Polymer Bulletin 29, 271–276 (1992)

Polymer Bulletin

Synthesis of soluble polyarylenes containing alternating 4,4′-(1,1′-binaphthyl) and 4,4′-(3,3′-diphenyl)biphenyl structural units

V. Percec, S. Okita, and J. Bae

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

SUMMARY

The synthesis and Ni(0) catalyzed homocoupling polymerization of 4,4'-bis[5-(trifluoromethanesulfonyloxy)-2-biphenylyl]-1,1'-binaphthyl (**9**) are described. This polymerization reaction produces a soluble polyarylene containing alternating 4,4'-(1,1'-binaphthyl) and 4,4'-(3,3'-diphenyl)biphenyl structural units.

INTRODUCTION

Some previous publications from our laboratory reported the synthesis of soluble polyarylenes, [1-5] and polyarylene ethers, [6,7] by increasing the configurational entropy of their backbone.[8] This concept is based on the generation of a linear extended chain conformation via a proper combination of kinked structural units (extended conformation based on conformational isomerism). The extended conformation based on conformational isomerism increases the configurational entropy of the backbone and brings the melting temperature in the close proximity or below the glass transition temperature. Solubility of these polymers is therefore, due to their amorphous state.[8] The synthetic strategy employed in the design of these polymers is based on the insertion of alternating isomeric biphenyl (i.e., 4,4'-biphenyl, 3,3'-biphenyl, 2,2'-biphenyl and 2,5-biphenyl) and 4,4'-(1,1'-binaphthyl) structural units within the main chain of the polymer.[1-8]

The goal of this communication is to describe a synthetic route for the preparation of a novel soluble polyarylene structure which contains 4,4'-(1,1'-binaphthyl) and 4,4'-(3,3'-diphenyl)biphenyl structural units.

EXPERIMENTAL

Materials

4-Bromo-3-nitroanisole (97 %), Fe powder (99.9+ %), n-butyllithium (2.5 M solution in hexane), boron tribromide (1.0 M CH_2Cl_2 solution), trifluoromethanesulfonic anhydride (triflic anhydride), triphenylphosphine (99 %), 2,2'-dipyridyl (DPY, 99%), $NiCl_2$ (99%), Et_4NI (98%) (all from Aldrich), $NaNO_2$ (99.7 %), LiCl (99.9 %) (both from J. T. Baker Chemicals), Na_2CO_3 (anhydrous, Fisher Scientific), sodium acetate (Matheson Coleman & Bell, 99 %), trimethyl borate (Fluka, >99 %), and $PdCl_2$ (Alfa, 99.9 %) were used as received. CH_2Cl_2 was dried over P_2O_5 and distilled. THF was dried over Na/benzophenone and distilled. Pyridine was dried over CaH_2 and distilled. $Pd(Ph_3P)_4$ was prepared according to a literature procedure.[9] [1,1'-Binaphthyl]-4,4'-diol was prepared from 1-naphthol by following a literature procedure.[10] Yield, 96.1 %. mp, 300°C (ref.[10], mp, 300°C). $Ni(Ph_3P)_2Cl_2$ was prepared as described previously.[6]

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer (TMS as internal standard). Relative molecular weights (versus polystyrene standards) were determined by gel permeation chromatography (GPC).[6]

Synthesis of monomers

The synthesis of the monomers is outlined in Scheme 1.

