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Poly(*p*-phenylene) graft copolymers with polytetrahydrofuran/polystyrene side chains

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Abstract

1,4-Dibromo-2,5-bis(bromomethyl)benzene was used as a bifunctional initiator in cationic ring opening polymerization (CROP) of tetrahydrofuran. The resulting macromonomer, with a central 2,5-dibromobenzene ring, was reacted in combination with 2,5-dihexylbenzene-1,4-diboronic acid by a Suzuki coupling, in the presence of $Pd(PPh_3)_4$ as catalyst, leading to a poly(*p*-phenylene) (PPP) with alternating polytetrahydrofuran (PTHF) and hexyl side chains. A polystyrene (PSt) based macromonomer with a central benzene ring bearing cyclic boronic acid propanediol diester groups, synthesized by atom transfer radical polymerization (ATRP), was also used as partner for PTHF in the cross-coupling reaction. A PPP with alternating PSt and PTHF side chains was obtained. PTHF macromonomer was also homopolymerized by a Yamamoto reaction. The resulting PPPs have high solubility in common organic solvents at room temperature. The new polymers were characterized by GPC, ^1H NMR, ^{13}C NMR, IR and UV analysis. Thermal behavior of the precursor PTHF macromonomer and the final polyphenylenes were investigated by TGA and DSC analyses and compared. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cationic polymerization; Macromonomer; Suzuki coupling

1. 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]. Recently, the application of poly(phenylene vinylene)s (PPV) to light emitting diodes [5,6] and light-emitting electrochemical cells [7] stimulated the investigations in the domain of polyaryl derivatives. Poly(*p*-phenylenes) (PPP) are one of the 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 [8,9].

Current methodologies for the direct synthesis of derivatized PPP and other soluble polyarylenes are primarily based upon nickel- and palladium-mediated cross-coupling reactions [10] largely due to their preservation of regiochemistry and nearly quantitative yields [11,12].

The cross-coupling of aryl halides and aryl boronic acids (Suzuki coupling) [13] is one of the most common methods for the synthesis of polyarylenes [14]. This method has several advantages. For example, the procedure is quite simple and the reaction is insensitive to moisture. Furthermore, this coupling reaction can be applied to monomers carrying functional groups [15]. In order to improve the solubility, by adapting this method to polymer synthesis, a series of functionalized PPP with pendant alkyl groups has been reported by Wegner et al. [16–18]. Moreover, PPPs containing oligo(oxyethylene) side chains, soluble in common organic solvents at room temperature were also obtained [19]. However, to our best knowledge, grafted copolymers having π-conjugated backbones are quite limited.

The reaction between organic halides and silver salts with non-nucleophilic counter anions generates species capable of initiating cationic ring opening polymerization (CROP) [20,21]. This method was used for grafting PTHF from halogenated polymers [22], for synthesis of star type polytetrahydofuran [23], and for synthesis of linear block copolymers with polystyrene [24]. Several other macromolecular architectures by using combination of CROP with atom transfer radical polymerization (ATRP) [25,26] and reverse ATRP [27] for the synthesis of linear and graft copolymers were also reported.

In previous works [28,29], we performed the synthesis of polystyrene based macromonomers with central 2,5-dibromobenzene (**1**) or benzene-2,5-bis(boronic acid propanediol

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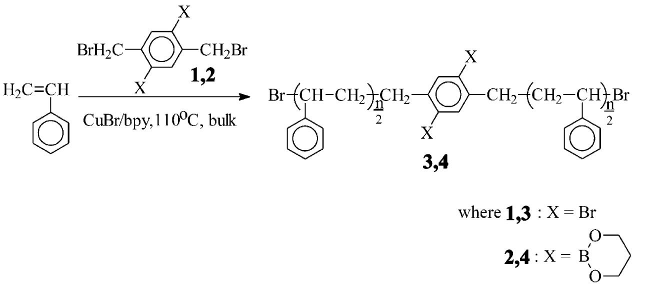


Scheme 1.

diester) (**2**) groups, via ATRP (Scheme 1), that were subsequently used in combination with 2,5-dihexylbenzene-1,4-diboronic acid or 2,5-dimethyl 1,4-dibromobenzene, respectively, for Suzuki couplings in the presence of $Pd(PPh_3)_4$ as catalyst. This way, comb-like PPP carrying vinyl polymers as side chains were obtained. The methodology opens new pathways to create materials with vastly different properties by varying the topology of the polymers.

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

2. Experimental

2.1. Materials

All the solvents were purified and dried by usual methods. Tetrahydrofuran (THF) was dried over potassium hydroxide, distilled over sodium wire, and finally distilled over sodium/benzophenone ketyl prior to use.

1,4-Dibromo-2,5-bis(bromomethyl)benzene (**1**) was prepared as in Ref. [30]. ^1H NMR ($CDCl_3$): δ(ppm) = 4.5 (s, 4H, CH_2), 7.65 (s, 2H, aromatic).

The synthesis of bifunctional initiator (**2**) and the preparation by ATRP of the corresponding polystyrene (**4**) was reported elsewhere [29]. $M_{n,GPC} = 4700$, $M_w/M_n = 1.24$.

