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Poly(*p*-phenylenes) with Well-Defined Side Chain Polymers

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Summary: 1,4-Dibromo-2,5-bis(bromomethyl)benzene and benzene-2,5-dibromomethyl-1,4-bis(boronic acid propanediol diester) were used as bifunctional initiators in Atom Transfer Radical Polymerization (ATRP) of styrene or in cationic ring opening polymerization (CROP) of tetrahydrofuran in conjunction with CuBr /2,2'-bipyridine or $AgSbF_6$, respectively. The resulting well-defined macromonomers with low polydispersities, bearing functional groups as bromine or boronic ester were used in Suzuki or Yamamoto type couplings, leading to poly(*p*-phenylene)s (PPPs) with polystyrene (PSt), polytetrahydrofuran (PTHF) or alternating PSt/PTHF side chains. The new polymers were characterized by GPC, ^{1}H-NMR, ^{13}C-NMR, IR and UV analysis. Thermal behavior of the precursors PSt or PTHF macromonomers and the final polyphenylenes were investigated by TGA and DSC analyses and compared.

Introduction

Fully conjugated polymers represent an attractive class of materials for a large number of applications in electronic conductivity[1,2] and optoelectronics[3,4]. Poly(*p*-phenylene)s (PPPs) are one of potentially most useful polymers for organic conducting materials and organic polymeric ferromagnets due to their extended planar conjugated π system, along with high strength and high heat resistance[5,6]. Different synthetic methods of PPPs have been developed in the recent years. The oxidative coupling of benzene in the presence of Lewis acids and oxidants[7], the Wurtz-Fittig reaction between dibromobenzene with metallic Na[8], the Ni-catalyzed coupling reaction of Grignard reagents[9] and the coupling reactions of dihalobenzenes catalyzed by $NiCl_2$[10] have been the typical methods for the synthesis of PPPs. The above mentioned classical methods are inadequate due to the presence of side reactions that introduce regiochemical irregularities and limit the molecular weight. Electrochemical polymerizations[11], also a method for the PPP synthesis, do allow the fabrication of thin

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films, but the molecular weight of the polymer is limited by its insolubility, and regiochemically flaws again appear to be present[12]. On the other hand, elegant strategies have been developed for the synthesis of defect-free high molecular weight samples of underivatized PPP[13] using soluble precursor routes. Current methodologies for the direct synthesis of derivatized PPP and other soluble polyarylenes are primarily based upon nickel- and palladium- mediated cross-coupling reactions[14] due largely to their preservation of regiochemistry and nearly quantitative yields[15, 16].

The cross-coupling of aryl halides and aryl boronic acids (Suzuki coupling)[17] is one of the most prevalent methods for the synthesis of polyarylenes and can be applied to monomers carrying functional groups[18]. In order to improve the solubility, by adopting this method to polymer synthesis, a series of functionalized PPP with pendant alkyl groups has been reported by Wegner *et al*[19-21]. Moreover, PPPs containing oligo(oxyethylene) side chains, soluble in common organic solvents at room temperature were obtained, too [22].

Living polymerizations are chain growth reactions that proceed in the absence of irreversible chain transfer and chain termination[23]. So, polymers can be end-functionalized and block copolymerized with other monomers. Thus, it has opened new pathways to create many new materials with vastly differing properties by varying the topology of the polymer (comb, star, dendritic, etc.), the composition of the polymer (random, periodic, graft, etc.), or the functional groups at various sites of the polymer (end, center, side)[24]. Atom Transfer Radical Polymerization (ATRP), introduced by Matyjaszewski[25, 26], has been proven to be effective for a wide range of monomers and appears to be a powerful tool for the polymer chemists, providing new possibilities in structural and architectural design and allowing the development of new products with monomers currently available. ATRP was also used for obtaining linear copolymers with one conjugated sequence[27].

