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Polystyrene macromonomer with boronic acid propanediol diester functionality prepared by ATRP for synthesis of comb-like polyphenylenes

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Summary

Benzene-2,5-dibromomethyl-1,4-bis(boronic acid propanediol diester) was used as initiator in Atom Transfer Radical Polymerization (ATRP) of styrene in conjunction with CuBr/2,2'-bipyridine as catalyst. The resulted macromonomer, with a central benzene ring bearing cyclic boronic acid diester groups and polystyrene segments at each side, was used in combination with 1,4-dibromo-2,5-dimethylbenzene for a Suzuki coupling in the presence of $Pd(PPh_3)_4$ as catalyst. The obtained polyphenylene, with alternating polystyrene side chains and methyl groups, has high solubility in common organic solvents at room temperature. The new polymer was characterized by ^{1}H-NMR, IR and UV analysis. Thermal behaviour of the precursor polystyrene macromonomer and the final polyphenylene was investigated by DSC and compared.

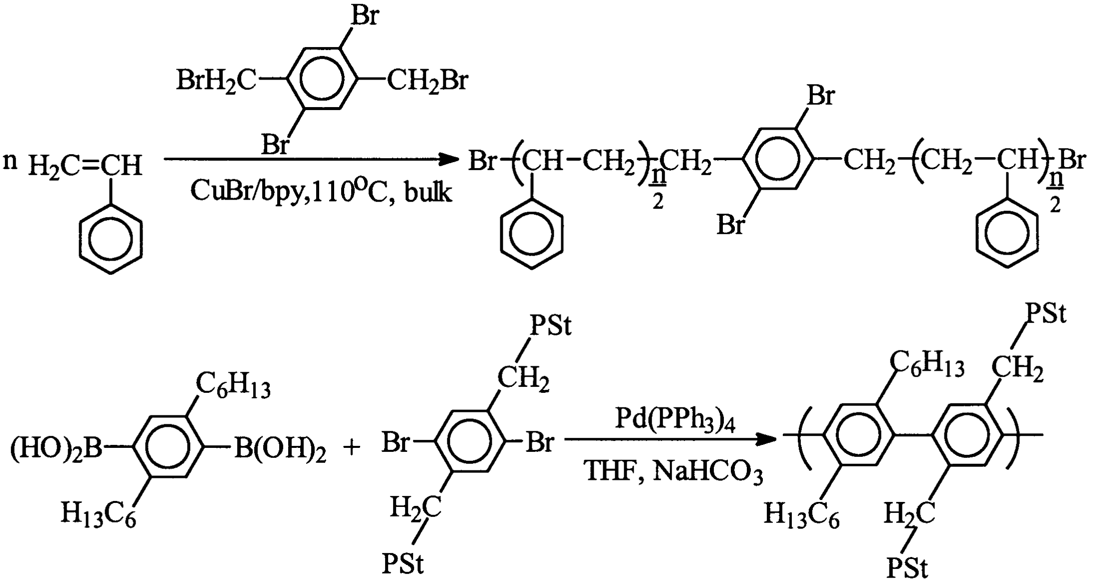
Introduction

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*-phenylenes) (PPP) 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 PPP 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 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. The final average molecular weight of the polymer can be adjusted by varying the initial monomer/initiator ratio, while maintaining a narrow molecular weight distribution ($M_w/M_n < 1.5$) [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]. 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].

In a previous work [28] we reported the synthesis of a polystyrene based macromonomer with a central 2,5 dibromobenzene ring and polystyrene segments at each side that was used in combination with 2,5-dihexylbenzene-1,4-diboronic acid, for a Suzuki coupling in the presence of $Pd(PPh_3)_4$ as catalyst, providing a polyphenylene, with alternating polystyrene and hexyl side chains (Scheme 1).



Scheme 1. Synthesis of a polyphenylene with polystyrene (PSt) side chains

The purpose of this contribution is to report the synthesis of a boronic acid propanediol diester functionalized polystyrene that can provide also comb-like polyphenylenes by Suzuki coupling.

Experimental

Materials

All the solvents were purified and dried by usual methods. Styrene (St) was distilled in vacuum from CaH_2 just before use. 1,3- Propandiol, N-bromosuccinimide (NBS) (Fluka) bipyridine(bpy), CuBr, $Pd(PPh_3)_4$ (Aldrich) were used as received. 1,4-dibromo-2,5-dimethylbenzene (**2**) was obtained by dibromination of *p*-xylene at 2,5-positions with Br_2 [29].