2-Bromo-5-methoxyaniline (2)

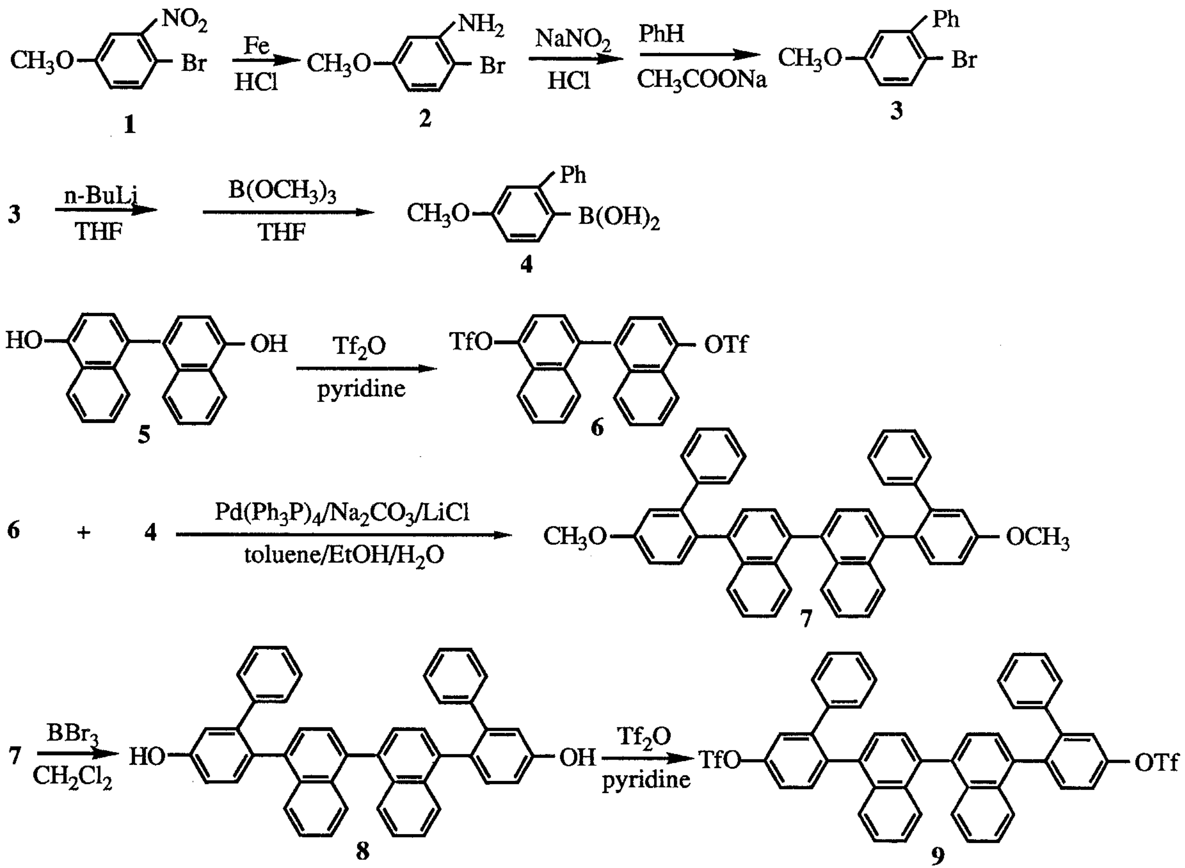
4-Bromo-3-nitroanisole (11.87 g, 51.13 mmol), Fe powder (16.92 g, 0.303 mol), benzene (50 mL) and water (35 mL) were placed in a 500-mL round bottom flask equipped with condenser and stirred vigorouly. To this mixture, concentrated HCl (25 mL) was added slowly from the top of the condenser. The reaction mixture was heated at reflux temperatute with stirring for 62h. Since TLC (silica gel/benzene) did not show the spot of 4-bromo-3-nitroanisole, the reaction mixture was cooled to room temperature. To the cooled reaction mixture, 25 % NaOH aqueous solution (140 mL) was added and stirred to generate the free amine. The unreacted Fe powder was removed by filtration. The Fe powder was washed with hot benzene and the combined filtrate was transferred into a separatory funnel to separate the benzene layer. The benzene layer was dried over anhydrous $MgSO_4$ and the solvent was removed on a rotary evaporator. The oily residue was purified by column chromatography on silica gel using benzene as eluent and the pure product was obtained as an orange oil. The yield was 9.085 g (87.9 %). ^{1}H-NMR ($CDCl_3$, δ, ppm) : 3.64 (s, 3H, $-OC\underline{H}_3$), 3.85 (br. s, 2H, $-N\underline{H}_2$), 6.14 (dd, 1H, J = 9, 2.5 Hz, Ph-$\underline{H}$ para to NH_2), 6.23 (d, 1H, J = 2.5 Hz, Ph-$\underline{H}$ ortho to NH_2), 7.18 (d, 1H, J = 9 Hz, Ph-$\underline{H}$ meta to NH_2).