2,5-Dihexylbenzene-1,4-diboronic acid was synthesized following literature procedures [16]. ^1H NMR (acetone-d_6): δ(ppm) = 0.87 (m, 6H, CH_3), 1.3 (m, 12H, CH_2), 1.55 (m, 4H, βCH_2), 2.74–2.78 (t, 4H, αCH_2), 7.09 (s, 4H, B-OH), 7.33 (s, 2H, aromatic).

$AgSbF_6$, $Pd(PPh_3)_4$ (Aldrich), $NiCl_2$, Zn (Merk), 2,2′-bipyridine (bpy) and triphenylphosphine (PPh_3) (Flukes), were used as received.

2.2. Synthesis of dibrominated PTHF (7) by CROP

The polymerization was carried out under nitrogen atmosphere. Five millilitre of freshly distilled THF (61 mmol) was introduced into a Schlenk tube, heated in vacuo with a heat gun and flushed with dry nitrogen. 0.75 g of **1** (1.78 mmol) and 1.22 g (3.55 mmol) of $AgSbF_6$ were added under efficient stirring at 0 °C. After 20 min, methanol was added to the reaction mixture to terminate the polymerization. After centrifugation, the polymer was poured into methanol and cooled to −30 °C. The precipitated polymer was filtered off and dried in vacuo. An additional purification by passing the polymer through a silicagel column using THF as eluent and reprecipitating in methanol was performed. (Yield 58%). ($M_{n,HNMR} = 4200$, $M_w/M_n = 1.34$) Anal. $(C_4H_8O)_nC_{10}H_{12}O_2Br_2$. For $n = 54$ Calcd C 64.35; H 10.61; Br 3.78. Found C 64.67; H 10.49; Br 3.64.

2.3. Synthesis by Suzuki coupling of PPP with PTHF and hexyl alternating side chains (9)

An 100 ml three neck round bottom flask equipped with a condenser, a rubber septum, nitrogen inlet–outlet, and magnetic stirrer, was charged with 20 ml 1 M $NaHCO_3$ aqueous solution and 30 ml of THF. The solvents were previously degassed by bubbling nitrogen over a period of 30 min. The mixture was refluxed under nitrogen, 4 h, then it was let to arrive at room temperature.

A 20 ml three necks round bottom flask equipped in the same way as the previous one was charged under inert atmosphere with 1.26 g (0.3 mmol) PTHF (**7**), 0.1 g (0.3 mmol) 2,5-dihexylbenzene-1,4-diboronic acid (**8**) and 0.0052 g (0.0045 mmol) $Pd(PPh_3)_4$. Three millilitre of the mixture of solvents was introduced with a syringe through the septum. The reaction was maintained at reflux under vigorous stirring and with the exclusion of oxygen and light. After 12 h a supplementary 3 ml of the mixture of solvents was added. After 48 h the polymer was obtained by precipitation in cold methanol (−30 °C). Reprecipitation from THF solution provided a white powder (yield 75%). ($M_{n,GPC} = 28{,}500$ and $M_w/M_n = 1.71$) Anal. $[(C_4H_8O)_nC_{28}H_{40}O_2]_x$. For $n = 54$ Calcd C 68.11; H 11.05. Found C 67.96; H 10.92; Br 0.16.

2.4. Synthesis by Suzuki coupling of PPP with PTHF and PSt alternating side chains (10)

Grafted PPP with PTHF and PSt was prepared following the same procedure as above using 0.63 g (0.15 mmol) PTHF (**7**), 0.705 g (0.15 mmol) PSt (**4**) ($M_{n,GPC} = 4700$, $M_w/M_n = 1.24$) and 0.0026 g (0.00225 mmol) $Pd(PPh_3)_4$ in 2.2 ml of mixture of solvents. After 24 h a supplementary amount (2 ml) of mixture of solvents was added. After 48 h the polymer was precipitated into methanol at room temperature and a sticky light brown gum with tendency of coagulation was obtained (yield 87%). The same behaviour was obtained after several reprecipitations from THF or $CHCl_3$ in methanol. ($M_{n,GPC} = 40{,}850$ and $M_w/M_n = 1.67$) Anal. $[(C_4H_8O)_n(C_8H_8)_mC_{28}H_{18}O_2Br_2]_x$. For $n = 54$ and $m = 41$ Calcd C 78.58; H 9.12; Br 1.86. Found C 78.85; H 9.27; Br 1.93.

2.5. Synthesis by Yamamoto reaction of PPP with PTHF side chains (*11*)

A 20 ml three necks round bottom flask equipped with condenser, rubber septum, nitrogen inlet–outlet and magnetic stirrer was charged under nitrogen with 1.05 g (0.25 mmol) PTHF (**7**) 0.02 g (0.076 mmol) PPh_3, 0.506 g (7.74 mmol) Zn, 0.0019 g (0.0125 mmol) bpy, 0.0016 g (0.0125 mmol) $NiCl_2$ and 1.2 ml of dry dimethyl acetamide. The reaction was performed at 85 °C, under nitrogen. After several minutes the colour of the solution changed to brown, due to the complex formation. The mixture was stirred at the above-mentioned temperature for 24 h. Then, the polymer was precipitated in excess methanol/HCl mixture (v/v = 9/1), filtered and dried. The polymer was then redissolved in THF, passed through a silicagel column and precipitated in methanol. A white powder (yield 78%) was obtained ($M_{n,GPC} = 21{,}150$ and $M_w/M_n = 1.82$). Anal. $[(C_4H_8O)_nC_{10}H_{12}O_2]_x$. For $n = 54$ Calcd C 66.89; H 11.02. Found C 66.62; H 10.89; Br not detected.