^{1}H-NMR (**3**) ($CDCl_3$): 2.30 (s, 6H, CH_3), 7.35 (s, 2H, aromatic).

IR (**3**) (cm^{-1}): 2940, 1432, 1058, 1035, 980, 885, 750.

Benzene-2,5-dimethyl-1,4-diboronic acid (**3**) was prepared in three steps from (**2**) following literature procedure [19].

^{1}H-NMR (**3**) (acetone-d_6) δ = 2.24 (s, 6H, CH_3), 7.22 (s, 4H, OH), 7.37 (s, 2H, aromatic).

IR (**3**) (cm^{-1}): 3350-3256, 2940, 1395, 1340, 1195, 1116,1076, 1025, 827.

Bis(1,3-propanediol) ester of benzene-2,5-dimethyl-1,4-diboronic acid (**4**) was prepared as follows [30]: 1,1617g (0.006 mol) of (**3**) and 1.03 mL (0.0144 mol) of 1,3-propandiol in 30 mL of dichloromethane were refluxed in a Dean-Stark apparatus for 6 h. After removing the solvent the crude product was passed through a silicagel column using as eluent benzene and finally recrystallized from benzene/hexane (1/2

vol.) yielding 1.12g (68%) of white crystals, m. p. (DSC): 148-149°C.
^{1}H-NMR (**4**) ($CDCl_3$): 1.95-1.99 (t, 4H, O-CH_2-CH_2-CH_2-O), 2.35 (s, 6H, CH_3), 4.05-4.09 (t, 8H, O-CH_2), 7.34 (s, 2H, aromatic).
IR (**4**) (cm^{-1}): 2940, 1473, 1421, 1357, 1263, 1148, 1122, 1030, 843
Bis(1,3-propanediol) ester of benzene-2,5-dibromomethyl-1,4-diboronic acid (**5**) was obtained from (**4**) by bromination of CH_3 groups with N-bromosuccinimide: 0.75g (0.0026 mol) of (5) and 0.96 g (0.0053 mol), 0.02 g of benzoyl peroxide (POB) and 5 mL of dry CCl_4 were heated slowly with stirring, under nitrogen, until reflux and maintained at that temperature 4h. At the finish of the reaction the formed succinimide was filtered off and washed two times with small amounts of CCl_4. The two solutions were combined, washed with water and dried over anhydrous $MgSO_4$. After removing of the solvent, the crude product was purified by cromatography using a silicagel column and CCl_4 as eluent. Final recristallization from CH_2Cl_2/hexane mixture (1/1 vol.) yielded 0.875g (77.9%) white crystals, m.p. (DSC) 197-198°C.
^{1}H-NMR (**5**) ($CDCl_3$): 2.03-2.11 (t, 4H, O-CH_2-CH_2-CH_2-O), 4.05-4.10 (t, 8H, CH_2, O-CH_2), 4.87 (s, 4H, CH_2Br), 7.36 (s, 2H, aromatic).
IR (**5**) (cm^{-1}): 2940, 1471, 1420, 1385, 1360, 1263, 1210, 1148, 1120, 918, 842, 780, 720

Synthesis of polystyrene functionalized with boronic ester groups by ATRP

A 20mL round bottom-flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Catalyst (CuBr, 0.1435g, 1 mmol), ligand bipyridine (bpy, 0.4036g, 3 mmol), initiator (**5**), 0.2158 g, 0.5 mmol) and styrene (5 mL) were introduced under inert atmosphere. The flask was placed in an oil bath warmed at 110°C and stirred at that temperature. After a 50 minutes, the mixture was diluted with THF and poured into ten-fold methanol. The solid was collected after filtration and drying at 40°C in a vacuum overnight. The polymer was purified by passing through a silicagel column using THF as eluent and reprecipitating into methanol. Yield 2.1612g (47,5%). $M_{n,GPC}$=4700 ($M_{n,th}$=4750), M_w/M_n=1.24.