2-Bromo-5-methoxybiphenyl(3) [11]

2-Bromo-5-methoxyaniline (8.889 g, 0.044 mol) was mixed with water (11 mL) and concentrated HCl (11 mL), and heated at 100°C with stirring to form its hydrochloride. The mixture was cooled in an ice/water bath. To the cooled mixture, a cold aqueous solution of $NaNO_2$ (3.32 g, 0.048 mol in 15 mL of water) was added dropwise in the course of 15 min. During this time, the temperature was maintained at 0-5°C. The resulting yellow suspension was poured into cold benzene (100 mL, about 10°C) and then, the mixture was vigorously stirred. A cold aqueous solution of CH_3COONa (14.16 g, 0.173 mol in 35 mL of water) was slowly added. The mixture was gradually warmed to room temperature without external heating over 2h and stirring was continued for 24h. The reaction mixture was extracted four times with benzene and the extract was washed three times with 10 % HCl, twice with water, three times with 10 % KOH aqueous solution, three times with water, and dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator and the oily residue was extracted five times with boiling petroleum ether. The extract was concentrated on a rotary evaporator and purified by column chromatography on silica gel using petroleum ether as eluent. The first colorless fraction was collected and the solvent was removed on a rotary evaporator to give a colorless oil. The yield was 6.164 g (53.3 %). Purity (HPLC), >99.9 %. ^{1}H-NMR ($CDCl_3$, δ, ppm) : 3.78 (s, 3H, $-OC\underline{H}_3$), 6.75 (dd, 1H, J = 8.5, 2.5 Hz, 4-$\underline{H}$), 6.87 (d, 1H, J = 2.5 Hz, 6-$\underline{H}$), 7.37-7.45 (m, 5H), 7.53 (d, 1H, J = 8.5 Hz, 3-$\underline{H}$).

5-Methoxy-2-biphenylboronic acid(4)

2-Bromo-5-methoxybiphenyl (5.920 g, 22.50 mmol) was dissolved in freshly distilled THF (35 mL) and the solution was cooled below -65°C in a dry ice/acetone bath under N_2. 2.5 M n-butyllithium solution in hexane (10.0 mL, 25.0 mmol) was added dropwise in the course of 15 min while the temperature of the reaction mixture was maintained below -65°C. The resulting yellow suspension was stirred below -65°C for 1h and trimethyl borate (6.0 mL, 5.30 g, 51.0 mmol) was added dropwise in the course of 15 min while the temperature of the reaction mixture was maintained below -65°C. The reaction mixture was gradually warmed to room temperature without any external heating



Scheme 1: Synthesis of 4,4'-bis[5-(trifluoromethanesulfonyloxy) -2-biphenylyl]-1,1'-binaphthyl (**9**)

and stirred overnight. 10 % HCl (100 mL) was added dropwise and the reaction mixture was extracted three times with diethyl ether. The extract was dried over anhydrous $MgSO_4$ and the solvent was removed on a rotary evaporator. To the resulting pale yellow oil, 200 mL of petroleum ether were added to solidify the product. The mixture was stirred at room temperature for 24 h to dissolve the organic impurities. The white crystals were collected by filtration, washed with petroleum ether and dried in vacuum. The yield was 1.814 g (35.3 %). mp, 124-5°C (the melt was turbid). ^1H-NMR (acetone-d_6, δ, ppm) : 3.85 (s, 3H, $-OCH_3$), 6.73-6.94 (m, 2H, Ph-H ortho to OCH_3), 7.21-7.47 (m, 5H), 7.60 (d, 1H, J = 8.5 Hz, Ph-H meta to OCH_3), $-B(OH)_2$ was not observed probably because this compound exists as anhydride under the conditions described above. The addition of D_2O did not change the NMR spectrum.