2.6. Analysis

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 250 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. GPC measurements were performed with an Agilent1100 RI apparatus equipped with three Waters Styragel columns HR series (4, 3, 2 narrow bore), at a flow rate of 0.3 ml/min and the temperature of the refractive index detector of 30 °C, and THF as eluent. Molecular weights were calculated using polystyrene standards. IR spectra were recorded on a Shimadzu IR-470 infrared spectrophotometer using films from CH_2Cl_2 solutions deposited on NaCl pellets. UV analyses were performed on a Lambda 2 Perkin Elmer Spectrometer from CH_2Cl_2 solutions with the same concentration (0.044 g l^{-1}).

DSC analyses were performed on a Perkin Elmer Differential Scanning Calorimeter DSC-6, in the range 20–300 °C, under nitrogen, with a scan rate of 10 °C/min. The glass transition temperature (T_g) is taken as the mid-point in the heat capacity change. Thermogravimetric data were obtained using a Shimadzu Thermogravimetric Analyzer TGA-50, between 20 and 800 °C, under nitrogen, with a scan rate of 10 °C/min.

3. Results and discussion

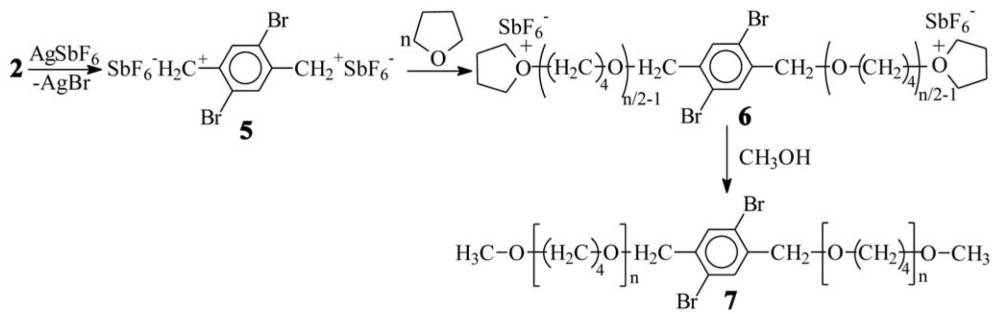
Many classes of halides were investigated using THF as both monomer and solvent [21]. From this survey it was concluded that benzylbromides (e.g. *p*-xylene dibromide) are capable of producing the benzyl carbonium anions, which in turn are efficient initiators of cationic polymerization. On the other hand, it was shown that arylhalides, even iodobenzene, do not initiate the polymerization of THF due to the higher strength of the C-halogen bond.

Accordingly, 1,4-dibromo-2,5-bis(bromomethyl)benzene (**1**), that was obtained starting from *p*-xylene, in two paths of bromination, was used as bifunctional initiator in cationic polymerization of THF, in combination with $AgSbF_6$ (Scheme 2). As it is expected, only the bromomethyl groups initiate the reaction.

The ^1H NMR ($CDCl_3$) spectrum of **7** (Fig. 1) contains near the usual absorptions of PTHF at 1.62 ppm (CH_2) and 3.41 ppm ($O{-}CH_2$), a small peak due to the aromatic protons of central benzene ring at 7.62 ppm. Due to the implied mechanism, the arom-CH_2 groups are in the vicinity of O atoms of the first THF repeating unit and the corresponding protons give a clear signal at 4.49 ppm. As the reaction was stopped by adding CH_3OH, the final OCH_3 protons appear as a signal at 2.17 ppm. The presence of these peaks permitted us to evaluate the molecular weight of the polymer. The value ($M_{n,HNMR} = 4200$) was considered to be more reliable than that obtained by GPC ($M_{n,GPC} = 5300$, after applying the correction factor [31]) and used for further calculations.

The ^{13}C NMR ($CDCl_3$) spectrum of macromonomer (Fig. 2) shows the usual peaks of PTHF at 26.45 ppm (CH_2) and 70.5 ppm ($CH_2{-}O$) but also the absorptions corresponding to the aromatic carbons of the central ring at 138.57 ppm ($C_{arom}{-}CH_2$), 132.10 ppm ($C_{arom}{-}H$), 121.00 ppm ($C_{arom}{-}Br$), arom-$CH_2{-}O$ at 72.49 ppm and final OCH_3 at 58.37 ppm.

In the IR spectra of **7** (Fig. 3) the small absorptions from 1050 cm^{-1} ($C_{arom}{-}Br$) and 845 cm^{-1} (1,2,4,5-tetrasubstituted benzene ring) are due to the rest of the initiator in



Scheme 2.

