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Synthesis of polyarylene homopolymers and copolymers via nickel(0)-catalyzed homocoupling of arylenebismesylates derived from bisphenols

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Summary

A general and inexpensive procedure for the synthesis of poly(arylene)-type homopolymers and copolymers containing alternating oligophenylene and a functional group (X) (*e.g.* X = -O-, -CO-, $-SO_2-$, $-C(CH_3)_2-$, $-CH_2-CH(Et)-$, etc) is described. The synthetic method is based on the Ni(0)-catalyzed homocoupling of aryl bismesylates (MsOAr-X-ArOMs) derived from bisphenols. Symmetric X groups lead to regioregular crystalline and insoluble polymers whereas bulky, asymmetric X groups or the incorporation of comonomers yield regioirregular polymers and, respectively, copolymers with decreased crystallinity and increased solubility. This new synthetic method can be applied to the preparation of polymers with controlled rigidity which are amorphous, crystalline or liquid crystalline.

Introduction

Synthetic methods for the preparation of substituted and unsubstituted poly(*p*-phenylenes) (PPP) can be classified as *direct* and *indirect* methods. The most significant recent contributions to both methods were discussed briefly in a previous publication (1) and were also reviewed (2-8). Recently, we have elaborated the most convenient and inexpensive synthetic method for the preparation of functional biaryls *via* Ni(0)-catalyzed homo-coupling and cross-coupling of their mesylates (9-12). This represents an important development of the previous homocoupling method which was based on the very expensive aryl triflates (13). The first application of this novel reaction to the field of polymer synthesis consisted in the elaboration of the most convenient method for the preparation of substituted PPPs *via* Ni(0)-catalyzed homocoupling of the bismesylates of substituted hydroquinones and 4,4'-dihydroxybiphenyls (1,13-15).

The goal of this publication is report the synthesis of a novel class of polymeric materials containing biphenylene and other oligophenylene repeat units generated *via* Ni(0)-catalyzed homocoupling of bismesylates or mixtures of bismesylates obtained from commercially available or synthetically readily accesible bisphenols. The synthetic procedure is of great synthetic value, first since it provides a very inexpensive avenue to produce C-C bonds from phenolic C-O bonds during a polymerization reaction, and

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second, since it can create an extremely large variety of material properties *via* the manipulation of chain rigidity and linearity.

Experimental

Materials: All reagents including bisphenols were purchased from commercial sources (Aldrich or Lancaster) and used without purification except when reported. 2,2'-Bis(trifloromethyl)-4,4'-bis(methylsulfonyloxy)biphenyl (15) and 1-(4-hydroxyphenyl)-2-(4-hydroxy-4'-biphenylyl)butane (16), were synthsized as previously described. Pyridine (dried over CaH_2) and THF (dried over Na/benzophenone) were freshly distilled before use. Zn dust was stirred in CH_3COOH, washed with H_2O and dried *in vacuo* at 120 °C. $NiCl_2(PPh_3)_2$ was prepared as described in the literature (17, 18). (2-Ethylhexyl)-2,5-dihydroxybenzoate was prepared by the acid-catalyzed esterification of 2,5-dihydroxybenzoic acid with 2-ethyl-1-hexanol (19). Arylene bismesylates were prepared by the alkylation of the corresponding bisphenols with methanesulfonyl chloride (20).

Synthesis of monomers: 4,4'-Bis(methylsulfonyloxy)benzophenone: Methanesulfonyl chloride (9.6 g, 0.084 mmol) was added slowly to a stirred solution of 4,4'-dihydroxybenzophenone (6 g, 0.028 mmol), DMAP (trace) and pyridine (50 mL) at 0 °C. The mixture was warmed to 22 °C and stirred for 12h. The reaction mixture was poured into 10% aq. HCl (500 mL) and the resulting precipitate was washed with H_2O, dried and recrystallized (2x, benzene) to yield 6.2 g (70%) of white crystals: mp = 130-131 °C.; ^{1}H-NMR δ 7.88 (d, J = 8.3 Hz, 4H, *o* to carbonyl), 7.43 (d, J = 8.3 Hz, 4H, *m* to carbonyl), 3.24 (s, 6H, $-OSO_2-C\underline{H}_3$).

2,2-Bis(4-methylsulfonyloxypropane) (83%): white crystals; mp = 97-98 °C (benzene); ^{1}H-NMR δ 7.26 (d, J = 8.6 Hz, 4H, *m* to oxygen), 7.20 (d, J = 8.6 Hz, 4H, *o* to oxygen), 3.14 (s, 6H, $-OSO_2-C\underline{H}_3$), 1.68 (6H, $-C(C\underline{H}_3)_2-$).