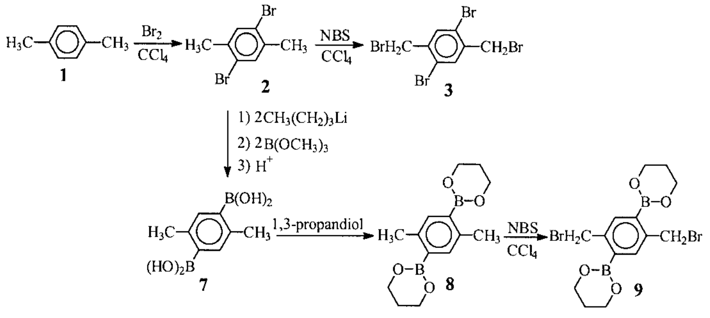
The reaction between organic halides and silver salts with nonnucleophilic counter anions generates species capable of initiating cationic ring opening polymerization (CROP) [28, 29]. This method was used for grafting PTHF from halogenated polymers[30], for synthesis of star type polytetrahydofuran[31] and to synthesize linear blockcopolymers with polystyrene[32]. Several other macromolecular architectures by using combination of CROP with ATRP[33] and reverse ATRP[34] for the synthesis of linear and graft copolymers were also reported.

The purpose of this contribution is to report the synthesis of comb-like PPPs carrying usual polymers as side chains, starting from well defined macromonomers obtained by ATRP or CROP.

Synthetic Strategies

Even numerous PPP bearing different types of pendant side groups were synthesized to induce different properties in PPP (see Table 1), grafted copolymers having π-conjugated backbones are quite limited.

Benzylbromides are efficient initiators for both ATRP[23] and CROP[30]. On the other hand arylhalides does not initiate these types of reactions. Accordingly, bifunctional initiators for the controlled polymerizations, that contain also groups that can react in Suzuki or Yamamoto couplings, were synthesized as shown in Scheme 1[54-56].



Scheme 1. Synthesis of bifunctional initiators for ATRP or CROP

Synthesis of Macromonomers

1,4-Dibromo-2,5-bis(bromomethyl)benzene (**3**) or benzene-2,5-dibromomethyl-1,4-bis(boronic acid propanediol diester) (**9**) were used as initiators in ATRP of styrene (St) in conjunction with CuBr /2,2'-bipyridine as catalyst (Scheme 2). As these polymers were intended to be used in further polymerization reactions, the efforts were directed toward obtaining a low molecular weight combined with a low polydispersity. Some results of the ATRP experiments for styrene are summarized in Table 1.

As can be seen from the Table 1, **3** and **9** are effective initiators for ATRP of styrene and the theoretical molecular weights fit very well with the measured ones. The GPC traces are unimodal and narrow, indicating that no side reaction occurred. Due to the low molecular weights, the results from the last three experiments could be verified by ^{1}H-NMR analysis. The found values are close to those found from GPC analysis.

Table 1. Types of PPPs containing different side groups and some of their properties

