Synthesis of Aromatic Polyethers by Scholl Reaction. VI.[†] Aromatic Polyethers by Cation–Radical Polymerization of 4,4′-, 3,3′-, and 2,2′-Bis(1-naphthoxy)biphenyls and of 1,3-Bis(1-naphthoxy)benzene[‡]

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ABSTRACT: This paper reports the development of a novel method for the synthesis of fully aromatic polyethers. It consists of the cation–radical polymerization of bis(1-naphthoxy)aryls. The particular examples described in this paper refer to the polymerization of 4,4′-bis(1-naphthoxy)biphenyl (**12**), 2,2′-bis(1-naphthoxy)-biphenyl (**13**), 3,3′-bis(1-naphthoxy)biphenyl (**19**), and 1,3-bis(1-naphthoxy)benzene (**24**). All polymerizations were performed in nitrobenzene with $FeCl_3$ as oxidant. Aromatic polyethers with number average molecular weights up to 90 500 g/mol were obtained.

Introduction

Aromatic polyethers contain most frequently ketones, sulfones, imides, and other electron-withdrawing groups since they are required to activate the leaving groups used in aromatic nucleophilic substitution polymerization reactions[1–9] or are generated during aromatic sulfonylation and aroylation polymerization reactions.[3–7]

The most notable exception from this class of polyethers is provided by poly(2,6-disubstituted-1,4-phenylene oxide)s which are synthesized either by the oxidative polymerization of 2,6-disubstituted-phenols[9] or by the single electron transfer catalyzed polymerization of 4-bromo-2,6-disubstituted-phenol.[10] The only other synthetic method which seems to be applicable to the synthesis of fully aromatic polyethers is the Ullmann reaction.[11]

Recently, two novel synthetic procedures were applied to the synthesis of aromatic poly(ether ketone)s and poly(ether sulfone)s. Both polymerization reactions involve the formation of a carbon–carbon bond during the polymerization process. One of them refers to the Ni(0)-catalyzed homocoupling of various aromatic dihalides containing sulfone[12] or ketone[13] groups. The other refers to the cation–radical polymerization of various bis(aryloxy) derivatives (Scholl reaction) which was used to synthesize both poly(ether sulfone)s and poly(ether ketone)s.[14]

The goal of this paper is to report on the development of a novel and general synthetic method for the preparation of fully aromatic polyethers based on the cation–radical polymerization of bis(aryloxy)aryl derivatives. The particular examples used to demonstrate this polymerization reaction refer to the synthesis and polymerization of 4,4′-bis(1-naphthoxy)biphenyl (**12**), 2,2′-bis(1-naphthoxy)biphenyl (**13**), 3,3′-bis(1-naphthoxy)biphenyl (**19**), and 1,3-bis(1-naphthoxy)benzene (**24**).

Experimental Section

Materials. 1-Bromonaphthalene (98%), 1-chloro-2-nitrobenzene (99%), 1-chloro-4-nitrobenzene (99%), 2,4-dichloronitrobenzene (97%), 2,2′-dipyridyl (99+%), ferric chloride (anhydrous, >98%), iron powder (99.9+%), nickel chloride (99%), resorcinol (99%), tetraethylammonium iodide (98%), triphenylphosphine (99%) (all from Aldrich), anhydrous potassium carbonate, cuprous chloride (96.1%), sodium methoxide (all from Fisher), hypophosphorous acid (50% solution in water, Fluka), and 1-naphthol (99%, Lancaster Synthesis) were used as received. Benzene, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP), nitrobenzene, and toluene were distilled from CaH_2. Benzonitrile was distilled from P_2O_5. Pyridine was distilled from NaOH pellets. Tetrahydrofuran (THF) was distilled from $LiAlH_4$. $Ni(PPh_3)_2Cl_2$ was prepared according to a literature procedure.[15]

Techniques. ^1H NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as internal standard. Gel permeation chromatography (GPC) measurements were performed on a Perkin-Elmer series 10 LC instrument equipped with an LC-100 column oven, an LC 600 autosampler, and a Nelson Analytical 900 series data station. The measurements were made with use of a UV detector set at 254 nm, chloroform as solvent (1 mL/min, 40 °C), a set of PL-gel columns (500 and 10^4 Å), and a calibration plot constructed with polystyrene standards (Supelco). Purity was similarly determined by high-performance liquid chromatography (HPLC) using a 100 Å PL-gel column. A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, was used to determine the glass transition temperatures of the polymers at a heating rate of 20 °C/min. The glass transition temperatures were read at the middle of the change in the heat capacity of the second DSC heating scan.

Synthesis of Monomers. The synthesis of monomers is outlined in Schemes I–IV.

1-(4-Nitrophenoxy)naphthalene (4). 1-Naphthol (6.98 g, 48.4 mmol), anhydrous K_2CO_3 (8.05 g, 58.3 mmol), dry DMSO (100 mL), and dry toluene (100 mL) were placed into a 500-mL three-neck round-bottom flask equipped with nitrogen inlet, Dean–Stark trap, and condenser, and the reaction mixture was heated at 160 °C. After no more water was collected, toluene was distilled off. The reaction mixture was allowed to cool to room temperature, 6.97 g (44.3 mmol) of 1-chloro-4-nitrobenzene was added, and the reaction was stirred at 160 °C for 12 h. The cooled reaction mixture was poured into 1 L of water and extracted three times with dichloromethane. The dichloromethane layer was washed twice with 5% aqueous NaOH and three times with water. The solution was dried over anhydrous $MgSO_4$, and the solvent was removed on a rotary evaporator. The resulting brown crystals were recrystallized from a mixture of ethanol and benzene to produce 9.07 g (77.3%) of brown crystals. Mp: 139–140 °C (lit.[16] mp 141–142 °C, lit.[17] mp 144–146 °C). ^1H NMR ($CDCl_3$, δ, ppm): 7.05 (d, 2 H, Ph-*H* meta to NO_2), 7.21 (d, 1 H, 2-*H* of the naphthalene unit), 7.42–7.73 (m, 3 H, 3-*H*, 6-*H*, and 7-*H* of the naphthalene unit), 7.83 (d, 1 H,

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[‡] Dedicated to Professor Robert Simha in honor of his 80th birthday.

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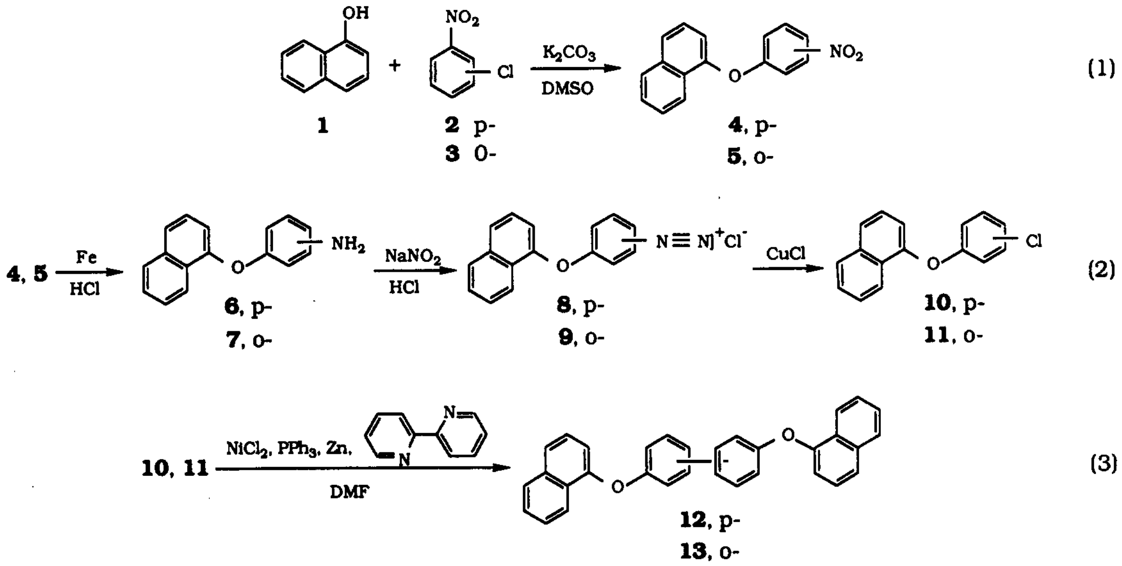
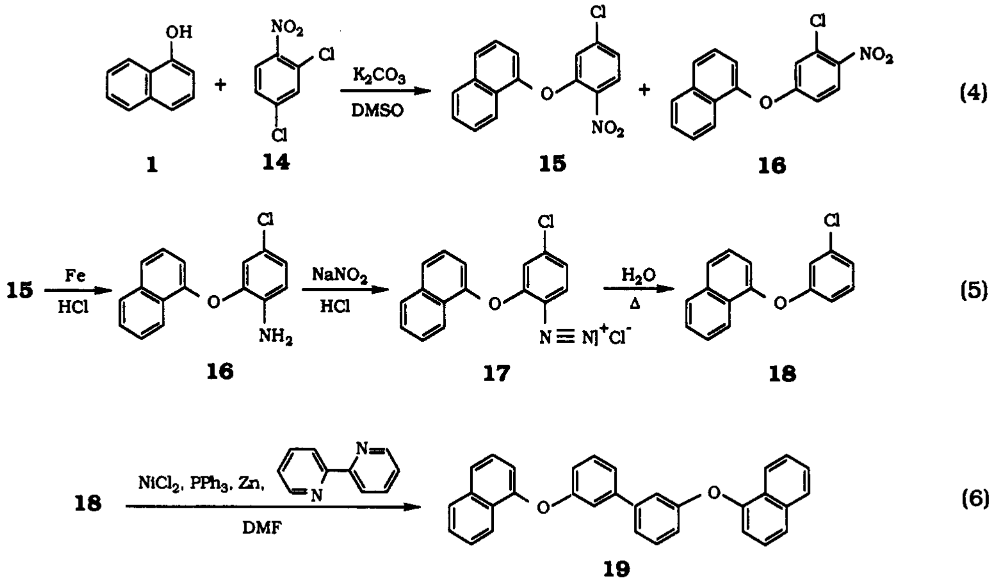
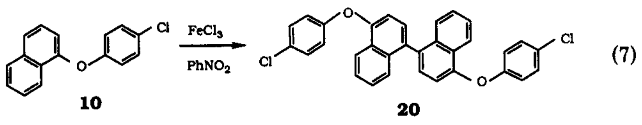
Scheme I



Scheme II



Scheme III



4-*H* of the naphthalene unit), 7.96 (d, 2 H, 5- and 8-*H* of the naphthalene unit), 8.23 (d, 2 H, Ph-*H* ortho to NO_2).