2-(3-Methylsulfonyloxyphenyl)-2-(4'-methylsulfonyloxyphenyl)propane. (63%): colorless oil; ^{1}H-NMR δ 7.46-7.19 (m, 8H, aromatics), 3.14 (s, 3H, $-OSO_2-C\underline{H}_3$ *m* to $-C(CH_3)_2-$), 3.10 (s, 3H, $-OSO_2-C\underline{H}_3$ *p* to $-C(CH_3)_2-$), 1.69 (s, 6H, $-C(C\underline{H}_3)_2-$).

4,4'-Bis(methylsulfonyloxy)phenyl ether: (89%): white crystals; mp= 140-141 °C (chloroform); ^{1}H-NMR δ 7.28 (d, J = 8.9 Hz, 4H, *o* to $-OSO_2-CH_3$), 7.05 (d, J = 8.9 Hz, 4H, *m* to $-OSO_2-CH_3$), 3.17 (s, 6H, $-OSO_2-C\underline{H}_3$).

4,4'-Bis(methylsulfonyloxy)phenyl sulfone. (80%): white crystals; mp = 150-151 °C (benzene); ^{1}H-NMR δ 8.02 (d, J = 8.4 Hz, 4H, *o* to $-SO_2-$), 7.45 (d, J = 8.4 Hz, 4H, *m* to $-SO_2-$), 3.22 (s, 6H, $-OSO_2-C\underline{H}_3$).

1,1'-Bis(methylsulfonyloxyphenyl)cyclohexane. (61%): white crystals; mp = 116-117 °C (benzene); ^{1}H-NMR δ 7.31 (d, J = 8.5 Hz, 4H, *m* to oxygen), 7.19 (d, J = 8.5 Hz, 4H, *o* to oxygen), 2.89 (s, 6H, $-OSO_2-C\underline{H}_3$), 2.25 (br s, 4H, aliphatic protons), 1.51 (br s, 6H, aliphatic protons).

3,3'-Bis(4-methylsulfonyloxyphenyl)-1-[3H]isobenzofuranone. (70%): white crystals; mp = 166-167 °C (benzene); ^{1}H-NMR δ 7.98 (d, J = 7.5 Hz, 1H, *o* to carbonyl), 7.76 (m, 1H, *p* to carbonyl), 7.65-7.55 (m, 2H, *m* to carbonyl), 7.41 (d, *J* =8.5 Hz, 4H, *m* to $-OSO_2-CH_3$), 3.16 (s, 6H, $-OSO_2-C\underline{H}_3$).

(2Ethylhexyl)-2,5-bis(methylsulfonyloxy)benzoate. (73%): viscous oil; ^{1}H-NMR δ 7.85 (br s, 1H, *o* to $-CO_2-$), 7.52 (br s, 2H, *m* and *p* to $-CO_2$), 4.25 (d, *J* = 5.6 Hz, 2H, $-CO_2C\underline{H}_2CH(CH_2CH_3)CH_2-$), 3.31 (s, 3H, $-OSO_2-C\underline{H}_3$), 3.31 (s, 3H, $-OSO_2-C\underline{H}_3$), 1.73 (m, 1H, $-CO_2CH_2C\underline{H}(CH_2CH_3)CH_2-$), 1.51-1.25 (m, 8H, $-CO_2CH_2CH(C\underline{H}_2CH_3)(C\underline{H}_2)_3CH_3$), 0.98-0.83 (m 6H, $CO_2CH_2CH(CH_2C\underline{H}_3)(CH_2)_3C\underline{H}_3$).