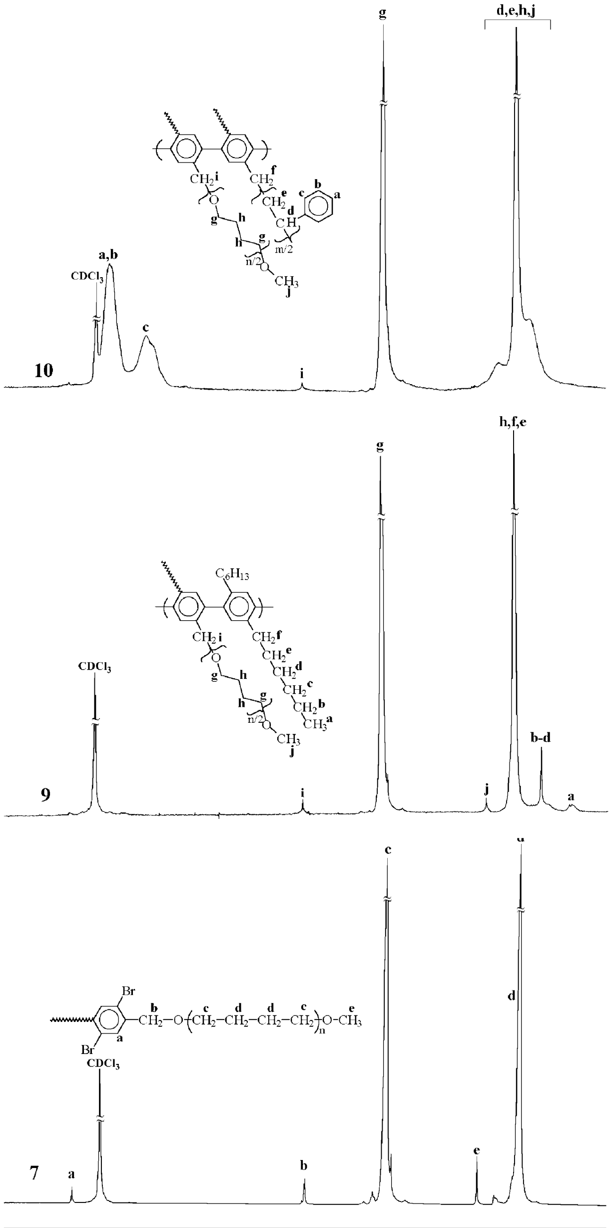


Fig. 1. ^{1}H NMR spectra of starting PTHF (**7**) and the synthesized PPPs by Suzuki coupling (**9**, **10**).

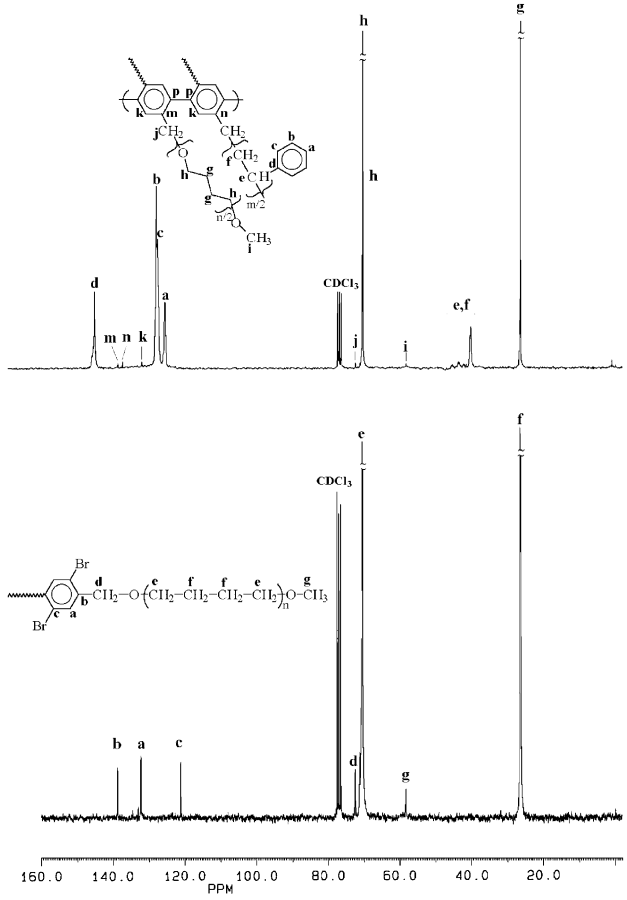


Fig. 2. ^{13}C NMR spectra of **7** and **10**.

the polymer structure. Other strong peaks are due to PTHF (cm^{-1}): 2940, 2850, 1442, 1363, 1240, 1205, 1105.

PTHF (**7**), having two bromine atoms directly connected to the central benzene ring, is an appropriate macromonomer for synthesizing PPPs, through Yamamoto coupling reactions using $NiCl_2$ catalyst, or Suzuki cross-coupling with a diboronic acid or its diester in the presence of a Pd(0) catalyst. Scheme 3 presents the cross-coupling reaction between **7** and 2,5-dihexylbenzene-1,4-diboronic acid (**8**).

A white powder soluble in usual organic solvents was obtained. The characteristics of resulted poly(*p*-phenylene) (**9**) are close to those of starting PTHF (solubility in usual organic solvents, melting over 30 °C).