4,4'-Bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (6) [12]

[1,1'-Binaphthyl]-4,4'-diol (1.435 g, 5.011 mmol) was dissolved in 35 mL of dry pyridine and stirred under nitrogen. The solution was cooled in an ice/water bath and trifluoromethanesulfonic anhydride (2.0 mL, 3.35 g, 11.9 mmol) was added dropwise via a syringe. The reaction mixture was stirred at 0°C for an hour and then at room temperature overnight. The mixture was poured into 300 mL of water and extracted three times with diethyl ether. The extract was washed twice with 10 % hydrochloric acid and twice with water, and dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was purified by column chromatography on silica gel using toluene as eluent. The pure product was obtained as a slightly yellow oil which crystallized upon standing. The yield was 1.803 g (65.4 %). mp, 103-5°C. Purity (HPLC), >99.9 %. ^1H-NMR ($CDCl_3$, δ, ppm) : 7.32-7.73 (m, 10H), 8.20 (d, 2H, J = 8.5 Hz, 8-H or 5-H).

4,4'-Bis(5-methoxy-2-biphenylyl)-1,1'-binaphthyl (7)[13]

In a 100 mL round bottom flask equipped with condenser, 4,4'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (1.570 g, 2.852 mmol) was dissolved in 15 mL of toluene. To this solution, $Pd(Ph_3P)_4$ (0.141 g, 0.122 mmol), 1M Na_2CO_3 aqueous solution (8 mL, 8 mmol), EtOH (13 mL), 5-methoxy-2-biphenylboronic acid (1.462 g, 6.410 mmol) and LiCl (0.160 g, 3.774 mmol) were added in this order and the mixture was heated at reflux temperature under N_2 for 2.5h. The product precipitated out of the reaction mixture after being cooled to room temperature. The crude product containing Pd catalyst residue was collected by filtration and purified by recrystallization from a mixture of EtOH and $CHCl_3$. The product was obtained as pale yellow crystals and the yield was 1.459 g (82.6 %). mp, 234-5°C. Purity (HPLC) , 96.8 %. ^1H-NMR ($CDCl_3$, δ, ppm) : 3.96 (s, 3H, $-OCH_3$), 7.01-7.40 (m, 4H), 7.48 (d, 2H, J = 8.5 Hz), 7.69-7.83 (m, 2H).

4,4'-Bis(5-hydroxy-2-biphenylyl)-1,1'-binaphthyl (8)[14]

In a 100 mL round bottom flask, 4,4'-bis(5-methoxy-2-biphenyl)-1,1'-binaphthyl (2.054 g, 3.319 mmol) was dissolved in 15 mL of dry CH_2Cl_2 and the solution was cooled in a dry ice/acetone bath under N_2, which became a white suspension due to the precipitation of 4,4'-bis(5-methoxy-2-biphenyl)-1,1'-binaphthyl. To this suspension, boron tribromide solution in CH_2Cl_2 (1M solution, 6.5 mL, 6.5 mmol) was added dropwise via a syringe over 10 min. The reaction mixture was gradually warmed to room temperature without any external heating and stirring was continued overnight. The resulting white suspension was poured onto crashed ice, and 10 % HCl (120 mL) was added. The reaction mixture was extracted twice with diethyl ether and the extract was dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was solidified by adding hexanes. The crude product was recrystallized from a mixture of hexanes and toluene. The product was obtained as a white solid. Yield, 1.792 g (90.8 %). mp, 116°C (peak temperature on the first heating scan of the DSC; on the second DSC heating scan this compound exhibits a glass transition temperature at 108°C). Purity

(HPLC), >99.9 %. ^{1}H-NMR ($CDCl_3$, δ, ppm): 4.99 (s, 2H, -OH), 6.97-7.45 (m, 26H), 7.75 (m, 2H).