Suzuki coupling of polystyrene based macromonomer with 1,4-dibromo-2,5-di-methylbenzene

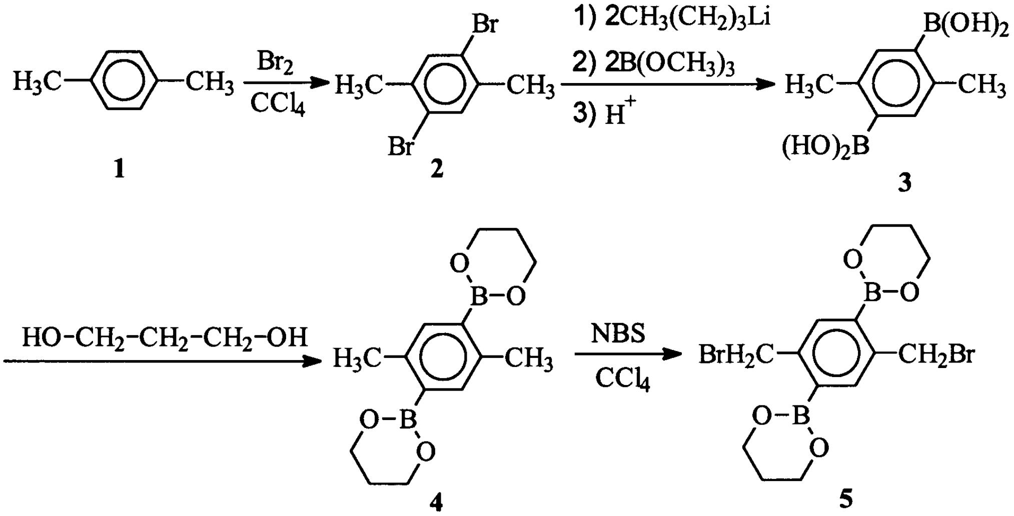
A 100 ml three necks round bottom flask equipped with a condenser, a septum, nitrogen inlet-outlet, and magnetic stirrer, was charged with 20 mL 1M $NaHCO_3$ solution and 30 mL of THF. The solvents were previously degassed by bubbling nitrogren over a period of 30 minutes. The mixture was refluxed under nitrogen, 4 hours.
A 20 ml three necks round bottom flask equipped in the same way as the previous one was charged under inert atmosphere with 0.47 g (0.1 mmol) polystyrene, 0.0264 g (0.1 mmol) 1,4-dibromo-2,5-di-methylbenzene (**2**) and 0.0017 g (0.0015 mmol) $Pd(PPh_3)_4$. 3mL of the mixture of solvents were introduced with a syringe through the septum. The reaction was maintained under vigorously stirring and with the exclusion of oxygen and light at reflux. After 48h a supplementary amount of 3 mL of mixture of solvents was added through the septum and stirred 1 day more. After that the polymer was obtained by precipitation in methanol. The product was filtrated, washed several times with water for removing the inorganic salts, dried and reprecipitated two times in methanol, first from chloroform and final from THF. The polymer resulted as a white-yellowish powder (yield 88%).

Analysis

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 250 MHz spectrometer with $CDCl_3$ or acetone-d_6 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, using THF as eluent and polystyrene standards for calculation of molecular weight.
IR spectra were recorded on a Shimadzu IR-470 Infrared Spectrophotometer using films from CH_2Cl_2 solutions deposed on NaCl pellets. UV analyses were performed on a Lambda 2 Perkin Elmer Spectrometer from CH_2Cl_2 solutions.
DSC analyses were performed on a Perkin Elmer Differential Scanning Calorimeter DSC-6, under nitrogen, with a scan rate of 10°C/min.

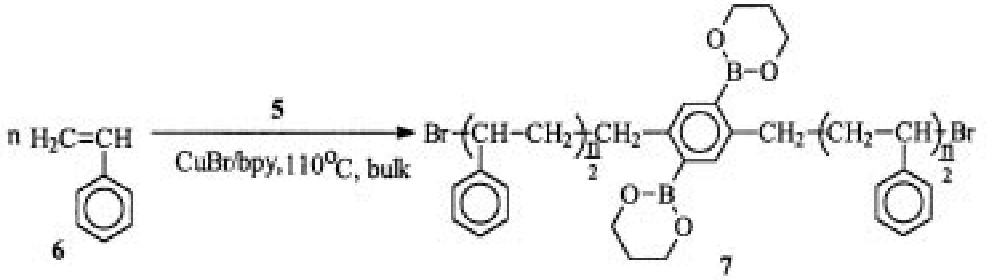
Results and Discussion

Bis(1,3-propanediol) ester of benzene-2,5-dibromomethyl-1,4-diboronic acid (**5**) was obtained according to the reactions from Scheme 2.