The GPC analysis of the polymer was performed. A broad peak with shoulders was obtained (Fig. 4). Multimodal GPC traces were reported for polyarylenes with side alkyl radicals, by other authors, as well [32]. Due to the expected non-linear nature of the macromolecules, with very long polystyrene side chains, the obtained molecular weight ($M_n = 28{,}500$ and $M_w/M_n = 1.71$) does not give sufficient information about the polymerization degree. It is quite possible that the length of PPP backbone could be much smaller than the length of the PTHF side chains. Despite this, Fig. 4 shows that the GPC trace of the new polymer is shifted to higher molecular weights, as comparing with that of starting macromonomer.

The spectral data of **9** indicates the presence of hexyl groups in the structure of the polymer.

^{1}H NMR ($CDCl_3$) spectrum of **9** (Fig. 1) shows new peaks at 0.86 ppm (CH_3 from hexyl group) and 1.25 ppm (the last three CH_2 groups of hexyl), near those of PTHF. Due to the increasing the molecular weight, broadening the distribution and overlapping with the $CDCl_3$ peak, signals in the aromatic region could not be clearly identified.

In the IR spectra of **9** (Fig. 3), the usual absorptions of

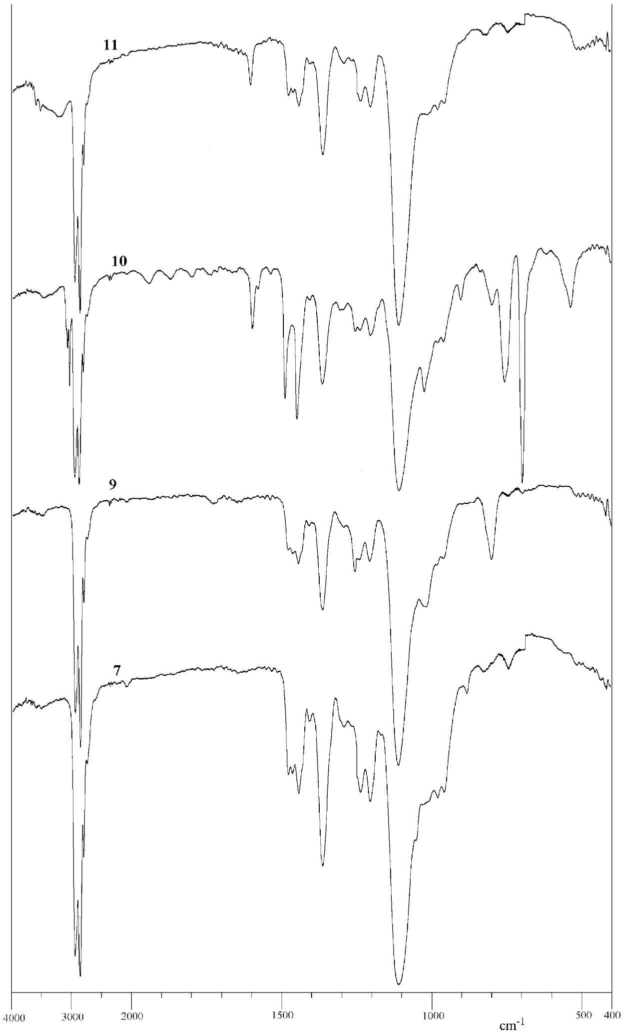
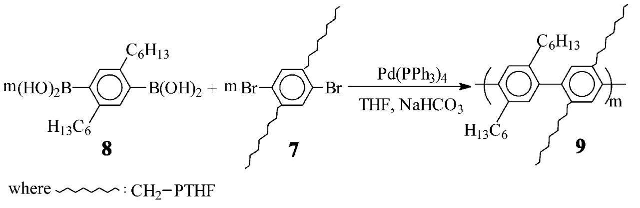


Fig. 3. IR spectra of starting PTHF (**7**) and the synthesized PPPs.

PTHF can be identified, but also a strong and broad peak centred at 800 cm^{-1} and another small one at about 745 cm^{-1} (out-of-plane deformation of C_{arom}–H from the PPP backbone). Moreover, the peak from 1050 cm^{-1}, attributed to C_{arom}–Br linkage [15] in the spectrum of **7**, disappears completely in the case of **9**.

Fig. 5 presents the UV spectra of PTHF (**7**) and the obtained PPP (**9**) registered in CH_2Cl_2 solutions with the same concentration (0.044 g l^{-1}). Unsubstituted and alkyl substituted PPP has two UV absorptions in the region 200–300 nm [15]. A strong absorption with the maximum at 228 nm and an additional shoulder between 250 and 270 nm in the case of **9** was taken as further evidence for the formation of poly(*p*-phenylene) backbone.



Scheme 3.

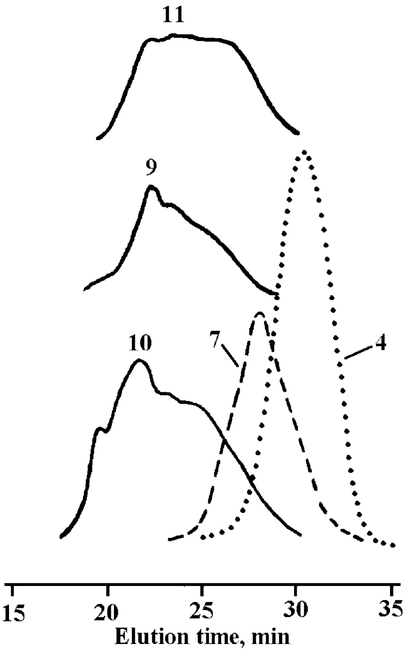


Fig. 4. GPC traces of PPPs as compared with the starting macromonomers **4** and **7**.