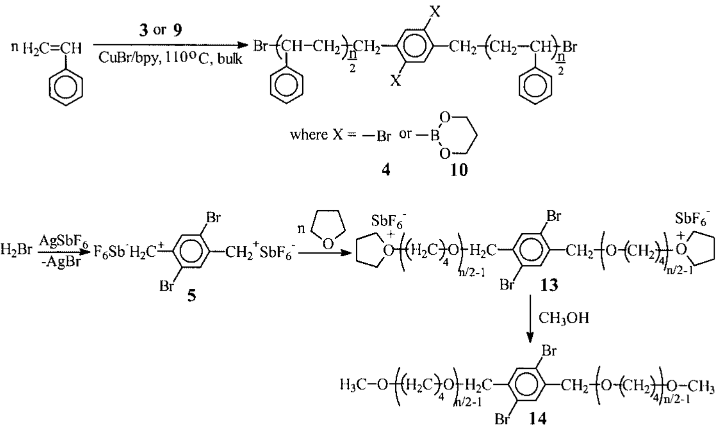
Type of PPP		Method of Synthesis	Properties	Ref.
PPPs with alkyl, **alkoxy, or hydroxy side groups**	$(CH_2)_n$-CH_3, n=5 - 7	Yamamoto	Soluble in common organic solvents, DP < 15	35
	$(CH_2)_n$-CH_3, n=0 - 15	Suzuki	Soluble in common organic solvents, DP > 100, Exhibits thermotropic liquid crystalline behaviour (R=dodecyl)	19, 21
	-CH_2-O-R; R= butyl, hexyl, C_6H_4CN	Suzuki	Soluble in common organic solvents, DP = 30-65	36, 37
	-$(CH_2)_x$OPh-R; x=1,6; R=H, CO_2CH_3,	Suzuki	Applied in LED	38,39
	-O-CH_2-CH(CH_3)-CH_2-CH_3	Suzuki	Optically activite	40
	-OH	Yamamoto	Soluble in DMF	41
PPPs with carboxyl or sulfonic ester groups	-COOH	Suzuki	Insoluble in organic solvents in free acid form, Soluble in dilute aqueous base, Highly birefringence in film form.	42
	-O$(CH_2)_3SO_3$Na, -SO_3R; R= p-tolyl or 3,5-(di-*t*-butyl)benzene, -O-CH_2-C_6H_4-SO_3Na	Suzuki	Polyelectrolyte, Dopable (n-type or p-type) in lyotropic solution in DMSO or thin film on ITO glass	43-45
PPPs with diketo or diethynyl side groups	-COR; R = C_6H_5, C_6H_{13},	Suzuki	Precursors for ladder polymers	46, 47
	-C C-C_6H_4-OR; R= *n*-alkyl	Suzuki	Precursors for ladder polymers	48
	-CO-CH_3; -CHO; -COC_6H_5 (*m*-PPP)	Yamamoto	Soluble in DMF, DMAc, DMSO, THF, NMP	49
Dendronized PPPs	-CH_2-O-C_6H_3(CH_2OC_6H_3)$_2$... (Frechet-type dendritic fragments of low generations)	Suzuki	Exceptionally rigid and attain a cylindrical shape in solution and when adsorbed on surfaces	50, 51
PPPs with polymeric side chains	oligo(etyhylene oxide)	Suzuki,	Amphiphilic, Applied as separators in rechargeable solid state Li cells,	22, 52
		Yamamoto	Exhibits liquid crystalline properties	53

Table 2. Conditions and Results of ATRP of Styrene using 1,4-Dibromo-2,5-bis(bromometyl)benzene in the Presence of CuBr/bpy Complex*

Sample	Initiator	$[I]_o \times 10^2$ mol L^{-1}	Time, min	Conversion, %	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n	$M_{n,H\text{-}NMR}$
A	**3**	2	240	35	16450	16830	1.42	nd
B	**3**	4	120	47	11000	10700	1.33	nd
C	**3**	10	45	32	3330	3350	1.31	3542
D	**3**	10	55	38	3880	3800	1.39	3750
E	**9**	10	50	47.5	4750	4700	1.24	4400

* T = 110°C; Init./CuBr/bpy mol ratio = 1/2/6, $[St]_o$ = 8.7 mol/L(bulk)
nd - not determined

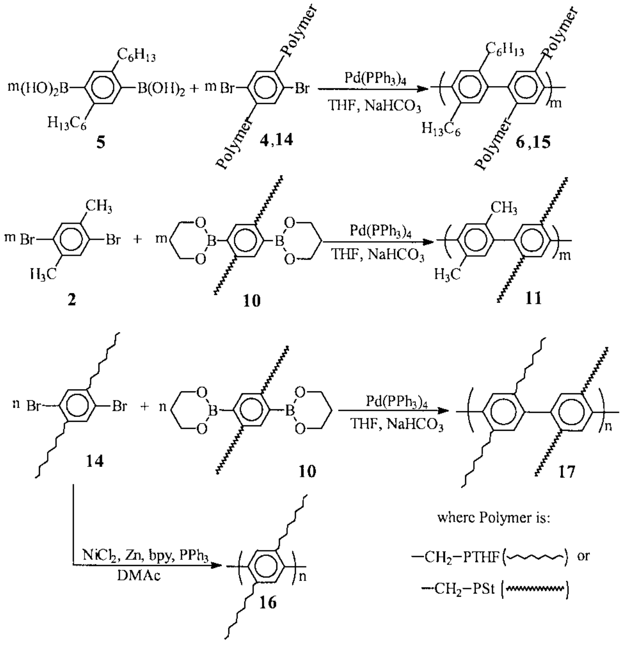
3 was also used for CROP of THF in accordance with Scheme 2[56]. The molecular weight of the resulted PTHF calculated from ^{1}H-NMR spectrum ($M_{n,HNMR}$=4200) was considered to be more reliable than that obtained by GPC ($M_{n,GPC}$ = 5300, M_w/M_n = 1.34, after applying the correction factor [57]) and used for further calculations.