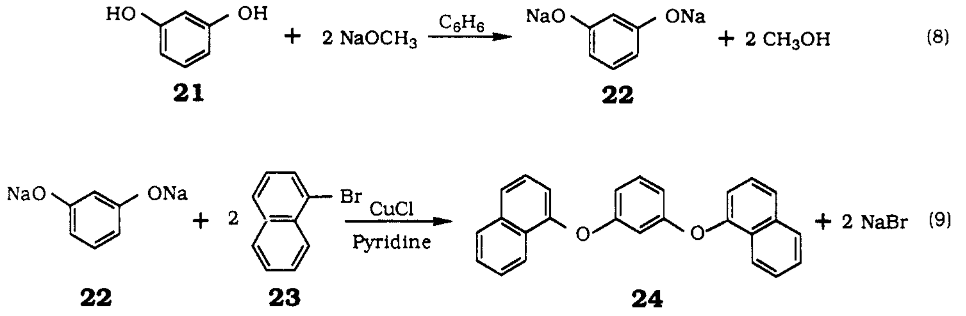
1-(2-Nitrophenoxy)naphthalene (5). 1-(2-Nitrophenoxy)-naphthalene was synthesized by the etherification of 1-chloro-2-nitrobenzene with 1-naphthol by following the same procedure used for the synthesis of 1-(4-nitrophenoxy)naphthalene. The resulting crude oily product was subjected to purification by column chromatography (silica gel, benzene/*n*-hexane 1/2, v/v). The yellow band was collected, and the solvent was removed on a rotary evaporator to produce 1-(2-nitrophenoxy)naphthalene as an orange oil in 84.3% yield. 5 was reported previously, however no information about its synthesis and characterization was presented.[18] ^1H NMR ($CDCl_3$, δ, ppm): 6.87 (dd, 1 H, 6-*H* of the phenylene unit), 7.01 (d, 1 H, 2-*H* of the naphthalene unit), 7.15 (td, 1 H, 4-*H* of the phenylene unit), 7.33–7.63 (m, 4 H, 5-*H* of the phenylene unit, 3-*H*, 6-*H*, and 7-*H* of the naphthalene unit), 7.69 (d, 1 H, 4-*H* of the phenylene unit), 7.84–7.93 (m, 1 H, 5-*H* of the naphthalene unit), 8.00 (dd, 1 H, 3-*H* of the phenylene unit), 8.08–8.20 (m, 1 H, 8-*H* of the naphthalene unit).

1-(2-Nitro-5-chlorophenoxy)naphthalene (15). 1-(2-Nitro-5-chlorophenoxy)naphthalene was synthesized by the etherification of 1-nitro-2,4-dichlorobenzene with 1-naphthol following the synthesis of 1-(4-nitrophenoxy)naphthalene.

1-Naphthol (10.45 g, 72.5 mmol), anhydrous K_2CO_3 (12.05 g, 87.2 mmol), and 1-nitro-2-dichlorobenzene (15.31 g, 79.7 mmol) were reacted at 160 °C for 2 h. The crude oily product was purified by column chromatography (silica gel, benzene/*n*-hexane 1/2, v/v). The yellow band was collected, and the solvent was removed to give 14.59 g (61.1%) of 1-(2-nitro-5-chlorophenoxy)naphthalene (orange oil). ^1H NMR ($CDCl_3$, δ, ppm): 6.84 (br s, 1 H, Ph-*H* ortho to O), 7.07–7.20 (m, 2 H, Ph-*H* para to O and 2-*H* of the naphthalene unit), 7.42–7.67 (m, 3 H, 3-*H*, 6-*H*, and 7-*H* of the naphthalene unit), 7.74–8.17 (m, 4 H, Ph-*H* meta to O and 4-*H*, 5-*H* and 8-*H* of the naphthalene unit).

From the second fraction, 1.60 g (7.3%) of 1-(3-chloro-4-nitrophenoxy)naphthalene was obtained as yellow crystals. Mp: 133–136 °C. ^1H NMR ($CDCl_3$, δ, ppm): 6.60 (m, 1 H, Ph-*H* ortho to Cl), 7.01 (d, 1 H, 2-*H* of the naphthalene unit), 7.34–7.65 (m, 4 H, Ph-*H* para to Cl) and 3-*H*, 6-*H*, and 7-*H* of the naphthalene unit), 7.73 (d, 1 H, 4-*H* of the naphthalene unit), 7.81–8.00 (m, 1 H, 5-*H* of the naphthalene unit), 8.23 (m, 2 H, Ph-*H* ortho to NO_2 and 8-*H* of the naphthalene unit). The structure of these two fractions is in agreement with those obtained by the etherification of 1-nitro-2,4-dichlorobenzene with trifluoroethanol.[19]

Scheme IV



1-(4-Aminophenoxy)naphthalene (6). In a 100-mL round-bottom flask equipped with condenser, 1-(4-nitrophenoxy)naphthalene (3.87 g, 14.6 mmol) was dissolved in 15 mL of benzene and 8 mL of water, and Fe powder (5.02 g, 90.0 mmol) was added. To the vigorously stirred mixture was added slowly 6 mL of concentrated aqueous HCl from the top of the condenser. The reaction mixture was heated to reflux temperature (the bath temperature was about 100 °C) and stirred for 20 h. The reaction mixture was cooled to room temperature and 40 mL of 25% NaOH aqueous solution was added. Benzene (20 mL) was added and the reaction mixture was stirred vigorously for 1 h. The mixture was filtered through Celite and Fe powder was washed with hot benzene. The filtrate was transferred into a separatory funnel and the benzene layer was separated and dried over anhydrous $MgSO_4$, and the solvent was removed on a rotary evaporator. The oily red residue was slowly poured into a vigorously stirred 10% HCl aqueous solution (125 mL) to form the corresponding hydrochloride. The red solid was collected and washed with a small amount of chloroform. The hydrochloride was treated with 100 mL of 10% NaOH aqueous solution and stirred to liberate the free amine. Benzene (50 mL) was added to extract the amine and was stirred until all the hydrochloride was dissolved. The benzene layer was separated and dried over anhydrous $MgSO_4$. The solvent was removed on a rotavapor to yield a red viscous oil which crystallized on standing overnight. The yield was 2.41 g (70.3%). Mp: 53–55 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.43 (s, 2 H, N*H*$_2$), 6.65 (d, 2 H, Ph-*H* ortho to NH_2), 6.76 (d, 1 H, 2-*H* of the naphthalene unit), 6.91 (d, 2 H, Ph-*H* meta to NH_2), 7.24–7.61 (m, 4 H, 3-, 4-, 6-, and 7-*H* of the naphthalene unit), 7.79–7.99 (m, 1 H, 5-*H* of the naphthalene unit), 8.29–8.42 (m, 1 H, 8-*H* of the naphthalene unit).

1-(2-Aminophenoxy)naphthalene (7). 1-(2-Aminophenoxy)naphthalene was synthesized by the reduction of 1-(2-nitrophenoxy)naphthalene by using the same procedure with that described for the synthesis of 1-(4-aminophenoxy)naphthalene. 1-(2-Aminophenoxy)naphthalene was obtained as a red oil in 95.7% yield. ^{1}H NMR ($CDCl_3$, δ, TMS): 3.82 (br peak, 2 H, N*H*$_2$), 6.67–7.09 (m, 5 H, Ph-*H* and 2-*H* of the naphthalene unit), 7.38 (d, 1 H, 4-*H* of the naphthalene unit), 7.48–7.63 (m, 3 H, 3-, 6-, and 7-*H* of the naphthalene unit), 7.83–7.92 (m, 1 H, 5-*H* of the naphthalene unit), 8.30–8.41 (m, 1 H, 8-*H* of the naphthalene unit).

1-(2-Amino-5-chlorophenoxy)naphthalene (16). 1-(2-Amino-5-chlorophenoxy)naphthalene was synthesized by the reduction of 1-(2-nitro-5-chlorophenoxy)naphthalene by using the same procedure described for the synthesis of 1-(4-aminophenoxy)naphthalene. 1-(2-Amino-5-chlorophenoxy)naphthalene was obtained as a deep red oil in 98.1% yield. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.31 (br s, 2 H, N*H*$_2$), 6.75–7.12 (m, 4 H, Ph-*H* of the phenylene ring and 2-*H* of the naphthalene unit), 7.34–7.75 (m, 4 H, 3-, 4-, 6-, and 7-*H* of the naphthalene unit), 7.86–8.00 (m, 1 H, 5-*H* of the naphthalene unit), 8.21–8.39 (m, 1 H, 8-*H* of the naphthalene unit).