In a previous paper we reported the synthesis via ATRP of polystyrene based macromonomer (**4**) with a central benzene-2,5 boronic acid propanediol diester group, and low polydispersity.

PPP with alternating PTHF and PSt graft chains **10** was synthesized by using the corresponding macromonomers in the same synthetic strategy (Scheme 4).

The precipitation of the polymer from THF or chloroform solution in methanol, with stirring, led to the coagulation of the initially formed fine particles into a single big piece. A

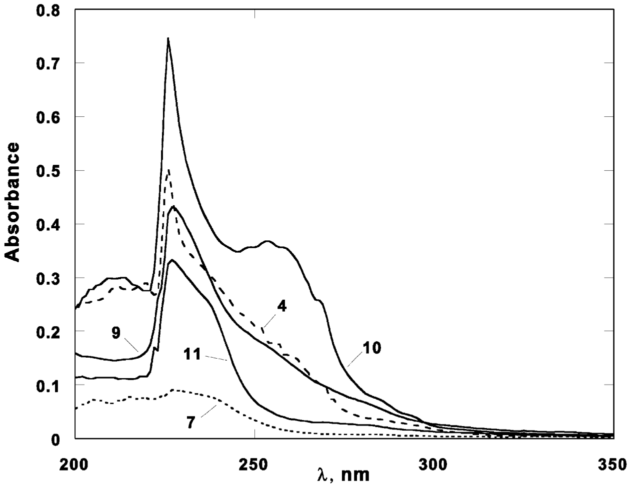
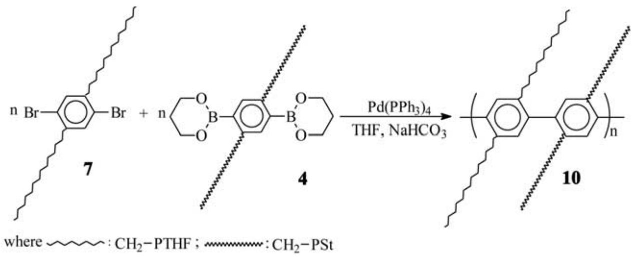


Fig. 5. UV absorption spectra of PPPs as compared with the starting macromonomers **4** and **7**.

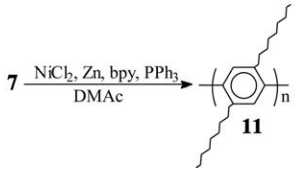


Scheme 4.

light-brown material with rubber aspect, that can be stretched, was obtained.

As can be seen from Scheme 1, polystyrene based macromonomer **4** possesses not only the boronic ester functionalities, but also secondary alkyl bromine groups at the ends of the macromolecules, due to the 'living' character of the ATRP reaction, applied in its synthesis. Further questioning invoked the possibility of their participation in the Suzuki coupling. As was demonstrated, the palladium-catalyzed cross-coupling reaction of arylorganoboronic compounds with aryl halides involves oxidative addition–transmetallation–reductive elimination sequences. Oxidative addition of aryl halides to a palladium(0) complex affords a stable *trans*-σ-palladium(II) complex. It has been considered that such reactions cannot be extended to alkyl halides with sp^3 carbon having β-hydrogens, due to the slow rate of oxidative addition of alkyl halides to palladium(0) complexes and the fast β-hydride elimination from σ-alkyl-palladium intermediates in the catalytic cycle [13]. Moreover, the order of reactivity in the step of reductive elimination of organic partners was shown to be diaryl → (alkyl)aryl → dipropyl → diethyl → dimethyl-palladium(II) which also suggested the participation of π-orbital of aryl groups during the bond formation. If a such kind of reaction is considered that could take place between the bromine end groups of macromonomer **4** and aryldiboronic ester ones, an alkyl–aryl C–C bound formation should occur. However, it was demonstrated that this type of linkages were formed in Suzuki coupling, only when primary iodoalkane was used, in 50% excess. Taking into account the above mentioned facts, Suzuki coupling of aryl-bromine containing macromonomer **7** with aryldiboronic acid containing macromonomer **4** (Scheme 5) yields only linear PPP chains with polytetrahydrofuran and polystyrene side groups, while hyperbranched polymers are not formed.

The GPC trace of **10** in comparison with those of the starting macromonomers is presented in Fig. 4. As in the case of **9**, the results ($M_{n,GPC} = 40{,}850$ and $M_w/M_n = 1.67$), does not give us valuable information regarding the dimension of the macromolecules. However, Fig. 4 clearly shows that a new polymer was formed.



Scheme 5.

^{1}H NMR spectrum shows signals of both PTHF and PSt moieties (Fig. 1). Moreover, the relation $I_{Ar}/5m = I_{OCH_2}/4n$ is verified, where I_{Ar} and I_{OCH_2} are the intensities of the peaks corresponding to the aromatic protons of PSt and the O–CH_2 protons of PTHF, respectively, and m and n are the polymerization degrees of the starting PSt and PTHF. The result confirms that PSt and PTHF chains are present in equal amounts in the PPP structure, as Suzuki cross-coupling leads to an alternating structure.