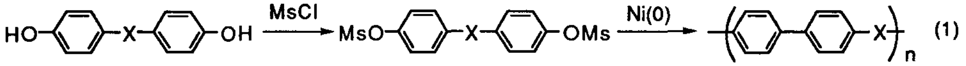
1-(4-Methylsulfonyloxyphenyl)-2-(4-methylsulfonyloxy-4'-biphenylyl)butane. (78%): white crystals; mp = 90-91 °C (toluene); ^{1}H-NMR δ 7.60 (d, *J* = 8.6 Hz, 2H, *m* to $-OSO_2-$ on the biphenyl), 7.46 (d, *J* = 8.6 Hz, 2H, *m* to $-CH_2-CH(CH_2CH_3)-$ on the biphenyl), 7.34 (d, *J* = 8.6 Hz, 2H, *o* to $-CH_2-CH(CH_2CH_3)-$ on the biphenyl), 7.18-7.04 (m, 6H, *o* to , $-OSO_2-CH_3$ on the monophenyl and on the biphenyl), 3.17 (s, 3H, $-OSO_2-C\underline{H}_3$ on the biphenyl), 3.13 (s, 3H, $-OSO_2-C\underline{H}_3$ on the monophenyl), 2.89 (m, 2H, $-C\underline{H}_2-CH(CH_2CH_3)-$), 2.68 (m, 1H $-CH_2-C\underline{H}(CH_2CH_3)-$), 1.75 (m, 2H, $-C\underline{H}_2CH_3$), 0.77 (t, 3H, *J* = 7.2 Hz, $-CH_2C\underline{H}_3$).

Polymerization: In a typical polymerization, a 125 mL Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (114 mg, 0.175 mmol), Zn (800 mg, 12.25 mmol), Et_4NI (675 mg, 2.625 mmol), 3,3-bis(4-methylsulfonyloxyphenyl)-1-[3*H*]isobenzofuranone (778 mg, 1.75 mmol) and a stir bar. The tube was sealed with a rubber septum and the contents were dried under vacuum ($1x10^{-3}$ mm Hg) at 22 °C for 3h. The reactants were then placed under an Ar atmosphere and 1.5 mL of dry THF were added *via* a syringe through the septum. The mixture was stirred first at 22 °C for 5 min (at which time the color of the mixture gradually changed to deep red-brown) then at 67 °C for 24h. The reaction mixture was poured into 100 mL of methanol acidified with 25 mL of conc. HCl. The resulting precipitate was filtered, dissolved in $CHCl_3$ (2 mL) the solution was filtered then precipitated into methanol (100 mL), filtered and dried *in vacuo* (350 mg, 70%). The polymer was further purified by reprecipitation into methanol from $CHCl_3$.

Techniques. Melting points are uncorrected and were determined with a Uni-Melt capillary melting point apparatus. ^{1}H-NMR (200 MHz) were recorded at 20 °C on a Gemini-200 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Relative molecular weights and purities were determined on a Perkin-Elmer Series 10-LC GPC/HPLC instrument, equipped with a LC-100 column oven, a Nelson Analytical 900 Series data station, and a UV detector using THF as solvent, (1mL/min, 40 °C) and two PL gel columns of $5\cdot10^2$ and 10^4 Å. A calibration plot constructed with polystyrene standards was used for the determination of the relative molecular weights. A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) calibrated with In and Zn standards and equipped with a TAC7/DX thermal analysis controller was used to record the thermal transitions at 20 °C/min. An Olympus BX40 optical polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor, was used to analyse the textures.

Results and Discussion

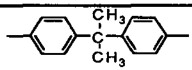
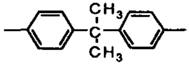
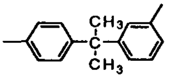
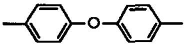
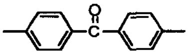
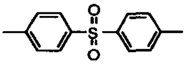
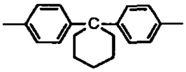
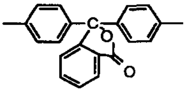
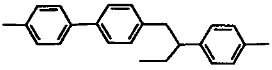
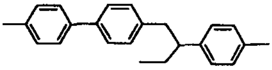
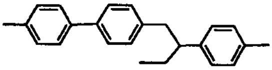
The general procedure for the preparation of aromatic biphenylene polymers is based on the Ni(0)-catalyzed homocoupling reaction of arylene bismesylates derived from bisphenols (eq 1):



The Ni(0) catalyst was prepared *in situ* from $NiCl_2(PPh_3)_2$, Zn, and Et_4NI in THF (9,21). Et_4NI is believed to function as a bridging agent between Ni and Zn, thus facilitating electron transfer in the reduction of Ni(II) to Ni(0) and of Ni(III) to Ni(I) (9).

The results obtained from the homopolymerization of various aryl bismesylates are summarized in Table 1. Relatively low yield and low molecular weight are obtained from 2,2-(bismethylsulfonyloxyphenyl)propane in the absence of additional PPh_3 (Table 1, entry 1). The resulting polymer is soluble however in common solvents such as $CHCl_3$.

