPO-*m* were repeated with **7a** and **7b**.

2.4.4. Acidic hydrolysis of CN–PBPO-*p*

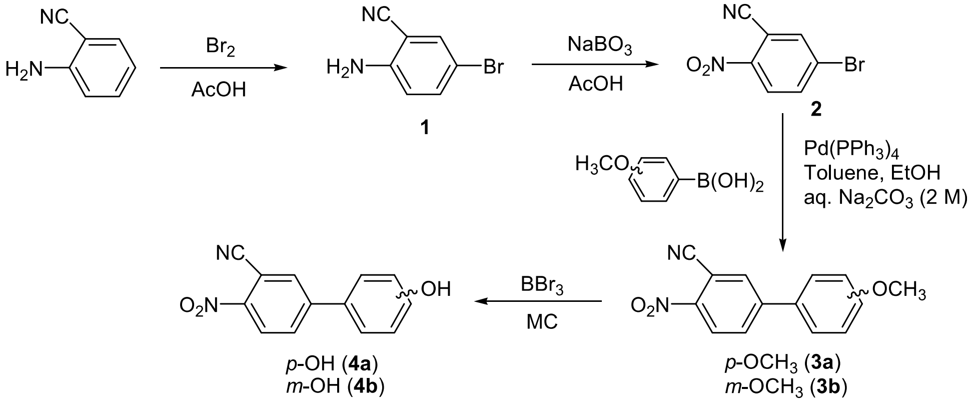
CN–PBPO-*p* (0.1 g) was mixed with 20 mL of 5 wt% sulfuric acid. The reaction mixture was stirred at 140 °C for 9 h. After cooling to room temperature, the reaction mixture was poured into cold water. The solid content was filtered and dried under vacuum at 80 °C. FT-IR (KBr, cm^{-1}): 1661, 1610, 1460, 1292, 1221.

2.4.5. Acidic hydrolysis of CN–PBPO-*m*

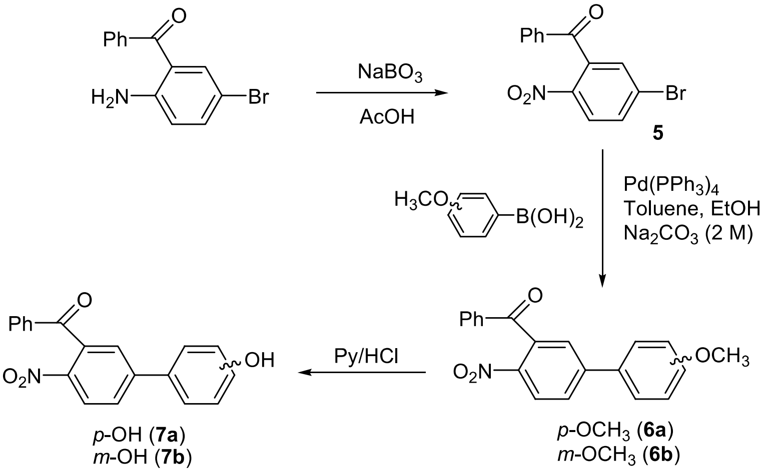
The above procedure was repeated with CN–PBPO-*m*. FT-IR (KBr, cm^{-1}): 1656, 1619, 1449, 1265.

3. Result and discussion

For the synthesis of substituted poly(biphenylele oxide)s (PBPOs), four AB-type monomers, which have a nitro group

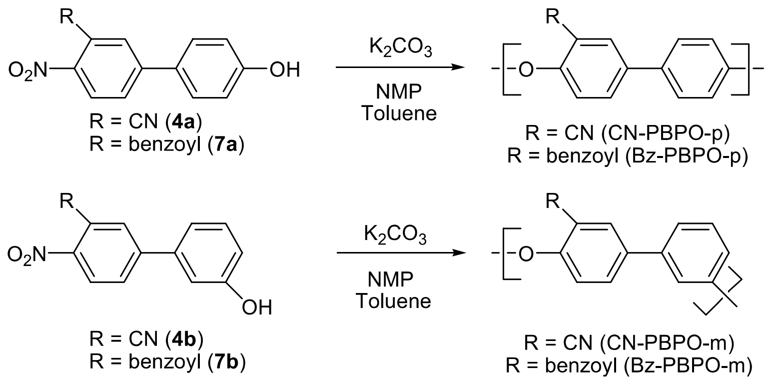


Scheme 1. Synthesis of nitrile substituted AB type monomers, **4a** and **4b**.