1-(4-Chlorophenoxy)naphthalene (10). In a 50-mL round-bottom flask was placed 1-(4-aminophenoxy)naphthalene (2.79 g, 11.9 mmol), and the contents was heated at about 80 °C. To the melted amine, was added 10 mL of 20% HCl aqueous solution and vigorously stirred to form the hydrochloride, which was cooled in an ice/water bath. Sodium nitrite (0.821 g, 11.9 mL) was dissolved in 10 mL of water and kept in a refrigerator. The cold sodium nitrite solution was added in portions to the stirred suspension of the hydrochloride while the temperature of the reaction mixture was kept below 5 °C. As the sodium nitrite solution was added, the hydrochloride dissolved to form a red solution. The solution of the diazonium salt was added in portions to a cuprous chloride solution (CuCl, 1.344 g, 13.6 mmol in 10 mL concentrated aqueous HCl) which had been prepared and maintained in a refrigerator before use. The reaction mixture became very thick, demonstrating the formation of the complex of CuCl with the diazonium salt. After the magnetic stirring became impossible, the mixture was stirred by a glass rod occasionally. The reaction mixture was allowed to warm up to room temperature without any external heating and then heated at 60 °C for 2 h with occasional stirring. The reaction mixture gradually evolved nitrogen and became thinner. Then it was allowed to cool to room temperature and was extracted four times with diethyl ether. The extract was washed twice with 10% NaOH aqueous solution, twice with water, with 10 mL of 2 N H_2SO_4, and finally again twice with water. The extract was dried over anhydrous $MgSO_4$, and the solvent was removed on a rotavapor. The brown oily residue was dissolved in a small amount of *n*-hexane and subjected to column chromatography (silica gel, *n*-hexane). 1-(4-Chlorophenoxy)naphthalene was obtained as a colorless oil (1.76 g, 58.3%). Bp: 130–135 °C (0.05 mmHg) (lit.[16] bp 148–148 °C (0.1 mmHg)). Purity (HPLC): >99.9%. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.95 (d, 3 H, Ph-*H* meta to Cl and 2-*H* of the naphthalene unit), 7.24–7.76 (m, 6 H, Ph-*H* ortho to Cl, 3-, 4-, 6-, and 7-*H* of the naphthalene unit, a doublet due to Ph-*H* ortho to Cl was observed at 7.27), 7.83–7.95 (m, 1 H, 5-*H* of the naphthalene unit), 8.11–8.24 (m, 1 H, 8-*H* of the naphthalene unit).

1-(2-Chlorophenoxy)naphthalene (11). 1-(2-Chlorophenoxy)naphthalene was synthesized by the same procedure as described for the synthesis of 1-(4-chlorophenoxy)naphthalene. 1-(2-Chlorophenoxy)naphthalene was obtained as a colorless oil. Even after it was distilled twice under vacuum, its purity was 72.7%. Yield: 42.6%. Bp: 138–140 °C (0.075 mmHg) (lit.[20] bp 135–140 °C (0.1 mmHg)). ^{1}H NMR ($CDCl_3$, δ, ppm): 6.82 (d, 1 H, 2-*H* of the naphthalene unit), 6.95 (d, 1 H, Ph-*H* ortho to O), 7.04–7.69 (m, 7 H, Ph-*H* meta and para to O and 3-, 4-, 6-, and 7-*H* of the naphthalene unit), 7.82–7.93 (m, 1 H, 5-*H* of the naphthalene unit), 8.19–8.32 (m, 1 H, 8-*H* of the naphthalene unit).

1-(3-Chlorophenoxy)naphthalene (18). The diazonium salt of 1-(3-aminophenoxy)naphthalene was prepared from 1-(2-amino-5-chlorophenoxy)naphthalene (10.11 g, 37.5 mmol) and sodium nitrite (2.60 g, 37.68 mmol) by using the same procedure as that described for the synthesis of 1-(4-chlorophenoxy)naphthalene. The solution of the diazonium salt was poured into 40 mL of hypophosphorus acid which was cooled in a refrigerator before use. The reaction mixture was kept in an ice/water bath with occasional stirring and allowed to warm up to room temperature overnight. Then it was extracted twice with diethyl ether, and the extract was dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator to yield a brown oil. The crude product was subjected to purification by column chromatography (silica gel, *n*-hexane). 1-(3-Chlorophenoxy)naphthalene was obtained as a colorless oil. Yield: 3.57 g (37.4%). Purity (HPLC): 83.9%. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.91 (d, 1 H, 2-*H* of the naphthalene unit), 6.99–7.13 (m, 3 H, Ph-*H* ortho and para to Cl), 7.25 (t, 1 H, Ph-*H* meta to Cl), 7.37–7.61 (m, 3

H, 3-, 6-, and 7-*H* of the naphthalene unit), 7.68 (d, 1 H, 4-*H* of the naphthalene unit), 7.86–7.97 (m, 1 H, 5-*H* of the naphthalene unit), 8.09–8.18 (m, 1 H, 8-*H* of the naphthalene unit).

4,4′-Bis(1-naphthoxy)biphenyl (12). A 50-mL three-neck round-bottom flask equipped with a condenser containing a nitrogen inlet/outlet and a septum was charged with $NiCl_2$ (0.040 g, 0.31 mmol), PPh_3 (0.510 g, 1.94 mmol), Zn powder (0.534 g, 8.166 mmol), and 2,2′-dipyridyl (0.042 g, 0.272 mmol).[21] The flask was evacuated under vacuum for 1 h and then was filled with nitrogen. The evacuation under vacuum and filling with nitrogen was repeated three times. Dry DMF (4 mL) was added via a syringe through the septum of the condenser and the reaction mixture was heated at 65–70 °C with stirring for 15 min. The color changed gradually to red brown in about 5 min. Then a solution of 1-(4-chlorophenoxy)naphthalene (1.27 g, 4.98 mmol) in 3 mL of dry DMF was added to the resulting catalyst via a syringe. The reaction mixture was heated at 65–70 °C with stirring. In about 20 min, the reaction mixture became very thick demonstrating the formation of the coupling product. After 1.5 h, the reaction mixture was allowed to cool to room temperature and then was filtered under vacuum. The mixture of Zn powder and crude product was washed with a small amount of DMF and then was recrystallized from benzene. 4,4′-Bis(1-naphthoxy)biphenyl was obtained as colorless needles. The yield was 1.47 g (66.8%). Purity (HPLC): >99.9%. MP: 206–207 °C. ^1H NMR ($CDCl_3$, δ, ppm): 7.02 (d, 2 H, 2-*H* of the naphthalene unit), 7.10 (d, 4 H, Ph-*H* ortho to O), 7.37–7.67 (m, 12 H, Ph-*H* meta to O and 3-, 4-, 6-, and 7-*H* of the naphthalene unit, a doublet at 7.52 can be assigned to Ph-*H* meta to O), 7.81–7.96 (m, 2 H, 5-*H* of the naphthalene unit), 8.19–8.34 (m, 2 H, 8-*H* of the naphthalene unit).

2,2′-Bis(1-naphthoxy)biphenyl (13). 2,2′-Bis(1-naphthoxy)biphenyl was synthesized by the coupling reaction of 1-(2-chlorophenoxy)naphthalene using a procedure similar to that described for the synthesis of 4,4′-bis(1-naphthoxy)biphenyl. The catalyst was prepared by the same procedure and the coupling reaction was continued for 20 h. The reaction mixture was allowed to cool to room temperature and filtered under vacuum to remove Zn powder. The filtrate was poured into 300 mL of water and extracted three times with benzene. The extract was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed on a rotavapor, and the residue was subjected to purification by column chromatography (silica gel, *n*-hexane). The first fraction yielded white crystals of 1-phenoxynaphthalene (43.4% yield, mp 54–56 °C, lit.[16] mp 55 °C), which was probably produced by reductive elimination of the chlorine from 1-(2-chlorophenoxy)naphthalene. The second fraction collected contained PPh_3. 2,2′-Bis(1-naphthoxy)biphenyl was obtained as white crystals from the third fraction. After recrystallization from a mixture of *n*-hexane and chloroform, the yield was 52.1%. Mp: 147–148 °C. Purity (HPLC): 96.2%. ^1H NMR ($CDCl_3$, δ, ppm): 6.78 (d, 2 H, 2-*H* of the naphthalene unit), 6.85 (d, 2 H, 3-*H* of the biphenylene group), 7.07–7.67 (m, 14 H, 3-, 4-, 6-, and 7-*H* of the naphthalene unit and 4-, 5-, and 6-*H* of the biphenylene group), 7.81 (d, 2 H, 5-*H* of the naphthalene unit), 8.16 (d, 2 H, 8-*H* of the naphthalene unit).

3,3′-Bis(1-naphthoxy)biphenyl (19). 3,3′-Bis(1-naphthoxy)biphenyl was synthesized by homocoupling of 1-(3-chlorophenoxy)naphthalene by the same procedure as that described for the synthesis of 2,2′-bis(1-naphthoxy)biphenyl. The crude product was subjected to purification by column chromatography (silica gel, *n*-hexane). The first fraction produced 3.1% of 1-phenoxynaphthalene, the second fraction PPh_3, while 3,3′-bis(1-naphthoxy)biphenyl was separated as a colorless viscous solid from the third fraction. It was purified by column chromatography (silica gel, *n*-hexane). The yield was 59.2%. T_g: 20 °C. Purity (HPLC): 96.4%. ^1H NMR ($CDCl_3$, δ, ppm): 6.99 (d, 4 H, 2-*H* of the naphthalene unit and 4-*H* of the biphenylene group), 7.24–7.70 (m, 14 H, 3-, 4-, 6-, and 7-*H* of the naphthalene unit and 2-, 5-, and 6-*H* of the biphenylene unit), 7.85–7.94 (m, 2 H, 5-*H* of the naphthalene unit), 8.18–8.27 (m, 2 H, 8-*H* of the naphthalene unit).

4,4′-Bis(4-chlorophenoxy)-1,1′-binaphthyl (20). A 100-mL three-neck round-bottom flask equipped with dropping funnel was charged with 1-(4-chlorophenoxy)naphthalene (1.28 g, 5.02 mmol). The flask was evacuated under and filled with nitrogen. Dry nitrobenzene (10 mL) was added, and a solution of $FeCl_3$ (0.987 g, 6.09 mmol) in 20 mL of nitrobenzene was added dropwise in the course of 30 min under stirring. The reaction was continued at room temperature for 2.5 h under nitrogen. The reaction mixture was poured into 350 mL of methanol and the resulting white precipitate was collected by filtration. The white solid was washed with methanol and recrystallized from a mixture of methanol and chloroform to yield 0.933 g (73.3%) of colorless needles. Mp: 210–211 °C. Purity (HPLC): >99.9%. ^1H NMR ($CDCl_3$, δ, ppm): 7.03 (d, 2 H, 2-*H* of the naphthalene unit), 7.09 (d, 4 H, Ph-*H* meta to Cl), 7.32–7.54 (m, 12 H, Ph-*H* ortho to O and 3-, 6-, 7-, and 8-*H* of the naphthalene unit), 8.29 (br d, 2 H, 5-*H* of the naphthalene unit).