Scheme 2. Synthesis of initiator for ATRP reaction

The esterification reaction of the diboronic acid was made for solubility reasons, as compound (**3**) is not soluble in CCl_4, the appropriate solvent for bromination of methyl groups with NBS. Intermediate (**5**) has a pair of CH_2Br groups and is expected to be effective as a bifunctional initiator in atom transfer radical polymerization (ATRP). Moreover, boronic ester functionalities, useful for Suzuki coupling in combination with dibromoarylene derivatives are present in this structure, too. The ATRP using the CuBr/bipyridine catalytic system provided a precursor polymer with a central benzene group substituted with two macromolecular chains of 20-21 units of styrene and preserving also the two ester boronic functionalities (Scheme 3). As the functionalized polystyrene was intended to be used in a further polymerization reaction, the conditions of ATRP (high concentration of initiator - 0.1M and low reaction time - 50 minutes) were chosen for obtainment a low molecular weight polymer, combined with a satisfactory conversion and polydispersity.



Scheme 3. ATRP of styrene using bis(1,3-propanediol) ester of 2,5-dibromomethyl-1,4-diboronic acid as initiator

The GPC curve was narrow and symmetrical (Figure 1, curve **a**) proving that bis(1,3-propanediol) ester of benzene-2,5-dibromomethyl-1,4-diboronic acid is an effective initiator for ATRP of styrene. Moreover, the theoretical molecular weight ($M_{n,th}$=4750) calculated by using the Equation 1 fits very well with the measured one ($M_{n,GPC}$=4700).

$$\overline{M}_{n,th} = \frac{[M_0]}{[I_0]}(M_w)(\text{conversion}) + M_I \qquad \textbf{(1)}$$

where M_0 and I_0 are the initial molar concentrations of monomer and initiator, respectively, and M_w and M_I are the molecular weights of the monomer and initiator, respectively.

Due to the relative low molecular weight, in the ^{1}H-NMR spectrum of the polymer can be also identified the final CHBr groups from the polystyrene chains at about 4.63 ppm (protons d) and the 8 protons from 2 and 4 positions of boronic ester groups at 4.15 ppm (protons **i**) (Figure 2, I). The presence of these signals permitted to calculate the molecular weight of the polymer using the Equation 2. The found value (M_n=4400) is close to that measured from GPC.

$$\overline{M}_{n,H-NMR} = M_w \frac{8I_{Ar} - 8I_{4.15}}{5I_{4.15}} + M_I \qquad (2)$$

where I_{Ar} and $I_{4.15}$ are the intensities of the peaks from the aromatic region and from 4.15 ppm, respectively.

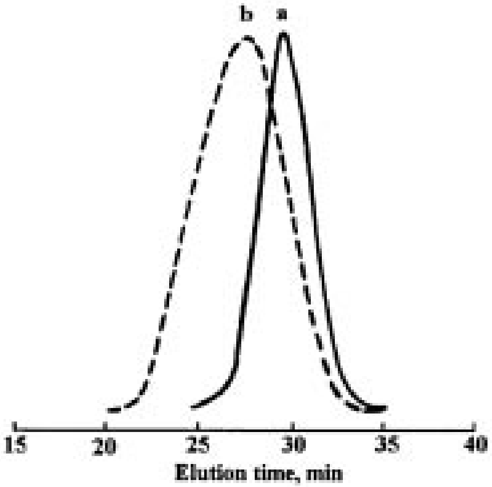
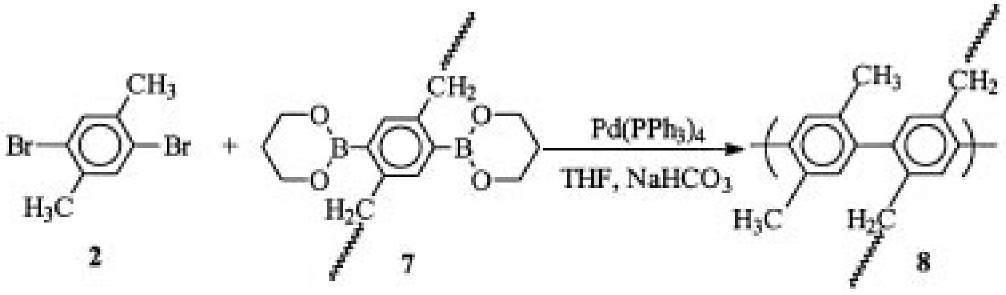