4,4'-Bis[5-(trifluoromethanesulfonyloxy)-2-biphenylyl]-1,1'-binaphthyl (**9**)[5]

4,4'-Bis(5-hydroxy-2-biphenylyl)-1,1'-binaphthyl (0.931 g, 1.566 mmol) was dissolved in 15 mL of dry pyridine and stirred under nitrogen. The solution was cooled in an ice/water bath and trifluoromethanesulfonic anhydride (1.0 mL, 1.68 g, 5.94 mmol) was added dropwise via a syringe. The reaction mixture was stirred at 0°C for an hour and then at room temperature overnight. The reaction mixture became a pinkish suspension due to the precipitation of the product. The mixture was poured into 100 mL of water and the product was collected by filtration, washed with 10 % HCl and water. The crude product was purified by crystallization from a mixture of hexanes and $CHCl_3$ to give white crystals. Yield, 0.996 g (74.4 %). mp, 248-9°C. Purity (HPLC) , 99.3 %. ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.11 (m, 8H), 7.30-7.51 (m, 14H), 7.66 (m, 6H).

Polymerizations

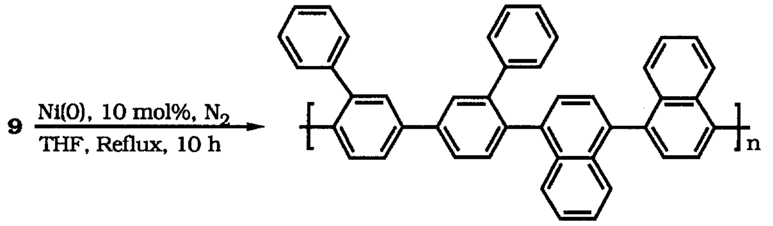
$Ni(Ph_3P)_2Cl_2$ (0.031g, 0.047 mmol), Zn powder (0.306g, 4.70 mmol) and Et_4NI (0.112g, 0.436 mmol) were placed in a 15 mL round bottom flask equipped with condenser and stopcock. The flask was evacuated under vacuum for 1 day and filled with N_2. Then, the evacuation and filling with N_2 was repeated four times. Freshly distilled THF (1.0 mL) was added via a syringe through the rubber septum from the top of the condenser. The mixture was stirred at room temperature for 10 min and during this time the color of the mixture gradually changed to deep red-brown. The monomer was dissolved in 1.0 mL of freshly distilled THF and added to the catalyst mixture via a syringe through the rubber septum. The reaction mixture was heated to the reflux temperature and stirred at this temperature for 10 h. The reaction mixture was then cooled to room temperature and poured into 50 mL of methanol acidified with HCl. The precipitate was collected by filtration and dissolved in 10 mL of $CHCl_3$. The solution was filtered to remove the trace of the catalyst and the filtrate was concentrated and poured into methanol. The precipitate was collected by filtration and vacuum dried. Yield, 0.090g (35%).

RESULTS AND DISCUSSION

The preparation of 4,4'-bis[5-(trifluoromethanesulfonyloxy)-2-biphenylyl]-1,1'-binaphthyl (**9**) was accomplished through the sequence of reactions outlined in Scheme 1. It started from 4-bromo-3-nitroanisole (**1**) which was reduced to the corresponding amine **2**. **2** was transformed into its diazonium salt which was coupled with benzene to yield 2-bromo-5-methoxybiphenyl (**3**). **3** was transformed into 5-methoxy-2-biphenylboronic acid (**4**) by lithiation followed by reaction with $B(OCH_3)_3$. **4** was cross-coupled with **6** via a variant of the Suzuki reaction,[13] to yield **7** which upon demethylation with BBr_3 and esterification with triflic anhydride in pyridine yielded **9**.