1,3-Bis(1-naphthoxy)benzene (24). 1,3-Bis(1-naphthoxy)benzene was synthesized by the Ullmann reaction of 1-bromonaphthalene with the disodium salt of resorcinol following literature reaction conditions.[22]

In a 250-mL single-neck round-bottom flask, sodium methoxide (5.3 g, 0.10 mol) was suspended in 100 mL of dry benzene by stirring under argon atmosphere. Resorcinol (5.5 g, 0.05 mmol) was subsequently added, and benzene and the resulting methanol were removed by distillation. Dry pyridine (100 mL) was added to the cooled disodium resorcinate powder, and when the reaction reached the reflux temperature, 1-bromonaphthalene (41.7 g, 0.20 mol) and cuprous chloride (1.5 g, 0.015 mol) were added. The reaction was continued for 16 h at reflux temperature (115 °C).

The Ullmann reaction was followed by taking aliquots of 0.2 mL from the raction mixture. The sample was added to 1.5 mL of water, acidified with 5 N aqueous HCl, and extracted with 1.5 mL of chloroform, and the chloroform layer was separated and dried with anhydrous $MgSO_4$. The chloroform solution was analyzed by HPLC. No unreacted resorcinol was observed after 16 h of reaction. The resulting product represents a mixture containing 94% 1,3-bis(1-naphthoxy)benzene, 6% 3-(1-naphthoxy)phenol, and the excess of unreacted 1-bromonaphthalene.

The cooled reaction mixture was poured into 600 mL of water and was acidifed with 5 N aqueous HCl. The aqueous layer was extracted with four portions of chloroform (200 mL). The chloroform phase was separated and dried with anhydrous $MgSO_4$. Chloroform was removed on a rotary evaporator yielding a yellow-brown oil, which was distilled under vacuum (140 °C (~1 mmHg)) to remove 1-bromonaphthalene. The resulting residue was dissolved in chloroform and washed with three portions of a solution of 2 N aqueous NaOH. The chloroform layer was then dried and anhydrous $MgSO_4$, and evaporated on a rotary evaporator. The residue was recrystallized from a mixture of ethanol and chloroform to yield white crystals. The conversion was 100% based on resorcinol. The isolated yield of 1,3-bis(1-naphthoxy)benzene was 54%. Purity (HPLC): 99.8%. Mp: 105–106 °C. ^1H NMR ($CDCl_3$, δ, ppm): 6.73 (s, 1 H, 2-*H* of the phenylene unit), 6.79 (d, 2 H, 4-*H* and 6-*H* of the phenylene unit), 7.03 (d, 2 H, 2-*H* of the naphthalene unit), 7.25 (t, 5-H of the phenylene unit), 7.34–7.64 (m, 6 H, 2-, 4-, and 6-*H* of the naphthalene unit), 7.86 (m, 2 H, 5-*H* of the naphthalene unit), 8.16 (m, 2 H, 8-*H* of the naphthalene unit).

Cation–Radical Polymerizations. The polymerization reactions were performed in dry nitrobenzene under nitrogen using $FeCl_3$ as oxidant. A few polymerization experiments were done in dry benzonitrile. The polymerization conditions are summarized in Table I. A typical polymerization example is provided below. 2,2′-Bis(1-naphthoxy)biphenyl (0.224 g, 0.51 mmol) was dissolved in 0.5 mL of dry nitrobenzene in a 25-mL round-bottom flask equipped with a nitrogen inlet/outlet. To the magnetically stirred solution of monomer, a solution of $FeCl_3$ (0.203 g, 1.25 mmol) in 1.0 mL of dry nitrobenzene was added dropwise during 20 min via a syringe with the needle penetrating through a rubber septum. The reaction mixture was stirred at room temperature for 5 h. The content was precipitated into 150 mL of methanol acidified with 2% hydrochloric acid. The precipitate was filtered, washed with methanol, and dried under vacuum. The yield was 0.204 g (92%). $\bar{M}_n$ = 13 900 g/mol, $\bar{M}_w/\bar{M}_n$ = 5.3. The polymer was dissolved in 5 mL of $CHCl_3$ and precipitated into 150 mL of acetone acidifed with 2% HCl. The precipitate was filtered, washed with acetone, and dried in vacuum. The yield of the acetone-insoluble fraction was 0.130 g (64%). $\bar{M}_n$ (GPC) = 30 300

Table I
Polymerization of 4,4′-Bis(1-naphthoxyl)biphenyl (12), 2,2′-Bis(1-naphthoxy)biphenyl (13), 3,3′-Bis(1-naphthoxy)biphenyl (19), and 1,3-Bis(1-naphthoxy)benzene (24)

	monomer solution		$FeCl_3$ solution							
exp no.	monomer (mmol)	$PhNO_2$, mL	$FeCl_3$, mmol	$PhNO_2$, mL	reaction temperature, °C	reaction time, h	polymer yield, %	$\bar{M}_n$, g/mol	$\bar{M}_w/\bar{M}_n$	T_g, °C
1	**12** (1.0)	4.0	2.0	1.25	115	5.0	58	4900	5.8	235
2	**12** (0.5)	4.0	1.2	1.2	95	0.5	*a*			
3	**12** (0.5)	4.0	1.2	2.4	80	0.5	*a*			
4	**12** (1.0)	4.0	4.0	2.5	115	5.0	*a*			
5	**12** (0.5)	6.0[b]	1.2	1.2[b]	90	24.0	0			
6	**13** (0.5)	3.0	1.2	1.2	25	5.0	85	7000	2.1	223
7	**13** (0.5)	3.0	1.2	1.2	25	24.0	86	7300	3.0	
8	**13** (0.5)	1.0	1.2	1.2	25	5.0	97	7300	3.1	222
9	**13** (0.5)	0.5	1.2	1.0	25	5.0	92	13900	5.3	235
10	**13** (0.5)	1.0	1.8	1.2	25	5.0	99	85100[c]	2.2	236
11	**13** (0.5)	1.0	2.4	1.2	25	0.5	99	90500[d]	2.4	234
12	**13** (0.5)	1.0[b]	1.2	1.2[b]	25	5.0	0			
13	**19** (0.5)	3.0	1.2	1.2	25	5.0		12600	3.7	210
14	**19** (0.5)	3.0	1.2	1.2	25	24.0		13300	3.3	
15	**19** (0.5)	1.0	1.2	1.2	25	5.0	93	8600	2.4	198
16	**19** (0.7)	1.4	2.5	1.2	25	5.0	87	34000	3.2	215
17	**24** (0.5)	0.6	1.2	0.6	25	0.5	67	4200	3.6	
18	**24** (0.5)	0.5	1.2	0.6	25	4.5	86	5200	4.7	185
19	**24** (0.5	0.6	1.2	0.8	25	12.0	87	5400	2.0	
20	**24** (0.5)	0.4	1.6	1.6	0.6	25	5.0	93[a]		
21	**24** (0.5)	0.4	1.9	0.8	25	5.0	96[a]			
22	**24** (0.5)	0.4	1.2+0.4[e]	0.8	25	6.0	82	22400[f]	2.3	218
23	**24** (0.7)	0.5	1.7+0.3[e]	1.0	25	3.0	83	13800[g]	2.5	213
24	**24** (0.3)	0.5	0.6+0.2[h]	0.3	25	6.5		14800[i]	4.4	217

[a] Insoluble polymer was obtained. [b] Benzonitrile was the polymerization solvent in this case. [c] Two other minor peaks were observed on the GPC chromatogram. The first peak, $\bar{M}_n$ = 361 3000 g/mol; $\bar{M}_w/\bar{M}_n$ = 1.19 (5.4% of the total area). The second peak, $\bar{M}_n$ = 2900 g/mol; $\bar{M}_w/\bar{M}_n$ = 1.12 (15.6% of total area). [d] One additional minor peak was recorded on the GPC chromatogram: $\bar{M}_n$ = 3100 g/mol; $\bar{M}_w/\bar{M}_n$ = 1.4 (19.6%) of total area. [e] In experiments 22 and 23, 1.2 and 1.7 mmol of $FeCl_3$ were respectively, added at the beginning of the polymerizations. After 1 h of polymerization, additional 0.4 and 0.3 mmol of $FeCl_3$ wee added respectively. [f] This is the main peak on GPC. Another minor peak (12.6% of total area) with $\bar{M}_n$ = 815 900 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.31 was also recorded on the GPC chromatogram. [g] Another high molecular weight fraction (5% of total area) with $\bar{M}_n$ = 2 770 800 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.52 was observed on the GPC chromatogram. [h] $FeCl_3$ (0.6 mmol) was added at the beginning of the polymerization; an additional 0.2 mmol $FeCl_3$ was added after 6 h of polymerization. [i] A high molecular weight fraction (2% total area) with $\bar{M}_n$ = 3 077 100 g/mol; $\bar{M}_w/\bar{M}_n$ = 1.20 was observed on the GPC chromatogram.