Figure 1. GPC traces of starting polystyrene (**a**) and the resulted polyphenylene (**b**)

The Suzuki coupling of polystyrene based macromonomer for obtaining polyphenylenes can be performed in combination with any convenient aryl dihalydes derivatives. The reaction was performed with 1,4-dibromo-2,5-dimethylbenzene (**2**), which was also an intermediate for obtaining the diboronic ester functionalized polystyrene (Scheme 4). The reaction, in the presence of $Pd(PPh_3)_4$ as catalyst, provided a polymer with the same solubility in organic solvents as polystyrene itself.



Scheme 4. The Suzuki coupling between the polystyrene based macromonomer and 1,4-dibromo-2,5-dimethylbenzene

Due to the expected shape of the macromolecules, with a central polyphenylene backbone and very long polystyrene side chains GPC can't give valuable information about the polymerization degree. Despite this, Figure 1 shows that the GPC trace of the new polymer (curve **b**) is shifted to higher molecular weights, as comparing with that of starting polystyrene (curve **a**). It is also interesting to notice that the GPC trace of polyphenylene, even broader, is also symmetrical.

The structure of polyphenylene (**8**), carrying PSt and methyl side groups, was investigated by spectral methods (^{1}H-NMR, IR, UV).

Even if the protons of the backbone of polyphenylene (**8**) appear together with aromatic polystyrene ones in the ^{1}H-NMR spectrum in Figure 2, II, by comparing with that of precursor polymer (**7**) (Figure 2, I), one can observe the disappearance of the boronic ester functionality (protons **i**), due to its consuming in Suzuki reaction.