Scheme 2. Synthesis of benzoyl substituted AB type monomers, **7a** and **7b**.

activated by a nitrile or a benzoyl group at the ortho position of the nitro group and a hydroxy group at para or meta position of the phenyl ring of the biphenyl unit, were synthesized as shown in Schemes 1 and 2. The synthesis involves the formation of biphenyl linkage by the Suzuki coupling reaction of two phenyl groups which have either activated nitro or methoxy group in each phenyl group. In the case of the cyano-activating monomer, 5-bromo-2-nitrobenzonitrile (**2**) was synthesized from 2-aminobenzonitrile through selective bromination and subsequent oxidation of the amino group by sodium perborate. In the case of the benzoyl-activating monomer, corresponding 5-bromo-2-nitrobenzophenone (**5**) was synthesized by oxidation of 2-amino-5-bromobenzophenone. The Suzuki coupling reaction of **2** or **5** with 3- or 4-methoxyboronic



Scheme 3. Synthesis of nitrile or benzoyl substituted PBPOs.

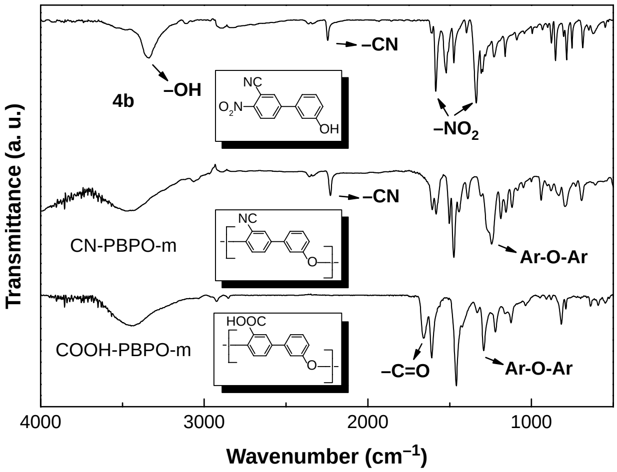


Fig. 2. FT-IR spectra of monomer **4b**, CN–PBPO-*m*, and COOH-PBPO-*m* (KBr pellet).

acid, followed by demethylation with either BBr$_3$ or pyridine hydrochloride produced the target monomers **4a/4b** and **7a/7b**, respectively. The structures of all AB-type monomers were confirmed by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

With these AB-type monomers, synthesis of nitrile or benzoyl substituted PBPO were carried out according to the conventional poly(arylene ether) synthesis with K$_2$CO$_3$ as a base in NMP at 140 °C as shown in Scheme 3. The solid content was maintained over 20 wt% and toluene was azeotropically distilled from the polymerization mixture for dehydration. The inherent viscosities of CN–PBPO-*p* and CN–PBPO-*m* were 0.93 and 0.45 dL/g, respectively, and flexible films were obtained by solution casting.

The structure of the polymers was confirmed with FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The strong hydroxyl stretching band at 3300 cm^{-1} and the sharp nitro stretching bands at 1526 and 1310 cm^{-1} were completely disappeared in FT-IR spectra of the polymers (Fig. 2). The absorption band near 2230 cm^{-1} corresponding to nitrile (C–N) stretching was observed in FT-IR spectra of both the monomers and the polymers, which shows the inertness of nitrile groups during the nitro displacement reaction. Substituted poly(biphenylene oxide)s showed an intense absorption band near 1240 cm^{-1} corresponding to the aryl ether linkages. ^{1}H NMR spectra of the monomers showed peaks at 10.0 and 9.75 ppm corresponding to the hydroxyl proton of monomers **4a** and **4b**, respectively, but these peaks disappeared in the ^{1}H NMR spectra of the corresponding polymers (Fig. 3). ^{13}C NMR spectra of CN–PBPO-*p* and CN–PBPO-*m* showed all expected 11 and 13 carbon peaks, respectively, as shown in Fig. 4. The high inherent viscosities and absence of detectable end groups in both FT-IR and NMR spectra support the formation of high molecular weight polymers.