The ^{13}C NMR spectrum (Fig. 2) also proves the presence of both components in the copolymer (ppm): 145.27, 127.93, 127.64, 125.60 (aromatic carbons of PSt), 45.95–40.4 (aliphatic carbons of PSt), 70.57 (CH$_2$–O) and 26.5 (CH$_2$) from PTHF. Small peaks at 72.56 ppm (arom-CH$_2$–O), 58.45 ppm (final CH$_3$–O of PTHF chains) can be also identified. The peak at 121 ppm attributed to C$_{arom}$–Br in the spectrum of **7**, is not present in the spectrum of **10**. The signals due to C$_{arom}$–PTHF (138.65 ppm), C$_{arom}$–PSt (137.54 ppm) and C$_{arom}$–H (132.16 ppm) are still present, while those corresponding to C$_{arom}$–C$_{arom}$ are covered by PSt absorptions.

IR spectra of PPP with PSt and PTHF (Fig. 3) side chains presents specific absorptions of both comacromonomers (cm^{-1}): 1940, 1867, 1798, 1742, 1598, 1489, 760, 695 for PSt, 1363, 1240, 1205, 1105 for PTHF. Peaks centred at 2930, 2850 or 1446 cm^{-1} can be attributed to both PSt and PTHF segments. The peaks at 1050 cm^{-1} (C$_{aromatic}$–Br in the spectrum of **7**) and 1260 cm^{-1} (B–O stretch, present in the spectrum of **4** [30]) does not appear in the spectrum of **10** due to the consumption of the corresponding functional groups in the Suzuki cross-coupling reaction.

UV absorption spectra of starting macromonomers (**4** and **7**) and final PPP (**10**) registered in CH$_2$Cl$_2$ at the same concentrations are shown in Fig. 5. The absorption band at 226 nm is much higher than those of **10** and precursor **4**. The shoulder at 254 nm in the spectrum of PSt becomes a very broad and pronounced peak in that of polyphenylene, due to supplementary phenylene rings of the main chain. This behaviour was noticed also in the case of PPP with PSt side chains synthesized from **3** and **4** in our previous works [28,29].

PTHF **7** bearing bromine atoms as functional groups was also homopolymerized by an Yamamoto coupling using the system NiCl$_2$/bpy/PPh$_3$/Zn, in DMAc (Scheme 5). A white powder was obtained.

As in the case of the **9** and **10**, the GPC trace of **11** indicates that a polymer with higher molecular weight was formed (Fig. 4).

Unfortunately ^{1}H NMR spectra does not give informations about the aromatic backbone. Due to the increasing molecular weight and polydispersity, the peaks corresponding to the aromatic protons are not visible. IR spectrum of **11** shows broad peaks centred at 825 and 750 cm^{-1} (out-of-plane deformation of C_{arom}–H.) UV spectrum of **11** shows the same strong absorption characteristics (Fig. 5).

3.1. Thermal behaviour of PPPs

The thermal behaviour of starting macromonomers and derived polymers was followed by thermogravimetrical analysis (TGA) and differential scanning calorimetry (DSC). In Table 1 are included the initial degradation temperature, the temperature for which the weight loss is 10% and the percent of char yield at 800 °C.

Usually the polyphenylenes are thermostable. This behaviour is derived from the conjugated structure of the main chain. If we take in account the TGA data presented in Table 1, the above-mentioned tendency was proved for the new synthesized polymers. The highest thermostability was showed by polymer **11**, synthesized by Yamamoto method. The starting macromonomer **7**, used for the synthesis of **11**, has two decomposition stages. The first one is in 230–297.5 °C range and the weight loss is about 3.5%. This experimental value was associated with the loss of bromine atoms directly linked to the phenylene ring. The initial degradation temperature of polymer **11** increased more than 80 °C as compared with the starting macromonomer **7** and the percent char yield at 800 °C with 14%.

Table 1
The TGA values of macromonomers and synthesized polyphenylenes (IDT, initial degradation temperature; T_{w10}, the temperature for which the weight loss is 10%; Y_{c800}, the percent of char yield at 800 °C)

Sample	IDT (°C)	T_{w10} (°C)	Y_{c800} (%)
7	230; 297.5	359	0.57
4	198.5	382	1.9
9	283	372	4.57
10	230	357.3	4.76
11	311.8	400	15