Table II
Polymerization of 4,4′-Bis(4-chlorophenoxy)-1,1′-binaphthyl (20)

	monomer solution		catalyst solution							
exp no.	monomer, mmol	solent (mL)	catalyst[a] (Ni mmol)	solvent (mL)	reaction temperature, °C	reaction time, h	polymer, yield, %	$\bar{M}_n$ g/mol	$\bar{M}_w/\bar{M}_n$	T_g, °C
1	1.0	DMF (1.0)	A (0.1)	NMP (9.0)	75	1.0		3700	1.5	
2	1.0	DMF (1.0)	A (0.1)	NMP (9.0)	75	5.0		5000	2.9	
3	1.0	DMF (1.0)	A (0.1)	NMP (9.0)	75	24.0	60	5500	2.4	231
4	1.0	DMF (1.0)	A (0.1)	DMF (1.0)	75	4.0	58	3200	6.4	
5	1.0	THF (2.0)	B (0.1)	THF (10)	55	24.0	8	2200	4.0	

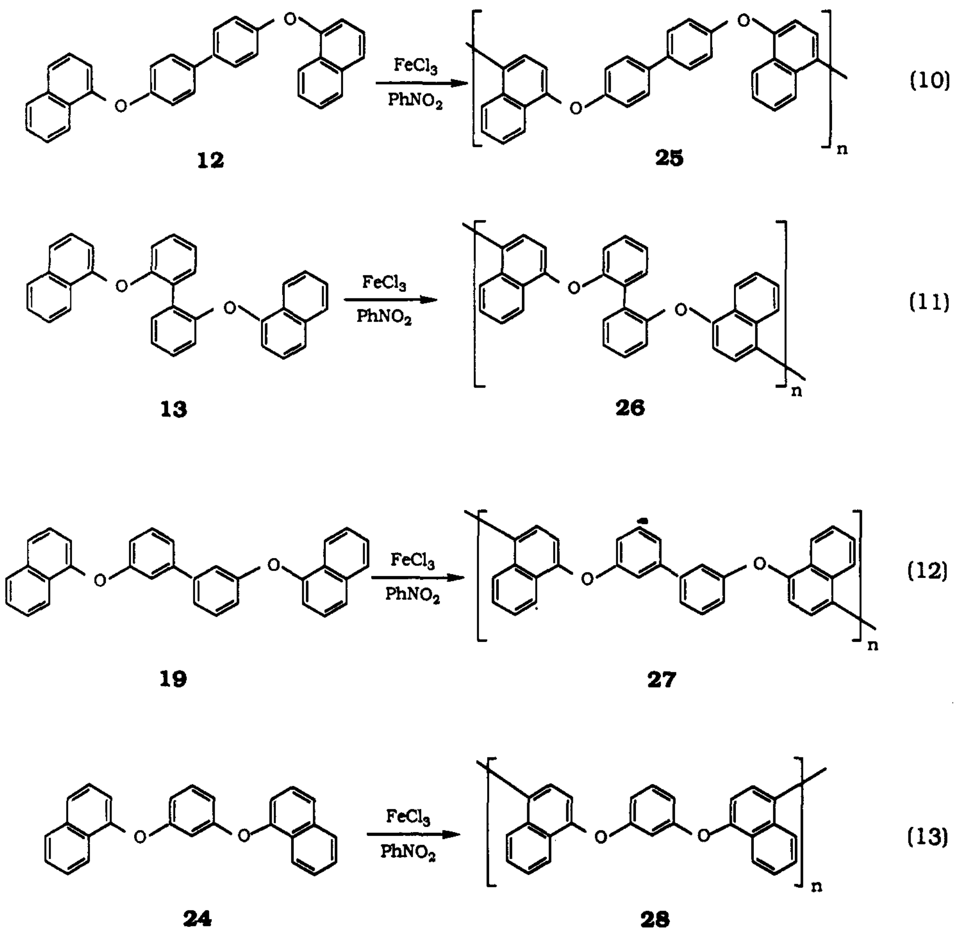
[a] Catalyst A: $NiCl_2/PPh_3/Zn/2,2'$-dipyridyl. Catalyst B: $Ni(PPh_3)_2Cl_2/Et_4I/Zn$.

g/mol, $\bar{M}_w/\bar{M}_n$ = 3.2. In some cases, the progress of the polymerization was monitored by withdrawing an aliquot of the polymerization mixture and precipitating it into a mixture of methanol and acetone (1/1, v/v). The filtered precipitate was dried in vacuum and subsequently analyzed by GPC. Alternatively, the aliquot was poured into water to remove $FeCl_3$, followed by extraction with $CHCl_3$. The $CHCl_3$ layer was dried over anhydrous $MgSO_4$ and finally analyzed by GPC.

Ni(0) Coupling Polymerizations. Method A. The Ni(0) catalyst was prepared by the same procedure described for the synthesis of 4,4′-bis(1-naphthoxy)biphenyl and the polymerization was performed under N_2.[12] The detailed polymerization conditions are provided in Table II. A typical polymerization example is given below. Ni(0) catalyst was prepared from $NiCl_2$ (0.014 g, 0.103 mmol), PPh_3 (0.199 g, 0.75 mmol), Zn powder (0.295 g, 4.52 mmol), 2,2′-dipyridyl (0.013 g, 0.083 mmol), and 1 mL of dry DMF. A solution of 4,4′-bis(4-chlorophenoxy)-1,1′-binaphthyl (0.755 g, 1.49 mmol) dissolved in 9 mL of dry NMP was added to the catalyst at 70 °C. The reaction mixture was stirred at 75 °C for 24 h. The reaction mixture was allowed to cool to room temperature, then diluted with 5 mL of DMF, and finally filtered to remove the unreacted Zn powder. The filtrate was poured into 150 mL of methanol acidified with 2% HCl. The precipitate was collected and boiled in 150 mL of acetone for 2 h to remove PPh_3. The polymer was collected by filtration, washed with acetone, and dried in vacuo. The yield was 0.389 g (60%). $\bar{M}_n$ (GPC) = 5500 g/mol, $\bar{M}_w/\bar{M}n$ = 2.4. In experiments 1 and 2 from Table II, the polymerization was followed by withdrawing samples from the polymerization mixture via a syringe. The sample was first precipitated in methanol and then into acetone, after which the polymer was characterized by GPC.

Method B. The Ni(0) catalyst was prepared from $Ni(PPh_3)_2Cl_2$ in THF. The procedure used in experiment 5 from Table II is given below. The Ni(0) catalyst was prepared from $Ni(PPh_3)_2Cl_2$ (0.133 g, 0.204 mmol), Zn powder (0.210 g, 0.321 mmol), Et_4NI (0.052 g, 0.203 mmol), and 2 mL of freshly distilled THF under N_2 at 55 °C.[23] A solution of 4,4′-bis(4-chlorophenoxy)-1,1′-binaphthyl (0.507 g, 1.00 mmol) dissolved in 10 mL of THF at 50 °C was added and the reaction stirred for 24 h. Then reaction mixture was allowed to cool to room temperature, diluted with 10 mL of THF, and filtered to remove Zn powder. The filtrate was poured into 150 mL of methanol acidifed with 2% HCl. The precipitate was collected and refluxed in 150 mL of acetone for 2 h to remove PPh_3. The polymer was collected by filtration, washed with acetone, and dried in vacuo. The yield was 0.036 g (8%). $\bar{M}_n$ (GPC) = 2200, $\bar{M}_w/\bar{M}_n$ = 4.0.

Scheme V



Results and Discussion

The synthesis of monomers 12 and 13 is described in Scheme I. Both compounds were prepared by the etherification of 2 and respectively 3 with 1 followed by the reduction of the resulting nitro derivatives 4 and 5 to the corresponding amines 6 and 7. The amines 6 and 7 were transformed into the corresponding diazonium salts 8 and 9 which were transformed into the chloride derivatives 10 and 11. Compound 4 was previously prepared in 9–12% yield by reacting *p*-nitrophenol with 1-bromonaphthalene under Ullmann reaction conditions.[16] Attempts to prepare compound 5 under similar conditions did not yield any product.[16] However, 5 was reported previously.[18] No analytical data and information about the synthetic procedure used in its preparation were provided.[18]

Compounds 10 and 11 were previously synthesized under Ullmann reaction conditions by reacting 2- and 4-chlorophenol with 1-bromonaphthalene.[16,20] Both compounds were obtained in yields lower than 18%. The synthetic procedures described here are more convenient and lead to products 10 and 11 in higher yields than the methods reported previously. 12 and 13 were synthesized by a Ni(0)-catalyzed homocoupling of 10 and respectively 11. The Ni(0) catalyst was generated in situ according to a literature procedure.[21]

Monomer 19 was synthesized by the sequence of reactions outlined in Scheme II. The essential product is 18 which can not be synthesized by the etherification of 1 with 1-chloro-3-nitrobenzene since the chloride group is not activated toward nucleophilic displacement by a nitro group present in the meta position. Therefore 18 was prepared by the sequence of reactions outlined in Scheme II. This procedure is based on the etherification of 14 with 1 which was assumed to lead to a mixture of 15 and 16 containing mostly the isomer 15. This assumption was based on literature information which showed that the etherification of 14 with trifluoroethanolate led to a 75/25 mixture of the ortho versus para substituted derivatives.[19] The other steps are based on conventional reactions.

Monomer 20 was synthesized by the cation–radical dimerization of 10 in nitrobenzene by using $FeCl_3$ as oxidant (Scheme III).

Finally, monomer 24 was synthesized by the Ullmann reaction (Scheme IV) of resorcinol (21) with 1-bromonaphthalene (23) by using literature reaction conditions.[22]

The cation–radical polymerization of 4,4′-bis(1-naphthoxy)biphenyl (12), 2,2′-bis(1-naphthoxy)biphenyl (13), 3,3′-bis(1-naphthoxy)biphenyl (19), and 1,3-bis(1-naphthoxy)benzene (24) is outlined in Scheme V. All polymerizations were performed under nitrogen in dry nitrobenzene, using $FeCl_3$ as oxidant. The results of these polymerizations are summarized in Table I.