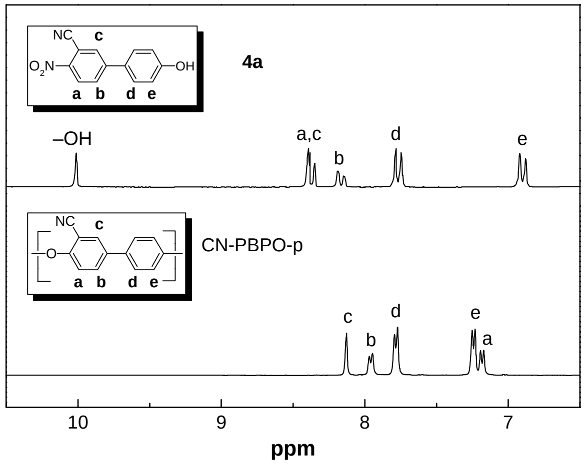


Fig. 3. ^{1}H NMR spectra of monomer **4a** (at 25 °C) and CN–PBPO-*p* (at 100 °C in DMSO-d_6).

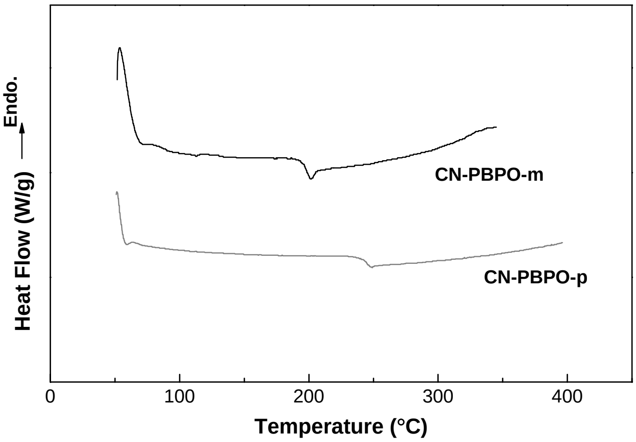
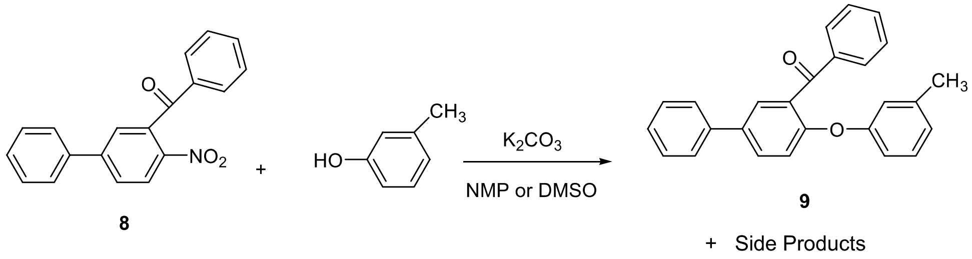


Fig. 4. DSC curves of CN–PBPO-*p* and CN–PBPO-*m*.

Also, PBPOs with benzoyl substituents were synthesized from the benzoyl-activated AB-type nitro monomers **7a** and **7b** but only low molecular weight polymers were obtained by the same polymerization condition. The attempt to optimize the polymerization condition such as solvent and temperature failed to get a high molecular weight polymer. Model reaction of 3-benzoyl-4-nitrobiphenyl (**8**) with *m*-cresol at 140 °C produced several side products along with the desired model compound (**9**) but detailed analysis of the side products was not performed (Scheme 4). Also, model reaction below 140 °C yields incomplete conversion of **8**. It seems that the benzoyl group at ortho position of the nitro leaving group is susceptible to the side reaction of the leaving nitrite ion (NO$_2^-$). Roughly purified side-products showed the loss of pendant benzoyl groups, which is identified from the loss of benzoyl carbonyl peaks around 193 ppm in ^{13}C NMR spectrum.

The physical properties of the polymers are summarized in Table 1. Thermal analysis shows that the polymers have high thermal stability. TGA showed 5 wt% weight loss temperatures at 534 °C for CN–PBPO-*p* and at 473 °C for CN–PBPO-*m* in nitrogen. The T_g's of CN–PBPO-*p* and CN–PBPO-*m* measured by DSC were 241 and 200 °C, respectively, and both polymers showed no melting transition until 400 °C (Fig. 4). It seems that introduction of nitrile groups effectively disturbs the highly crystalline characteristics of the parent PBPO. CF$_3$–PBPO has also high thermal stability (T_{d5} at 514 °C in nitrogen) but it's T_g (201 °C) is less than that of commercially available PPO™ (T_g = 210 °C) [8]. CN–PBPO-*p* shows improved physical



Scheme 4. Model reaction for benzoyl substituted nitro-displacement reaction.