Scheme 2. Synthesis of macromonomers by ATRP or CROP

Synthesis of Poly(p-phenylenes) with macromolecular side chains

The resulting macromonomers (Samples D and E from Table 1 in the case of PSt), having two functional groups (bromine or boronic diester) directly connected to the central benzene ring, are proper for obtaining PPPs with side polymeric chains through Suzuki polycondensation in combination with aromatic diboronic acids or aromatic dihalides, respectively, in the presence of a Pd(0) catalyst, or Yamamoto coupling reactions using Ni based catalysts. Thus, PPPs with alternating PSt/hexyl or methyl side chains (**6** or **11**, respectively) and PTHF/hexyl (**15**) were obtained by Suzuki polycondensations of macromonomers **4**, **10** and **14** in combination with the appropriate reaction partners. (Scheme 3). Moreover, by reacting two macromonomers with different functional groups (**10** and **14**) a PPP with alternating PSt and PHF side chains was obtained (**17**). The bromine containing macromonomers can also be homopolymerized by Yamamoto reaction. A PPP with PTHF side chains was synthesized by reacting this compound in the presence of $NiCl_2$ catalyst. White powders with good solubilities at room temperatures in common organic solvents were obtained. Polymer **17** resulted as a sticky light brown gum with tendency of coagulation.



Scheme 3.
Synthesis of poly(*p*-phenylene)s with macromolecular side chains

The GPC traces of PPPs in comparison with those of the starting macromonomers are presented in Figures 1 and 2 and the molecular weigths are shown in Table 3. Usually the GPC traces are multimodal and broader than those of the starting polymers. Multimodal GPC traces were reported for polyarylenes with side alkyl radicals, by other authors, as well[58]. Due to the expected shape of the macromolecules, with very long polystyrene side chains, the obtained molecular weights does not give sufficient information about the polymerization degrees. It is quite possible that the length of despite this, the GPC data shows that new polymers were obtained.

Table 3. GPC data for PPPs with polymeric side chains

Polymer	M_n	M_w/M_n
6	19800	4.7
11	18500	1.6
14	28500	1.71
15	21200	1.82
17	41000	1.67

Spectral characterization of the new PPPs (^{1}H-, ^{13}C-NMR, IR) was reported in our earlier works[54-56]

UV absorption spectra shows that important differences appear for the PPPs as compared with the starting macromonomers. UV absorption spectra of **4** and **6** registered in CH_2Cl_2 solutions with the same concentrations are shown in Figure 1. The absorption from 226 nm is present in both spectra, but much higher in the case of polyphenylene. The shoulder from 254 nm in polystyrene spectra becomes a very broad and pronounced peak in polyphenylene. Normal and alkyl substituted PPP has two absorptions in UV in the same region (200-300 nm) [19]. In our case, the increase in the absorbance at 226 nm and the appearance of the second strong absorption band are due to the presence of supplementary phenylene rings from the main chain. The same behaviour was found when UV spectra of macromonomer **10** and polyphenylene **11** were registered from solutions with the same concentrations.