The polymerization experiments of 4,4′-bis(1-naphthoxy)biphenyl (12) are listed as experiments 1–5 from Table I. Due to the low solubility of monomer 12 in nitrobenzene, low monomer concentration and elevated temperature were required to completely dissolve the monomer. At a $FeCl_3/12 = 2/1$ (mol/mol) (experiment 1, Table I), the polymerization results in polymer 25 (Scheme V) of $M_n = 4900$ g/mol and $M_w/M_n = 5.8$ in 58% polymer yield. The glass transition temperature (T_g) of the polymer was 235 °C. Since the monomer concentration is limited by its low solubility, attempts to increase the molecular weights of the resulting polymers by conducting polymerizations

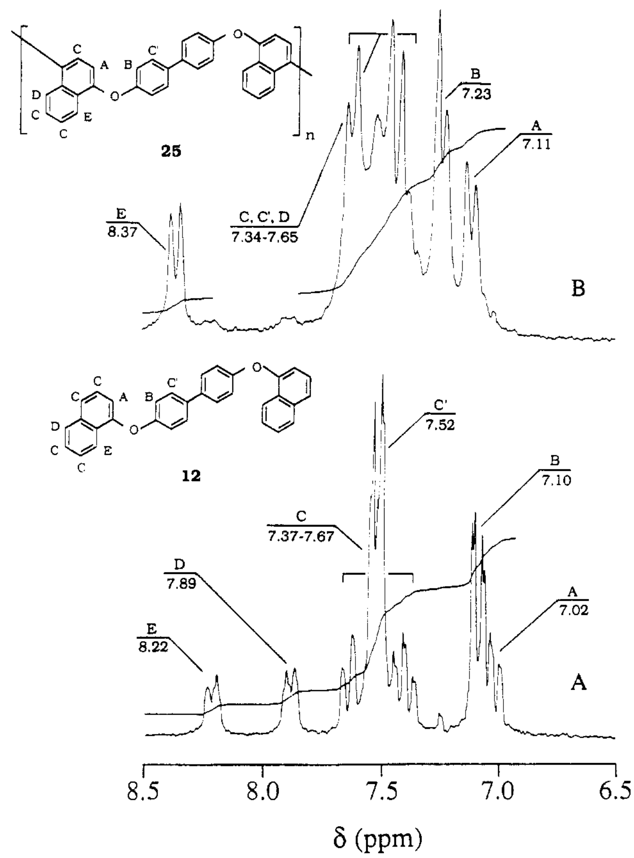


Figure 1. ^{1}H NMR spectra (200 MHz, $CDCl_3$, TMS) of 4,4'-bis(1-naphthoxy)biphenyl (**12**, spectrum A) and poly[4,4'-bis(1-naphthoxy)biphenyl] (**25**, spectrum B, sample 1, Table I). (An expansion of the δ = 6.5–8.5 ppm region).

at higher $FeCl_3$/**12** molar ratios failed (experiments 2–4, Table I). These polymerizations led to an insoluble polymer. An attempt to polymerize monomer **12** in an alternative polymerization solvent (experiment 5, Table I), i.e. benzonitrile, did not produce any polymer.

The solubility of polymer **25** is higher than that of its parent monomer **12**. Polymer **25** is soluble in common organic solvents such as chloroform and tetrahydrofuran. The structure of polymer **25** was determined by ^{1}H NMR spectroscopy. Representative 200-MHz ^{1}H NMR spectra of monomer **12** and polymer **25** along with the peak assignments[24] are present as spectra A and B in Figure 1. These spectra demonstrate that the polymer obtained from **12** has the structure **25** from Scheme V.

The synthesis of polymer **25** was also achieved by the Ni(0)-catalyzed homocoupling reaction of 4,4'-bis(4-chlorophenoxy)-1,1'-binaphthyl (**20**) as outlined in Scheme VI (identical NMR spectrum to Figure 1B). The results of these polymerization experiments are summarized in Table II. Two different experimental approaches were used for the Ni(0)-catalyzed polymerization of **20**. In the first method,[12] a solution of the monomer **20** in NMP was added to the DMF solution of the Ni(0) catalyst generated from $NiCl_2$, PPh_3, Zn powder, and 2,2'-dipyridyl. These polymerizations (experiments 1–3, Table II) led to polymer **25** with a maximum yield of 60%, and M_n in the range of 3700–5500 g/mol. The T_g of polymer **25** synthesized by Ni(0)-catalyzed polymerization of **20** (sample 3, Table II) is 231 °C and agrees with the T_g of the polymer **25** prepared by the cation–radical polymerization of monomer **12** (experiment 1, Table I).

Representative GPC traces of the polymer **25** obtained after 1 h, 5 h, and 24 h of polymerization time are presented as curves A, B, and C in Figure 2. Even though oligomers are present in all these polymers, it is obvious that the average molecular weight shifts toward higher values as the Ni(0)-catalyzed polymerization proceeds.

Due to the low solubility of monomer **20** in the reaction mixture, the polymerization (experiment 4, Table II) in DMF resulted in a polymer **25** with $\bar{M}_n$ of 3200 g/mol. The heterogeneity of the polymerization system has significantly broadened the polydispersity of the resulting polymer, i.e. $\bar{M}_w/\bar{M}_n$ = 6.4.

The second Ni(0) polymerization procedure consists of the addition of monomer solution in THF to the Ni(0) catalyst generated from $Ni(PPh_3)_2Cl_2$, Et_4NI, and Zn powder in THF.[23] However, after 24 h of polymerization, this method produced polymer **25** in only 8% yield. The resulting polymer has a $\bar{M}_n$ of 2200 g/mol and a polydispersity of 4.0.

The synthesis of poly[4,4'-bis(1-naphthoxy)biphenyl] (**25**) by the cation–radical polymerization of **12** (Scheme V) led to polymer **25** of a $\bar{M}_n$ lower than 5000 g/mol. This low $\bar{M}_n$ was determined by the low solubility of the monomer **12**. Therefore, monomers **13**, **19**, and **24** of higher solubilities than monomer **12** were synthesized and polymerized under similar reaction conditions.

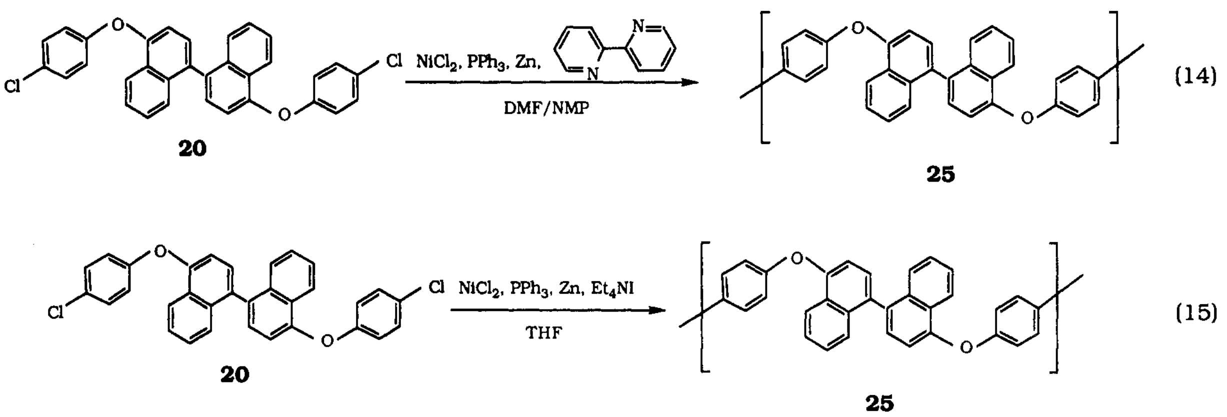
The results of the polymerization of 2,2'-bis(1-naphthoxy)biphenyl (**13**) are listed as experiments 6–12 from Table I. Polymerization experiments 6–8 from Table I were performed at low monomer concentrations and a $FeCl_3$/**13** = 2.4/1 (mol/mol). These polymerizations produced polymers of yields ranging from 85 to 97%. The number average molecular weights of the polymers are ranging from 7000 to 7300 g/mol and their polydispersities from 2.1 to 3.1. A representative GPC trace of polymer **26** (experiment 8, Table I) is shown in Figure 3. The polymerization performed at higher monomer concentration (experiment 9, Table I) resulted in a polymer **26** with $\bar{M}_n$ of 13 900 g/mol and a polydispersity of 5.3. The glass transition temperature of this polymer is 235 °C.

2,2'-Bis(1-naphthoxy)biphenyl (**13**) was also polymerized at higher $FeCl_3$/**13** molar ratios (experiments 10 and 11, Table I). These polymerizations produced polymers of higher molecular weights. Their $\bar{M}_n$ values were in the range of 85 100–90 500 g/mol. However, in addition to the main elution peak these two polymers displayed additional peaks on their GPC chromatograms. The heterogeneity of the polymerization medium at a higher monomer concentration and at higher $FeCl_3$/**13** molar ratios are the cause of the appearance of these additional peaks. Previous polymerization experiments performed with 1,3-bis[4-(1-naphthoxy)benzoyl]benzene have demonstrated a similar effect of the monomer concentration and $FeCl_3$/monomer molar ratio on the molecular weight distribution of the resulting polymers.[14] The polymerization of monomer **13** performed in benzonitrile (experiment 12, Table I) failed.

3,3'-Bis(1-naphthoxy)biphenyl (**19**) was polymerized at a $FeCl_3$/**19** molar ratio of 2.4/1 (experiments 13 and 14, Table I), to yield polymer **27** with $\bar{M}_n$ of 12 600 and 13 300 g/mol. These experiments were performed with identical monomer and $FeCl_3$ concentrations as those used in the polymerization of monomer **13** (experiments 6 and 7, Table I). The molecular weights of polymers derived from **19** are significantly higher than those of polymers derived from **13**. The polymerization of **19** at a higher $FeCl_3$/**19** molar ratio (experiment 16, Table I) resulted in a polymer **27** of higher molecular weight, i.e. 34 000 g/mol.

1,3-Bis(1-naphthoxy)benzene (**24**) is a monomer which has a *m*-phenylene central unit instead of the biphenyl

Scheme VI



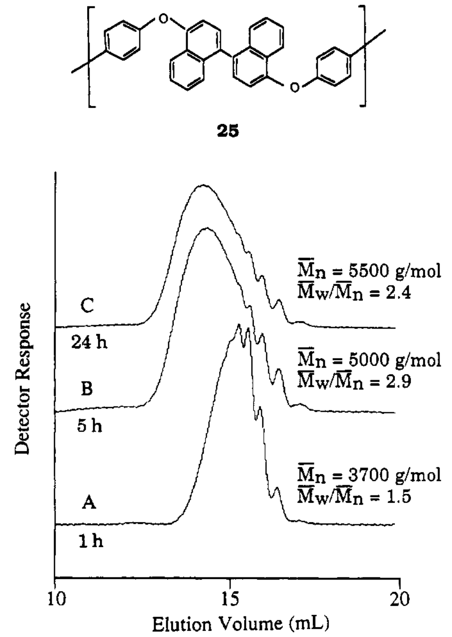


Figure 2. GPC traces of poly[4,4'-bis(1-naphthoxy)biphenyl] (**25**) as a function of the polymerization time: (A) $t = 1$ h; (B) $t = 5$ h; (C) $t = 24$ h.

central unit. The polymerization of monomer **24** at a $FeCl_3$/**24** molar ratio of 2.4/1.0 (experiments 17–19, Table I) led to polymers with $\bar{M}_n$ up to 5400 g/mol. However, attempts to polymerize monomer **24** at $FeCl_3$/**24** molar ratios of 3.2/1.0 and 3.8/1.0 (experiments 20 and 21, Table I) produced an insoluble polymer. Subsequently, we have modified the procedure used in the addition of the $FeCl_3$ solution (experiments 22 to 24, Table I) and obtained polymer **28** with $\bar{M}_n$ from 13 800 to 22 400 g/mol. This modification consists of the addition of 2.2–2.4 equiv of $FeCl_3$ to the monomer at the beginning of the polymerization followed by subsequent addition of more $FeCl_3$ oxidant after respectively 1 and 6 h of polymerization time. However, the resulting polymers displayed additional minor peaks on the molecular weight distribution presumably as a result of the heterogeneity of the polymerization medium.