Table 1
Properties of substituted PBPOs

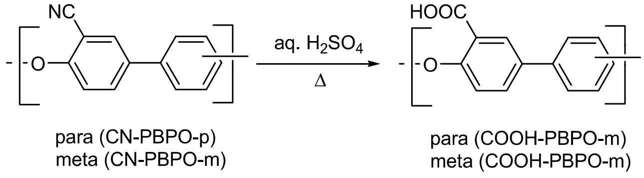
Polymers	Linkage	η_{inh}[a] (dL/g)	T_g[b] (°C)	$T_{d5,N2}$[c] (°C)	$T_{d5,Air}$[d] (°C)	Residue (wt%)[e]
CN–PBPO-*p*	Para	0.93	241	534	537	75
CN–PBPO-*m*	Meta	0.45	200	473	418	68
CF_3-PBPO-*p*[f]	Para	0.77	201	514	466	–
CF_3-PBPO-*m*[f]	Meta	0.62	148	476	421	–

[a] Intrinsic viscosity, measured with a concentration of 0.5 g/dL in NMP at 30 °C.
[b] Measured by second scan of DSC with a heating rate of 20 °C/min in nitrogen.
[c] Five percent of weight loss temperature measured by TGA with a heating rate of 20 °C/min in nitrogen.
[d] Five percent weight loss temperature measured by TGA with a heating rate of 20 °C/min in air.
[e] Weight residue measured by TGA with a heating rate of 20 °C/min at 800 °C in nitrogen.
[f] See Ref. [9].

properties over both PPO™ and CF_3-PBPO. The high T_g of CN–PBPO-*p* may result from both the more rigid biphenylene linkages of PBPO and the relatively small size of nitrile substituents. Lower thermal stability and T_g of CN–PBPO-*m* may be caused by the decreased chain rigidity due to the meta-linked polymer structure.

The solubility behaviors of the substituted PBPOs are characterized. The polymers were quite soluble in aprotic polar solvents such as NMP and DMAc but CN–PBPO-*p* was only soluble in DMSO on heating and partially soluble in DMF at room temperature. Both polymers were not soluble in chlorinated solvents like 1,2-dichlorobenzene and chloroform, where usual poly(arylene ether)s such as poly(ether sulfone)s are highly soluble. These solubility characteristics of the substituted PBPOs may also originate from the introduction of highly polar nitrile group. For comparison, poly(biphenylene oxide)s containing trifluoromethyl groups were highly soluble in chloroform and tetrahydrofuran [8].

The pendent nitrile groups of CN–PBPO-*p* and CN–PBPO-*m* can be hydrolyzed in aqueous acidic condition, resulting in PBPO with carboxylic acid groups as shown in Scheme 5. Hydrolysis by 5 wt% sulfuric acid at 140 °C produced polymers insoluble in any organic solvents. The nitrile stretching band at 2230 cm^{-1} was completely disappeared and the absorption band of carboxylic acid near 1660 cm^{-1} was newly appeared in FT-IR spectra of the resulting polymers, which supports the full conversion of nitrile groups to carboxylic acid groups as shown in Fig. 1. PBPO with carboxylic acids showed no glass transition or melting transition up to 400 °C in DSC.



Scheme 5. Hydrolysis of CN–PBPOs into COOH–PBPOs.

4. Conclusions

A series of properly designed AB type monomers containing hydroxyl and nitro leaving groups activated by nitrile and benzoyl groups were synthesized and polymerized to substituted poly(biphenylene oxide)s (PBPOs) via nitro displacement reaction. While the benzoyl groups were not suitable for the synthesis of high molecular weight polymers, PBPOs with nitrile groups were effectively synthesized in NMP at 140 °C. The polymers are amorphous, soluble in polar aprotic solvents, and formed tough and flexible films on casting. Para-linked PBPO with nitrile groups was highly thermally stable. The polymer showed a 5 wt% loss temperature at 534 °C and a T_g at 241 °C, which is higher than that of PPO™. The nitrile groups of PBPOs are easily transformed to carboxylic acid groups by acidic hydrolysis.

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