The Ni(0) catalyzed homopolymerization of **9** was performed via a method elaborated in our laboratory.[2] Table 1 summarizes two examples of polymerizations and outlines the structure of the resulted polymer. No attempts were made to optimize the Ni(0) catalyzed polymerization of **9** and therefore, polymers with a number average degree of polymerization of maximum 9 were obtained. Since the structural unit of this polymer contains 4 p-phenylene units, the overal number of phenylene units from the main chain corresponding to a degree of polymerization of 9 is 45. This value is quite large for poly(p-phenylene)s.[1,2] The obtained polymer is white since the p-phenylene units of its main chain are twisted and therefore, are nonconjugated. Nevertheless, this structure can be transformed into a conjugated one via a one electron transfer induced electrophilic

Table 1: Ni(0) catalyzed polymerization of **9**.



No	Catalyst System	Solvent and mon. conc	Yield	Mn	Mw/Mn	DP
	(mol ratio)	(mol/l)	(%)		GPC	
1	$Ni(Ph_3)_2Cl_2/Zn/Et_4/NI(1/100/9.3)$	THF(0.23)	35	5,120	1.65	8.2
2	NiCl2/PPh3/Zn/DPY(1/30/158/1.3)	DMF(0.20)	33	3,820	1.84	7.0

intramolecular cyclization[1] which leads to triphenylene and perylene structural units. These structural units force the main chain of this polymer into a conjugated structure.[1,15] Experiments on this line are in progress.

ACKNOWLEDGMENT

Financial support by the Edison Polymer Innovation Corporation is gratefully acknowledged.

REFERENCES

1) V. Percec and S. Okita, *J. Polym. Sci: Part A: Polym. Chem.*, **30**, 1037(1992)
2) V. Percec, S. Okita and R. Weiss, *Macromolecules*, **25**, 1816(1992)
3) V. Percec and S. Okita, *J. Polym. Sci: Part A: Polym. Chem.*, in press
4) V. Percec and S. Okita, *J. Polym. Sci: Part A: Polym. Chem.*, in press
5) V. Percec, C. Pugh, E. Cramer, S. Okita and R. Weiss, *Makromol. Chem., Macromol. Symp.*, **54/55**, 113(1992)
6) V. Percec, S. Okita and J. H. Wang, *Macromolecules*, **25**, 64(1992)
7) V. Percec and J. H. Wang, *Makromol. Chem. Macromol. Symp.*, **54/55**, 337(1992)
8) V. Percec, J. Wang and S. Okita, *Polym. Prepr.*, **33(1)**, 225(1992)
9) D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972)
10) M. Tanaka and T. Nakaya, *Makromol. Chem.*, **185**, 1915 (1984)
11) The procedure for the phenylation via diazonium salt in the synthesis of 2-chlorobiphenyl from o-chloroaniline was applied. A. I. Vogel, *Vogel's Textbook of Practical Organic Chemistry*, 5 th Ed., Longman Scientific & Technical, p. 942 (1989)
12) A general procedure for the synthesis of phenol triflates described in the following paper was applied. A. M. Echavarren and J. K. Stille, *J. Am. Chem. Soc.*, **109**, 5478 (1987)
13) A general procedure for the Pd(0) catalyzed cross-coupling reaction of phenol triflate with aryboronic acid described in the following papers was applied. a) A. Huth, I. Beetz and I. Schumann, *Tetrahedron*, **45** (21), 6679 (1989). b) T. Oh-e, N. Miyaura and A. Suzuki, *Synthesis*, 221 (1990)
14) A procedure for the synthesis of 3,3'-biphenol described in the following paper was applied. J. F. W. McOmie and D. E. West, *Org. Synth.*, **49**, 50 (1969)
15) U. Scherf and K. Müllen, *Polymer*, **33**, 2443(1992); U. Scherf and K. Mullen, *Synthesis*, 23(1992)

Accepted August 21, 1992 K