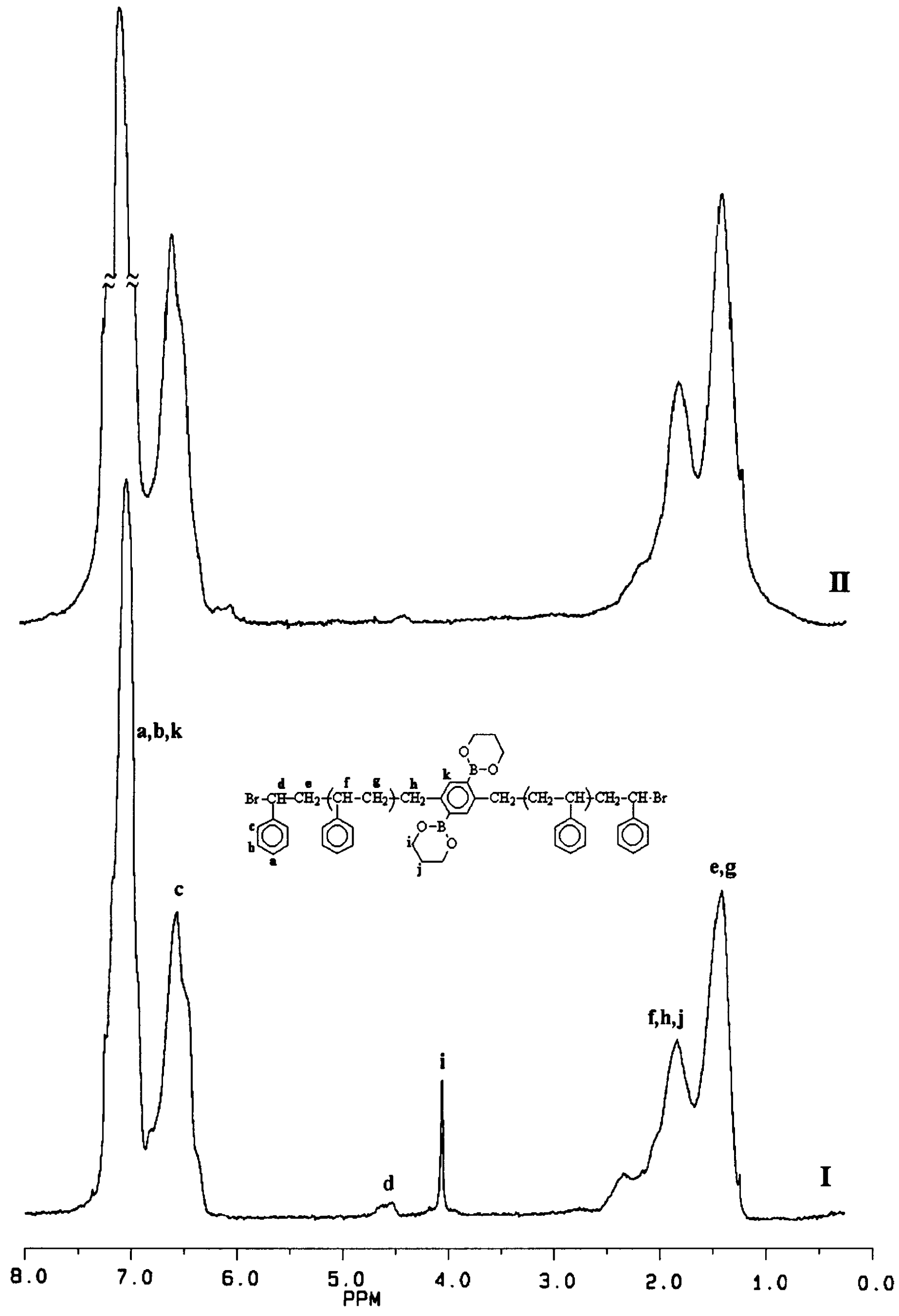


Figure 2. ^{1}H-NMR ($CDCl_3$) spectra of functionalized polystyrene (I) and final copolymer (II)

IR spectra of initial polystyrene (**7**) and final copolymer (**8**) are similar due to the high polystyrene content. The peak from 1260 cm^{-1} attributed to B-O stretch from the spectra of macromonomer is not present in that of polyphenylene (Figure 3), in agreement with ^{1}H-NMR result. Other absorptions are found in both spectra due to the high content of styrene units, that usually covers the peaks of phenylene rings from the main chain: 3048 cm^{-1}, 3024 cm^{-1} (aromatic CH stretching), 2928 cm^{-1}, 2848 cm^{-1} (aliphatic CH stretching), 1937 cm^{-1}, 1867 cm^{-1}, 1798 cm^{-1}, 1665 cm^{-1} and 760 cm^{-1} (out-of -plane hydrogen deformation), 1598 cm^{-1}, 1482 cm^{-1}, 1446 cm^{-1} (in-plane-bend -stretching vibrations of phenyl ring).