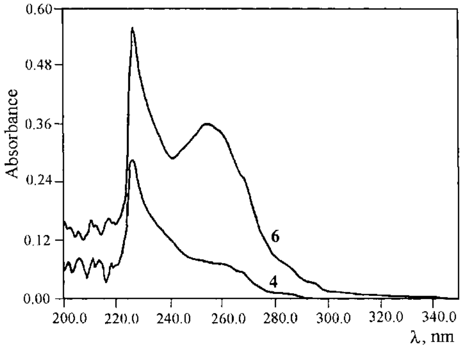


Figure 1. UV spectra of PSt macromonomer **4** and PPP with alternating hexyl and PSt side chains **6**

Even more evident are the changes in the UV spectra for the PTHF containing PPPs as comparing with the starting macromonomer **14** (Figure 2). A strong absorption with the maximum at 228 nm and an additional shoulder between 250-270 nm in the case of **15**, was taken as further evidence for the formation of poly(*p*-phenylene) backbone.

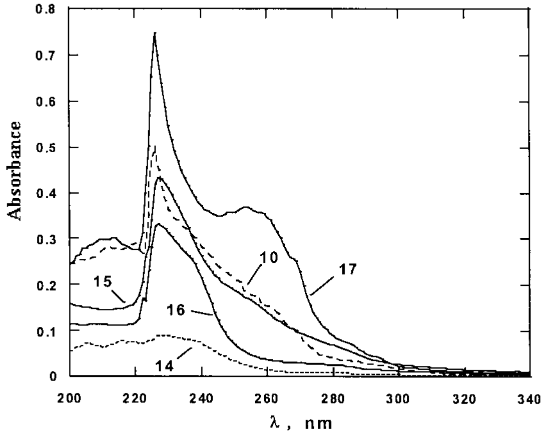


Figure 2. UV absorption spectra of PPPs with PTHF side chains as compared with the starting macro-monomers **10** and **14**

Polymer **17**, that contains both PSt and PTHF side chains has an UV absorption spectrum similar with those of PPPs containing only PSt (**6** and **11**) with an intense peak at 226 nm a very broad and pronounced one at 254 nm.

Thermal Behaviour of the PPPs with Macromolecular Side Chains

The thermal behaviour of synthesized polymers was investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), under nitrogen, the heating rate being 10°C/min. The results of TGA analyses are shown in Table 4. The starting macromonomers have two deccomposition stages. During the first one, the weight loss is between 3.5-5%. This stage is associated with the loss of the functional groups directly linked to the central benezene ring. The second deccomposition stage is due to the degradation of the main chain. The first stage is missing in the case of PPPs, as the functional groups were consumed during the coupling reactions. For these polymers the weight loss is associated only with the degradation of the polimeric side chains.

Usually the polyphenylenes are thermostable. This behaviour is shown for our polymers, too. While at 450°C the starting macromonomers are almost completely deccomposed, in the case of PPPs the char yield is significant and is due to the main conjugated chain that degradates at higher temperatures.

Table 4. The TGA values of macromonomers and synthesized polyphenylenes

Polymer	IDT (^{o}C)	T_{w10} (^{o}C)	Y_{C450} (%)
4	190; 300	340	1
6	258	360	10
10	198.5; 315	382	2
11	300	390	23
14	185; 297.5	359	1
15	283	372	12
16	311.8	400	15
17	230	357.3	7

IDT – initial degradation temperature

T_{w10} – The temperature for which the weight loss is 10%

Y_{C450} – The percent of char yield at 450 °C

DSC traces of PSt based macromonomers and the corresponding PPPs are presented in Figure 3. All the polymers presents the glass transition temperatures characteristic to polystyrene between 82-100^{o}C. In the case of **6**, the glass transition temperature (T_g = 82^{o}C) is lower that that of the starting macromonomer, **4**. The DSC trace of poly(*p*-phenylene) containing only hexyl moieties as pendant groups showed a transition near to 80^{o}C that was associated by the authors with the side chain melting [19]. The low transition temperature in this case can be due to the presence of hexyl groups alternating with PSt side chains. This behaviour is not found in the case of **10** where PSt alternates with methyl groups.