The 200-MHz ^{1}H NMR spectra of 1,3-bis(1-naphthoxy)benzene (**24**) and of a representative poly[1,3-bis(1-naphthoxy)benzene] (**28**) (sample 22, Table I) are presented as spectra A and B from Figure 4. Even though this polymer displays a minor peak (12.6% of total area) of higher molecular weight ($\bar{M}_n$ = 815 900 g/mol) on its GPC trace, the polymer exhibits an expected ^{1}H NMR spectrum which agrees with the structure **28** (Scheme V). The change in the shielding effect from monomer **24** to polymer **28** causes an inversion of the resonances of protons A and B. Thus in monomer **24** A is upfield from B, while in polymer **28** B is upfield from A. The integral of the resonance of proton A in **28** (s, 7.00 ppm) is half of that due to the proton B (d, 6.90 ppm). This indicates the absence of any possible 5-membered ring formation between the phenylene unit and the neighboring naphthalene unit, i.e. benzonaphthofuran ring.

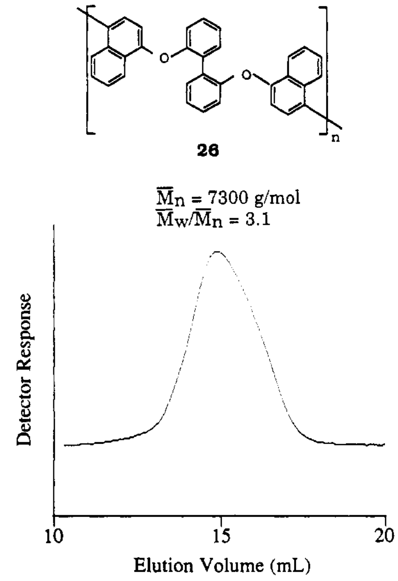


Figure 3. GPC traces of poly[2,2'-bis(1-naphthoxy)biphenyl] (**26**, sample 8, Table I).

The polymerization of 1,3-bis(1-naphthoxy)benzene (**24**) was monitored by taking samples which were subsequently analyzed by GPC. Figure 5 shows the GPC traces of the polymers obtained at different polymerization times. Curve A represents the GPC trace of the polymer **28** after 5 min of polymerization time. The sample was obtained by precipitating the polymerization aliquot into a mixture of methanol/acetone = 1/1 (v/v). This polymer has a $\bar{M}_n$ of 6300 g/mol and a polydispersity of 3.0. Therefore, this demonstrates that the polymerization of 1,3-bis(1-naphthoxy)benzene is very fast. In fact, all polymerizations performed at high monomer concentrations had to be diluted with polymerization solvent immediately after the complete dropwise addition of $FeCl_3$ solution in order to maintain an efficient stirring. As soon as a drop of $FeCl_3$ solution was added to the polymerization mixture containing monomer **24**, a large amount of HCl gas evolved immediately from the polymerization mixture.

Curve B is due to a sample of polymer **28** taken after 30 min of reaction time. However, this sample was

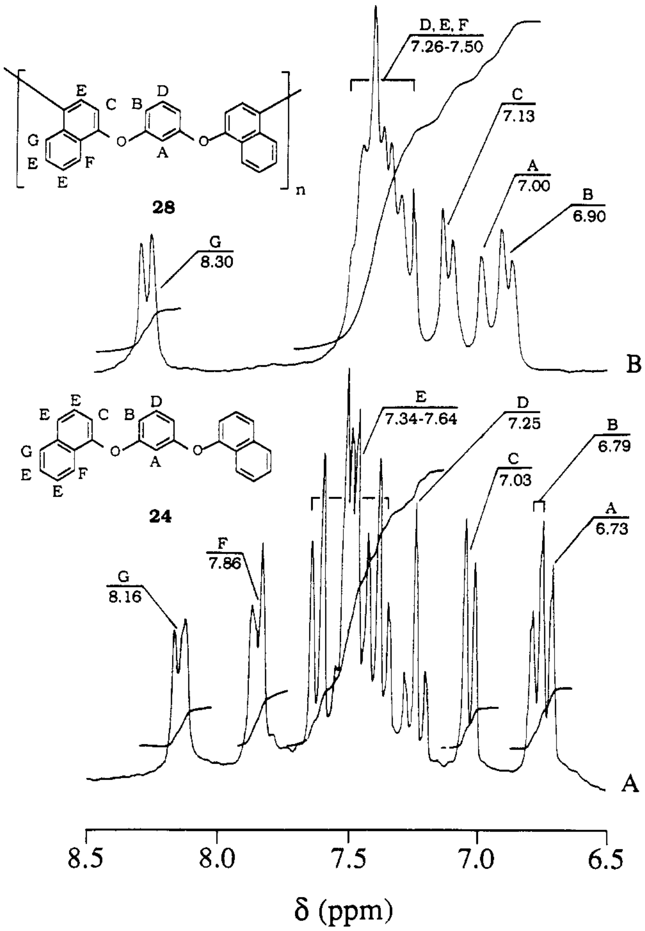


Figure 4. ^1H NMR spectra (200 MHz, $CDCl_3$, TMS) of 1,3-bis(1-naphthoxy)benzene (**24**, spectrum A) and poly[1,3-bis(1-naphthoxy)benzene] (**28**, spectrum B, sample 22, Table I). (An expansion of the δ = 6.5–8.5 ppm region).

separated by precipitating the polymerization aliquot into water, followed by extraction with $CHCl_3$. By this method, $FeCl_3$ is transferred into the aqueous phase and the unreacted monomer and oligomers (both soluble in $CHCl_3$) are separated from the reaction mixture. Samples of polymer **28** separated by precipitation in methanol/acetone contain less monomer and oligomers. After 30 min of polymerization time the amount of unreacted monomer was 1.5%. Curve C represents the GPC trace of a sample separated after 60 min of polymerization time. This sample was separated by precipitating the sample of the reaction mixture in methanol/acetone. This polymer has a $\bar{M}_n$ of 6900 g/mol and a $\bar{M}_w/\bar{M}_n$ value of 3.8. Besides the main polymer, curve C shows a trace of high molecular weight fraction which is responsible for the broadened polydispersity of the polymer. The polymerization was continued and additional 0.2 mmol of $FeCl_3$ (i.e. 0.67 equiv of the monomer) was introduced after 300 min of polymerization. Curve D displays the polymer sample taken 30 min after the second $FeCl_3$ addition (i.e after 390 min of polymerization time). The GPC trace of this polymer exhibits two peaks. The main peak (98% of total area) has a $\bar{M}_n$ of 14 800 g/mol and a $\bar{M}_w/\bar{M}_n$ of 4.4. The minor peak (2% of total area) has a relative number average molecular weight (versus polystyrene standards) of about 3×10^6 g/mol. In fact, all the polymers prepared by the two-step addition of $FeCl_3$ oxidant display this type of bimodal molecular weight distribution (experiments 22–24, Table I). The relative molecular weights of these high molecular weight fractions are listed in the footnotes in Table I.

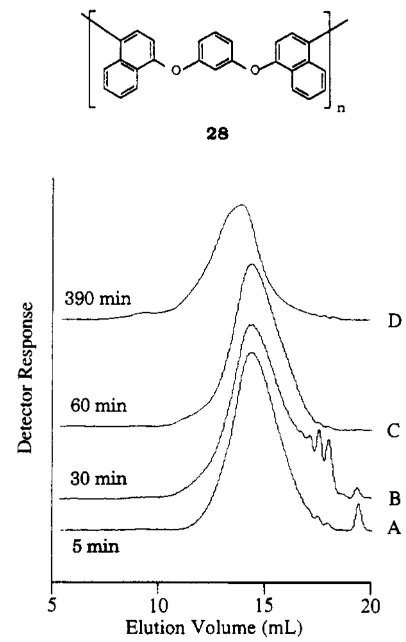


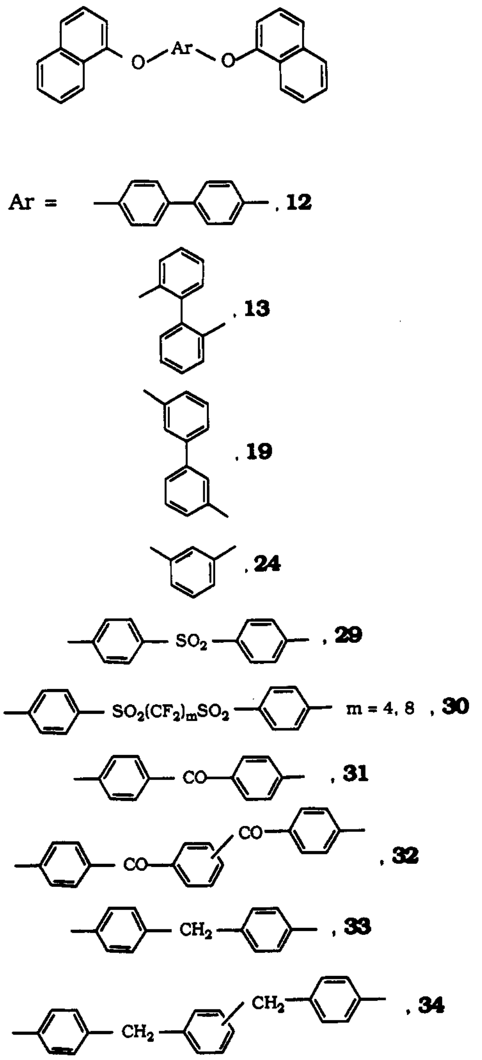
Figure 5. GPC traces of poly[1,3-bis(1-naphthoxy)benzene] (**28**) separated at different polymerization times of 1,3-bis(1-naphthoxy)benzene (**24**): (A) t = 5 min, sample obtained by precipitating the polymerization aliquot into methanol/acetone = 1/1, v/v; (B) t = 30 min, sample obtained by precipitating the polymerization aliquot into water and extracting with $CHCl_3$; (C) t = 60 min, sample obtained by precipitating the polymerization aliquot into methanol/acetone = 1/1, v/v; (D) t = 390 minutes, sample obtained by precipitating the polymerization aliquot into methanol/acetone = 1/1, v/v.