Table 1. Ni(0)-Catalyzed Homopolymerization of Aryl Bismesylates

Entry	Ar	Yield (%)	Mn	Mw/Mn	DP	Tg (°C)	Tm (°C)	Tni (°C)
1		54	1393	1.4	7	-	-	-
2		90	nd[a]	insoluble	-	128	-	-
3		94	2490	2.0	13	92	-	-
4		98	nd	insoluble	-	-	250	-
5		100	nd	insoluble	-	-	340	-
6		90	nd	insoluble	-	-	-	-
7		99	nd	insoluble	-	187	-	-
8		70	3440	1.5	12	-	-	-
9		79	2900	1.2	30	127	-	287
10		6	1063	1.17	3	-	-	206
11		11	755	1.14	2	45	-	81

[a] nd = not determined

The addition of extra PPh_3 to the catalyst significantly enhances the yield and molecular weight for less reactive and/or sterically hindered aryl bismesylates. Addition of 0.6 equiv. of PPh_3 to the reaction mixture increased the yield dramatically but lead to an insoluble polymer, probably due to the increased degree of crystallinity (Table 1, entry 2).

Increasing the configurational entropy of the main chain through a proper combination of kinked phenylenic units was employed in other cases to obtain soluble polyphenylenes (3). Polymerization of 2-(3-methylsulfonyloxyphenyl)-2-(4'-methylsulfonyloxyphenyl)propane resulted in the formation of a soluble polymer with an average degree of polymerization (DP) of 13 which indicates approximatively 26 phenylene units in the main chain (Table 1, entry 3). Although this polymer is very soluble, further increases in molecular weight were not obtained. This is consistent with the deactivating influence of *p*-alkyl substituents through an electron-donating effect in the Ni(0) catalyzed homocoupling reaction of aryl mesylates (9). In addition, in certain cases, the bulkiness of the substituent group may also impede the reaction. Polymerization of unsubstituted aryl bismesylates containing ether, carbonyl, and sulfonyl moieties gave insoluble polymers due to their regioregular microstructure which produced crystalline materials (Table 1, entries 4 to 6).

The effect of introduction of a bulky group between the two aryl units of the bismesylates was investigated (Table 1, entries 7-9). When this group was symmetyrical, a regioregular, insoluble, polymer was obtained (Table 1, entry 7). From these results (Table 1, entries 2 & 4 - 7) it can be deduced that the homopolymerization of symmetrical bismesylates of this type leads to insoluble polymers with a high degree of rigidity and crystallinity.

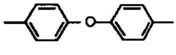
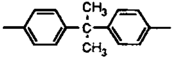
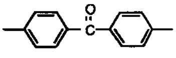
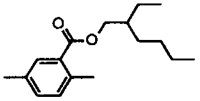
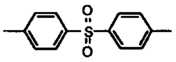
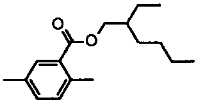
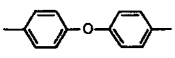
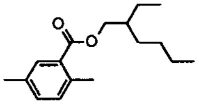
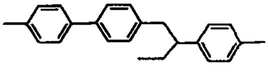
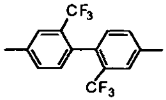
By contrast, the introduction of an unsymmetrical bulky unit between the two aryl groups resulted in an increase in the solubility of the corresponding polymers. The bismesylate derivative of phenolphtalein (3,3-bis(4-hydroxyphenyl)-1[3*H*]-isobenzofuranone) containing bulky benzofuranone groups was found to undergo Ni(0)-catalyzed polymerization, resulting in a quite soluble polymer, with an average DP of 12. (Table 1, entry 8).

The presence of an asymmetrical 1-(ethyl)ethyl linkage between a phenyl and a biphenyl unit in 1-(4-methylsulfonyloxyphenyl)-2-(4-methylsulfonyloxy-4'-biphenylyl)butane lead again to a soluble, regioirregular polymer with an average DP of 10, corresponding to 30 phenylene units (distributed in diads, triads and tetrads) (Table 1, entry 9). Linear, soluble, lower molecular weight oligomers of the same structure were also isolated (SiO_2, $CHCl_3$/Hexanes = 1/1) from a polymerization performed at lower monomer concentration (Table 1, entries 10 and 11). In these three cases, both the regioirregularity imparted by the random distribution of all the possible head/tail combinations as well as the presence of asymmetric substituents induced solubilization. A second effect of the depression in the melting temperature was to uncover a liquid crystaline phase. A typical Schlieren nematic texture was observed by optical polarized microscopy (Table 1, entries 9, 10 and 11).