DSC measurements of polymers containing PTHF evidence that melting points characteristic for this polymer appears for the starting macromonomer and for PPPs **15** and **16** between 31-35 °C (Figure 4). Polymer **15** shows also a glass transition at 147.5^{o}C. The presence of the glass transition proved the obtainment of a new poly-*p*-phenylene type material.

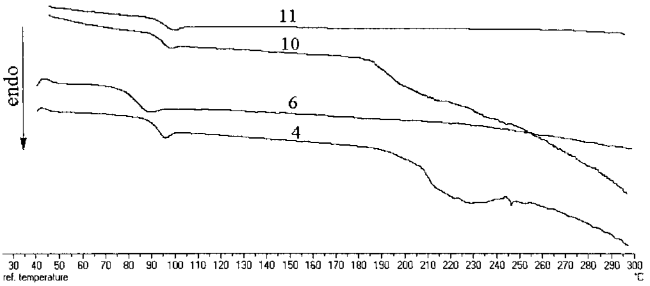


Figure 3. The DSC traces of PSt based polymers

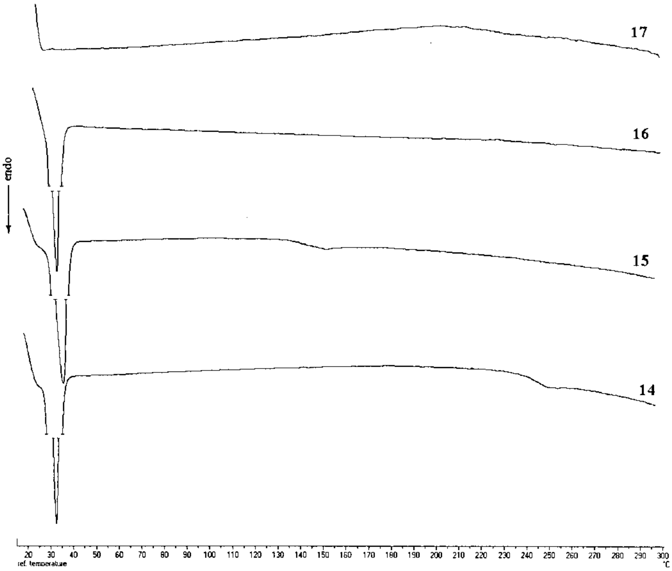


Figure 4. DSC traces of the polymers containing PTHF

It was shown in the case of PPP with polyethylene oxide side chains that long chains are less affected by the limited mobility than short ones [53]. In our case macromonomers **4**, **10** and **14** have sufficiently high molecular weights, so **6** and **11** preseved the transition temperature of PSt and **9** and **11** the crystalinity of the starting PTHF. A special behaviour appears in the case of **17**, the PPP that posses both PTHF and PSt alternating side chains. In the DSC trace of polymer **17** the endothermal peak associated to the melting phenomenon and the glass transition are missing. The absence of the melting characteristic for the PTHF side chains is due to the loss of the crystallinity that could be a consequence of alternation with the polystyrene side chains induced by Suzuki polycondensation. The absence of the glass transition specific to the PSt side chains can be also due to the alternating structure of **17**. The polymerization degree of PTHF side chain is higer than that of PSt side chains. Moreover, each repeating unit of PTHF is longer than that of PSt and we can suppose that an inclusion phenomenon of PSt chains inside of PTHF ones can take place, leading to a decreasing of freedom for PSt segments and hindering their thermal mobility.

Conclusions

By Atom Transfer Radical Polymerization (ATRP) or Cationic Ring Opening Polymerization (CROP) new macromonomers containing bromine or ester boronic functional groups were synthesized and characterized. Using them in Suzuki polycondensation or Yamamoto coupling, new PPPs graft copolymers with complex macromolecular architectures were obtained. The structures of the synthesized polymers were proved by spectral methods and thermal properties were studied by TGA and DSC. These new materials are more thermostable than the starting macromonomers due to the presence of conjugated main chain.

The PPPs graft copolymers may find applications in various areas such as light emitting diodes and for sensing devices. Further work would be required to understand their morphology and thermal properties.

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