The analysis of the molecular weight distribution versus polymerization time dependence (Figure 5) has shown that the polymer separated at an early stage of the polymerization has a monomodal molecular weight distribution. Due to the high rate of polymerization, the monomer concentration decreases rapidly and the viscosity of polymerization mixture increases. This makes the monomer and $FeCl_3$ oxidant concentrations not uniform throughout the polymerization system. As a result, a small fraction of high molecular weight which does not fit the main polymer peak emerges as a minor shoulder (i.e., after about 60 min of reaction time, curve C, Figure 5). The high molecular weight fraction increases and forms a different molecular weight distribution (i.e. as a separate peak on GPC trace, curve D, Figure 5) as a result of the addition of more $FeCl_3$ oxidant.

The structures of the other monomers containing 1-naphthoxy polymerizable groups investigated in our laboratory[14] are summarized in Scheme VII. The polymerization results of monomers **12**, **13**, **19**, and **24** have demonstrated that these monomers are highly reactive in these cation–radical polymerizations. A comparison of the present results with those of the polymerizations of the other monomers suggests that the monomers containing substituted biphenyl (**12**, **13**, and **19**) and phenylene (**24**) groups as the central units exhibit a comparable polymerizability to that of monomers **29**–**31** (Scheme VII). However, the polymerizability of the monomers **12**, **13**, **19**, and **24** is higher than that of monomers **32**–**34** (Scheme VII).

The cation–radical dimerization of anisole, 4-methoxybiphenyl, and other related compounds was investigated by electrochemical techniques.[25] On the basis of kinetic data obtained by derivative cyclic voltammetry (DCV),[25] the two mechanisms outlined in Scheme VIII were proposed for their dimerization. The first mechanism is

Scheme VII



Scheme VIII

$$M \underset{}{\overset{-e}{\rightleftharpoons}} M^{\cdot+} \qquad (16)$$

Radical-Radical Coupling (RRC):

$$M^{\cdot+} + M^{\cdot+} \xrightarrow{k_1} M{-}M^{2+} \qquad (17)$$

Radical-Substrate Coupling (RSC):

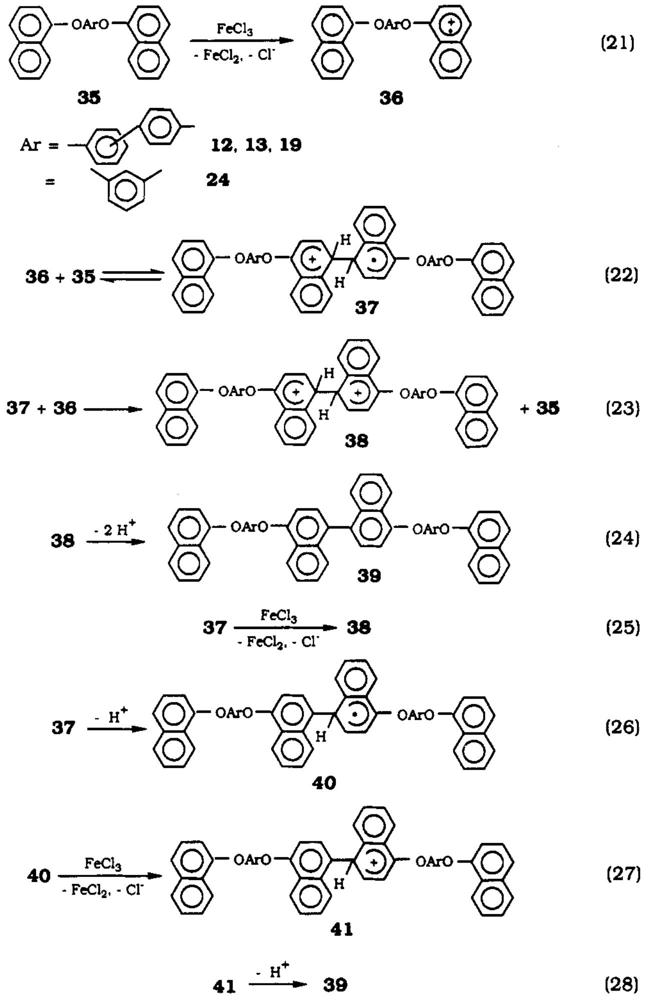
$$M^{\cdot+} + M \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M{-}M^{\cdot+} \qquad (18)$$

$$M{-}M^{\cdot+} + M^{\cdot+} \xrightarrow{k_3} M{-}M^{2+} + M \qquad (19)$$

$$\text{Rate} = \frac{k_2 k_3 [M^{\cdot+}]^2 [M]}{k_{-2} + k_3 [M^{\cdot+}]} \qquad (20)$$

a radical–radical coupling (RRC) reaction, in which two cation–radicals dimerize to produce a dimeric dication in a single step as outlined in eq 17. The second mechanism consists of the radical-substrate coupling (RCS) leading to a dimeric cation–radical (eq 18), followed by a single electron transfer from the dimeric cation–radical to the monomeric cation–radical to generate a dimeric dication and the neutral substrate (eq 19). Recent studies[26,27] suggest that out of these two mechanisms only the radical–substrate coupling (RSC) (eqs 18 and 19, Scheme VIII) is responsible for the dimerization reaction. The derived rate law for the RSC mechanism is outlined in eq 20 from Scheme VIII. The calculated rate constants by the reaction order approach for M = 4-methoxybiphenyl are as follows: $k_2 = 4.14 \times 10^4$ M^{-1} s^{-1}, $k_{-2} = 2.98 \times 10^6$ M^{-1} s^{-1}, and $k_3 = 10^{10}$ M^{-1} s^{-1} (this step was assumed to be diffusion controlled). Since $k_3 \approx (3 \times 10^3) k_{-2}$, at high substrate concentration, the overall rate of reaction reduces to $k_2[M^{\cdot+}][M]$, i.e. the forward reaction of eq 18 is the rate-determining step. At low substrate concentration, the overall rate reduces to $k_3[MM^{\cdot+}][M^{\cdot+}]$, i.e., eq 19 becomes the rate-determining step. The concentration at which the rate-determining step changes is (2.98×10^{-4})M. Subsequently all the available kinetic data could be explained in terms of the RSC mechanism alone.[26]

Scheme IX



On the basis of these results,[26,27] the most probable cation–radical polymerization mechanism of monomers **12**, **13**, **19**, and **24** is presented in Scheme IX. The single electron transfer oxidation of monomer **35** by $FeCl_3$ leads to its corresponding cation–radical **36** (eq 21). This reaction proceeds most probably by the excitation of an EDA complex **35**/$FeCl_3$. The radical–substrate coupling (eq 22) results in the dimeric cation–radical **37**, which gets oxidized through the one electron transfer reduction of the monomeric cation–radical **36** to produce the dication **38**. The transfer of one electron from the dimeric cation–radical **37** to the monomeric cation–radical **36** is favored since the cation–radical of 1,1′-dinaphthyl **37** is more easily oxidized than the monomeric naphthoxy cation–radical **36**. This is supported by the fact that the dimer derived from anisole is more easily oxidized than anisole itself.[25] However, in this oxidation reaction, an alternative electron transfer reaction (eq 25) is possible. It consists of one electron transfer from the dimeric cation–radical **37** to the $FeCl_3$ oxidant. Due to the presence of an equivalent amount of $FeCl_3$ to monomer in the polymerization reaction and due to the probably higher electronic affinity of $FeCl_3$ than that of the monomeric cation–radical **36**, the reaction from eq 25 might be at least as favorable as the reaction from eq 23. The dication **38** eliminates two protons to generate the neutral dimer **39** (eq 24).

A critical evaluation of the relative importance between reactions from eqs 23 and 25 requires the analysis of the kinetic data of this polymerization. The present results are not sufficient to discriminate between these two reactions.

The previous mechanisms suggested that this polymerization[14] did not take into consideration the single electron transfer step from eq 23. It was proposed that the dimeric cation–radical **37** first eliminates one proton (eq 26). The resulting radical **40** is oxidized by one electron transfer to $FeCl_3$ to produce the dimeric monocation **41** (eq 27) which subsequently eliminates the second proton to produce the neutral dimer **39** (eq 28). The sequence of reactions from eqs 26 to 28 can be eliminated only if we demonstrate that the dication **38** (eq 23) and the cation–radicals **36** and **37** are the only active species in this reaction. Presently we do not have experimental data which can discriminate between these two polymerization mechanisms.

The initial monomer concentration in these cation–radical polymerizations ranges from 0.9 to 1.4 M. If this polymerization proceeds through the sequence of eqs 21–24, this concentration is significantly higher than the concentration at which the one electron transfer (eq 19 in Scheme VIII, and eq 23 in Scheme IX) becomes the rate-determining step. Therefore, under these conditions, in the early stages of this polymerization, the forward reaction of eq 22 should represent the rate-determining step. As the polymerization proceeds, the decrease in the monomer concentration may make the one electron transfer from eq 23 the rate-determining step.

The synthesis and polymerization of 4,4′-, 3,3′-, and 2,2′-bis(1-naphthoxy)biphenyls and 1,3-bis(1-naphthoxy)benzene have demonstrated that the cation–radical polymerization of bis(1-naphthoxy)aryls represents a novel and general method for the synthesis of fully aromatic polyethers. Its application to the synthesis of novel aromatic polyethers, of functional aromatic polyethers, and of aromatic polyethers containing well-defined chain ends is in progress and will be reported in due time.

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