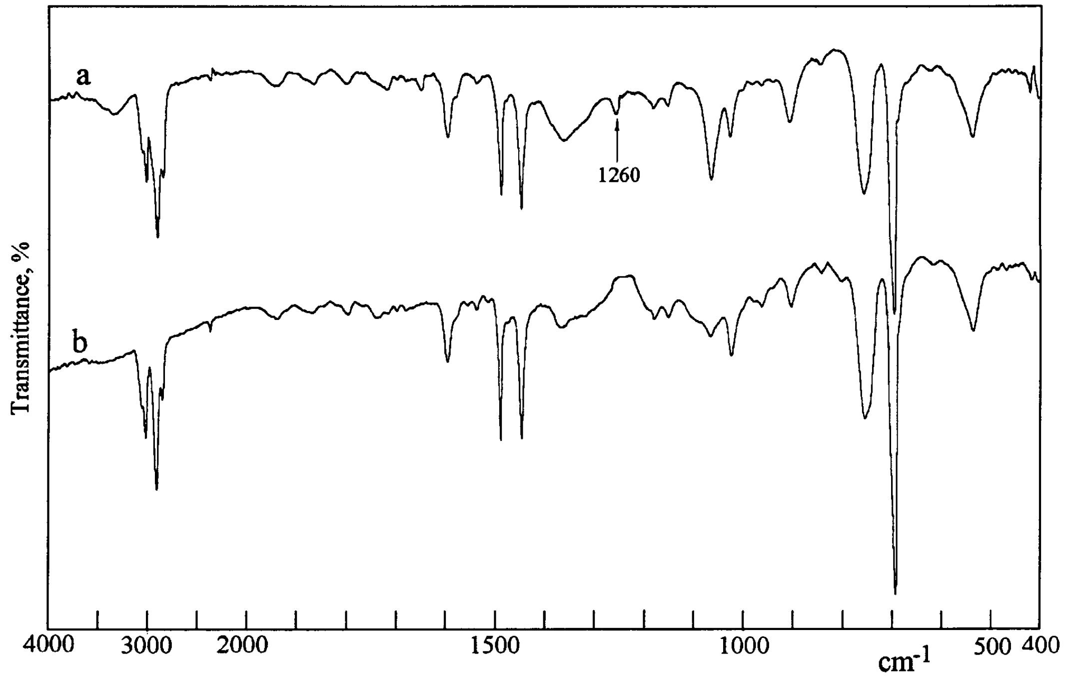


Figure 3. IR spectra of the starting macromonomer (**a**) and the resulting polyphenylene (**b**)

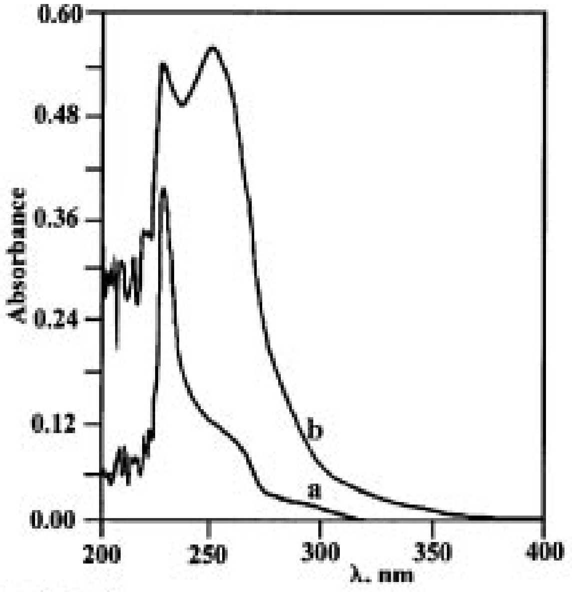


Figure 4. UV spectra of polystyrene (**a**) and polyphenylene (**b**)

Figure 4 shows important differences in UV absorption spectra of the starting PSt and the corresponding PPP registered in CH_2Cl_2 solutions with the same concentrations. The absorption from 226 nm is present in both spectra, but much higher in the case of polyphenylene (**8**). The shoulder at 254 nm observed in UV spectrum of macromonomer (Figure 4, curve **a**) becomes a broad and very pronounced peak in polyphenylene (**8**) (Figure 4, curve **b**). Normal and alkyl substituted PPP has two absorptions in UV 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.

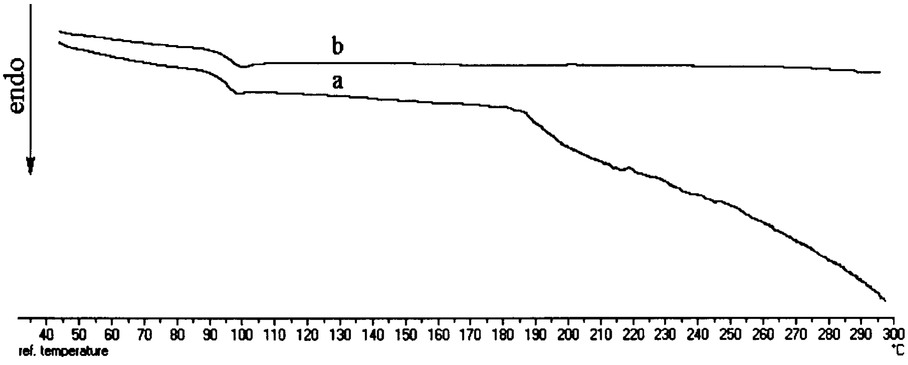


Figure 5. DSC traces (the second run) of polystyrene (**a**) and polyphenylene (**b**)

The thermal behaviour of the polymers was followed by differential scanning calorimetry, under nitrogen, with a heating rate of 10°C/min. A first run was performed until 150°C (lower than the well known initial degradation temperature of polystyrene), cooled down at 30°C and than reheated until 300°C (second run), for both polymers. The precursor polymer (**7**) and PPP (**8**) has close glass transition temperatures (around 95°C) characteristic for polystyrene. While for polymer (**7**) (Figure 5, curve **a**) an endothermic effect, starting at 185°C and associated with the beginning of degradation is present, no similar process was observed at polymer (**8**), proving a higher thermal stability until 300°C for this new polyphenylene.