Previously we have shown (14) that copolymerization of two different aryl bismesylates gave highly soluble, poly(*p*-phenylene)s due to a significant increase in configurational entropy of the main chain. Copolymerization of 4,4'-bis(methylsulfonyloxy)phenyl ether with 2,2-bis(4-methylsulfonyloxy)propane in a 1:1 mol ratio gave a highly soluble polymer containing approximatively 32 phenylene units in the main chain (Table 2, entry 1). Although parent homopolymers are insoluble (Table 1, entries 2 and 4), random copolymerization of the monomers which have similar reactivity towards the Ni(0) catalyst reduces the intermolecular chain packing forces and increases the chain entropy resulting in an enhanced solubility. Soluble and higher molecular weight polymers could threfore be obtained even from the highly crystallizable carbonyl, sulfonyl and ether containing symmetrical aryl bismesylates *via* copolymerization with (2-ethylhexyl)-2,5-bis(methylsulfonyloxy)benzoate (Table 2, entries 2-4).

Table 2 Ni(0) Catalyzed Copolymerization of Aryl Bismesylates

$$n\ \mathrm{MsO{-}Ar{-}OMs}\ +\ m\ \mathrm{MsO{-}Ar'{-}OMs}\ \xrightarrow{\mathrm{Ni(0)}}\ \left(\mathrm{Ar}\right)_n\left(\mathrm{Ar'}\right)_m$$

Entry	Ar	Ar'	Yield (%)	Mn	Mw/Mn	m+m	Tg (°C)	Tni (°C)
1			97	2820	1.8	16	135	-
2			94	3690	2.0	18	41	-
3			95	4150	1.8	19	64	-
4			89	3780	2.7	19	-	-
5			85	7400	1.4	64	164	316

We have previously shown that this monomer (14) induces solubilization in related PPP polymers prepared by Ni(0) catalyzed copolymerization reactions. The highest molecular weight was obtained with the strongly electron withdrawing sulfonyl containing aryl bismesylate (Table 2, entry 3). The sulfonyl containing monomer shows a high reactivity while the (2-ethylhexyl)-2,5-bis(methylsulfonyloxy)benzoate comonomer has a dimished reactivity due to severe steric hindrance. By copolymerization, numerous oligophenylene based constitutional isomers are generated in the main chain, and, in addition to the bulkiness of the 2-ethylhexyl group, these constitutional isomers increase the configurational entropy of the chain, decrease the crystallinity and, subsequently, increase the solubility.

In order to obtain high molecular weight polymers, the substituents on the phenyl rings should favor electronically the coupling reaction. Their size should be small enough so that they do not sterically hinder the reactive functionality. We have recently demonstrated that these requirements are satisfied by the trifloromethyl (-CF_3) or trifloromethoxy (-OCF_3) groups (15). Through its strong electron withdrawing effect, the -CF_3 group increases both the reactivity of the monomer and the acidity of the hydrogens on the phenylene units, in such a way that they can act as additional substituents, thereby increasing the polymer regioirregularity and solubility. Copolymerization of 1-(4-methylsulfonyloxyphenyl)-2-(4-methylsulfonyloxy-4'-biphenylyl)butane with 2,2'-bis(trifloromethyl)-4,4'-bis(methylsulfonyloxy)biphenyl in a 1:1 mol ratio lead to a very soluble, high molecular weight polymer with an average DP of 25, corresponding to approximatively 64 phenylene units (as diads and longer oligo(*p*-phenylene) sequences) (Table 2 entry 5). Both monomers contribute to the solubilization of the polymer, which, as in the case of their parent homopolymers (Table 1, entry 9 and reference 15) displayed a very broad (>150 °C) enantiotropic nematic mesophase.

Conclusions

A series of new poly(arylene)-type polymers and copolymers containing alternating oligophenylene segments and various functional groups (X) was synthesized using the general and inexpensive Ni(0)-catalyzed polymerization of bismesylates derived from commercially availble or synthetically readily accessible bisphenols. Symmetrical X groups lead to highly crystalline, insoluble polymers, whereas asymmetrical X groups as well as the use of comonomeric units generated soluble, relatively high molecular weight materials. Monomers containing both solubilizing and activating substituents (-CF_3) and asymmetrical X groups (-CH_2-CH(Et)-) afforded the highest molecular weight polymers. In certain cases, broad enantiotropic nematic phases were observed. Although these preliminary experiments were not optimized, they demonstrate that a large variety of polymeric properties can be obtained by using this new and very valuable synthetic procedure through the fine tuning of the monomer structure and by copolymerization.

Acknowledgment

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