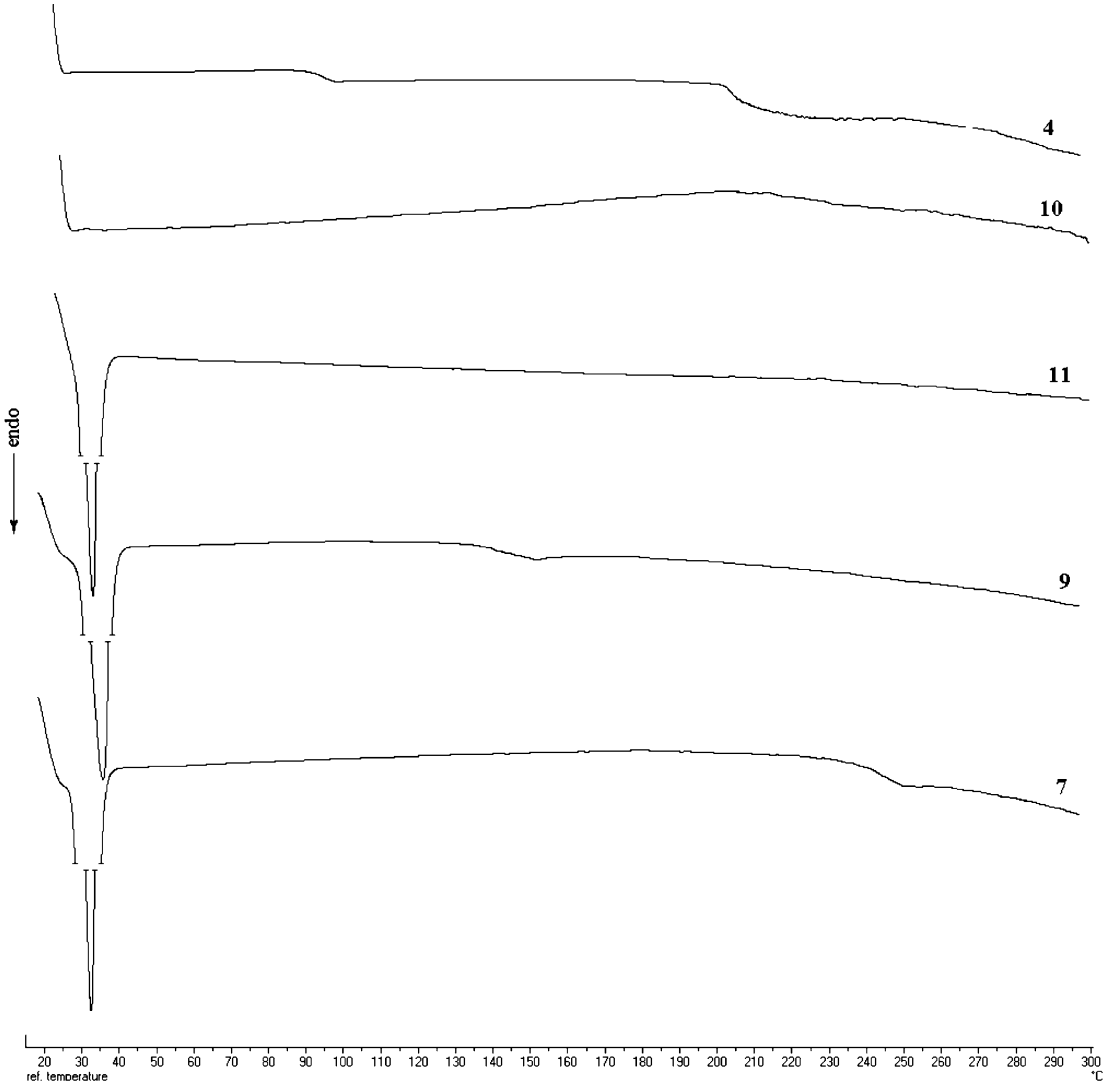


Fig. 6. DSC traces of PPPs as compared with the starting macromonomers **4** and **7**.

By DSC measurements the melting points characteristic to the PTHF side chains were evidenced at 33 and 31 °C for macromonomer **7** and polymer **11**, respectively (Fig. 6).

For the polymer **10**, obtained by Suzuki polycondensation starting from macromonomers **4** and **7**, the values obtained from TGA measurements were near to those of macromonomer **7**, excepting the char yield, Y_{c800}, which was higher. In the DSC trace of polymer **10** 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 **10**. The polymerization degree of PTHF side chain is higher 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 PTHF ones can take place, leading to a decrease of freedom for PSt segments and hindering their thermal mobility.

For the polymer **9** obtained also by Suzuki coupling and containing PTHF and hexyl side chains the thermostability is higher comparing with that of the starting macromonomer **7** (Table 1). By DSC measurements an endothermic peak centred at 36 °C was evidenced and was attributed to the melting of the PTHF side chains. We can conclude that the presence of the hexyl side groups, shorter than PSt does not disturb the crystallinity of the PTHF side chains in the case of polymer **9**.

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 [33]. In our case, macromonomer **7** has a sufficiently high molecular weight, so **9** and **11** preserved the crystallinity of the starting PTHF. The polymer **9** shows also a glass transition at 147.5 °C. The presence of the glass transition proved the obtainment of a new poly(*p*-phenylene) type material.

Most probably the chains of poly(*p*-phenylene)s reported above are short, and only oligomers were formed from the point of view of the aromatic backbone. One reason can be the low mobility of macromonomers with relatively high molecular weight as the reaction solution is viscous at the beginning. In the case of Suzuki coupling, it is difficult to assure the equimolecularity of the components in the reaction mixture, as their molecular weight cannot be determined precisely. On the other hand, the polymerization degree of **10** is probably sufficiently high as the side chains do not show their independent characteristics in DSC analysis, as shown above.

4. Conclusions

By cationic ring opening polymerization (CROP) a new macromonomer containing PTHF side chains was synthesized and characterized. By using it 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 macromonomer **7** 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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