Conclusions

Benzene-2,5-dibromomethyl-1,4-bis(boronic acid propanediol diester) was shown to be an effective initiator in ATRP of styrene by using CuBr/2,2'-bipyridine as catalyst. By this method, a polymeric precursor that posses a designed molecular weight with a narrow molecular weight distribution was prepared. The presence of a central benzene ring, disubstituted with the cyclic ester of boronic acid groups, made it proper for obtaining PPPs by subsequent Suzuki coupling with 1,4-dibromo-2,5-dimethylbenzene. The poly(*p*-phenylene) type polymer with alternating polystyrene side chains and methyl groups has a very good solubility in common organic solvents at room temperature and the structure was characterized by ^{1}H-NMR, IR and UV spectroscopy.

Acknowledgements.

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References

1. Feast WJ, Tsibouklis J, Pouwer KL, Groenendaal L, Meijer EW (1996) Polymer 22:5017
2. Kobayashi K, Yang TX, Muruyama K, Shimomura M, Miyauki S (1995) Synth Met 69:475
3. Hamaguki M, Yoshino K (1996) Appl Phys Lett 69:143
4. Cimrova V, Scherf U, Neher D (1996) Appl. Phys. Lett 69:608
5. Krivoshei IV, Skorobogatov VM (1991) Polyacetylene and Polyarylenes; Polymer Monographs; Gordon and Breach Science Publishers: Philadelphia, PA, Vol 10
6. Toshima N, Hara S (1995) Prog Polym Sci 20:155
7. Kovacic P, Jones MB (1987) Chem. Rev 87:357
8. Goldfinger G (1949) J Polym Sci. 4:93
9. Yamamoto T, Hayashi Y, Yamamoto A (1978) Bull Chem Soc Jpn 51:2091
10. Chaturvedi V, Tanaka S, Kaeriyama K (1993) Macromolecules 26:2607
11. Shi G, Xue G, Li C, Jin S, Yu B (1994) Macromolecules 27:3679
12. Rubenstein I (1983) J Polym Sci, Polym Chem Ed 21:3035
13. Gin DL, Conticello VP, Grubbs RH (1994) J Am Chem Soc 116:10934
14. Grob MC, Feiring AE, Auman BC, Percec V, Zhao M, Hill DH (1996) Macromolecules 29:7284
15. Yamamoto T (1992) Prog Polym Sci 17:1153
16. Schluter AD, Wegner G (1993) Acta Polym 44:59
17. Myaura N, Suzuki A (1995) Chem Rev 95:2457
18. Miura Y, Oka H, Morita M (1998) Macromolecules 31:2041
19. Rehahn M, Schluter A-D, Wegner G (1990) Makromol Chem 191:1991
20. Kallitsis JK, Rehahn M, Wegner G (1992) Macromol Chem 193:1021
21. McCarthy TF, Witteler H, Pakula T, Wegner G (1995) Macromolecules 28:8350
22. Lauter U, Meyer WH, Wegner G (1997) Macromolecules 30:2092
23. Matyjaszewski K (1998) Controlled Radical Polymerization; ACS Symposium Series; American Chemical Society: Washington DC, Vol. 685.
24. Webster OW, Science, (1991) 251:887
25. Wang, JS, Matyjaszewski K (1995) J Am Chem Soc 117:5614
26. Gaynor SG, Edelman S, Matyjaszewski K (1996) Macromolecules 29:1079
27. Alkan S, Toppare L, Hepuzer Y, Yagci Y (1999) J Polym Sci: Part A: Polymer Chemistry 37:4218.
28. Cianga I, Yagci Y, Macromolecules, submitted.
29. Ruggli P, Brand F (1944) Helv Chim Acta 27:274
30. Rulkens R, Schulze M, Wegner D (1994) Makromol Rapid Commun (1994) 15:669.