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Electrochemical synthesis of poly(4,4′-biphenylenevinylene)s (PBPVs)

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A series of three 2,2′-substituted 4,4′-dimethylbiphenyls have been prepared either by Grignard or Ullmann reactions and their benzylic bromination with NBS gave the corresponding 4,4′-bis(dibromomethyl)biphenyls. The cathodic reduction of these compounds, at a stirred mercury pool cathode led to the desired poly(4,4′-biphenylenevinylene)s, PBPVs, in good yields and in very smooth conditions. The obtained polymers have been spectroscopically characterized. After doping with iodine vapours, they exhibited electrical conductivities of the same magnitude as those observed for parent PPVs. Thermal analysis data (DSC and TG) are also presented and show their thermal stability both in air or nitrogen atmosphere.

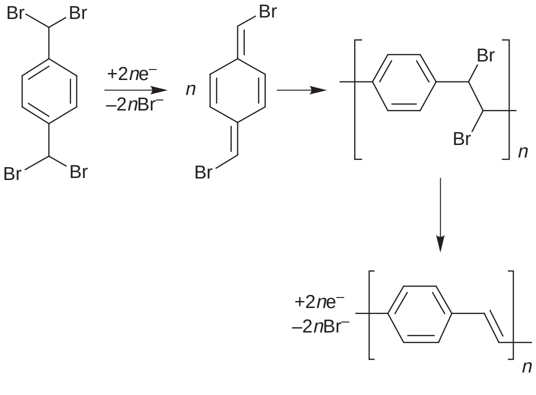
Poly(*p*-phenylenevinylene)s (PPVs) display a variety of interesting properties, such as electrical conductivity upon doping, nonlinear optical response, electro- and photoluminescence, which make them suitable for many applications.[1] They are usually prepared *via* pyrolysis of water-soluble precursor polymers (sulfonium route)[2] and obtained in the form of films or fibres.

We have recently synthesized a variety of poly(arylenevinylene)s (PAVs)[3,4] by the cathodic reduction of α,α,α′,α′-tetrabromo-*p*-xylenes. The reductions are carried out at a stirred mercury pool cathode and proceed to completion. As shown in Scheme 1, the reaction involves the formation of quinodimethane intermediates that polymerize to linear polymers. The insoluble polymers formed precipitate and the soluble fractions can also be easily separated by the addition of water to the catholite. This non-thermal method offers the possibility of producing a large range of polymers and copolymers with substituents that would not survive the pyrolysis or the strongly basic conditions used in the soluble precursor route.

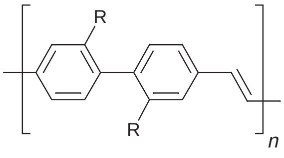
In this paper we report the electrosynthesis of three PPV-type conjugated polymers **1**, **2** and **3**, with alternating substituted biphenylene and vinylene units (Fig. 1).

We also report herein some of their spectroscopic data, thermal stability and electrical doped conductivities.

As far as we know, only one of these polymers **1** has been previously reported[5] and was prepared *via* a Heck reaction between 4,4′-bis(bromomethyl)biphenyl and ethylene gas, catalysed by palladium(II) acetate.



Scheme 1 Electrochemical route to PPV.



1 R = H
2 R = NO_2
3 R = OMe

Fig. 1 PBPVs.

Results and discussion

Preparation of precursors

4,4′-Dimethylbiphenyl **4**, 2,2′-dinitro-4,4′-dimethylbiphenyl **5** and 2,2′-dimethoxy-4,4′-dimethylbiphenyl **6** were obtained from *p*-bromotoluene, 4-chloro-3-nitrotoluene and 2-iodo-5-methylanisole, respectively, *via* Grignard or Ullmann reactions, according to procedures described in the literature.[6–8] The novel tetrabromo-compounds **7**, **8** and **9** were obtained by the treatment of **4**, **5** and **6** with an excess of *N*-bromosuccinimide (NBS), in the presence of visible light and peroxide (Scheme 2). ^1H NMR, IR and elemental analyses agreed with their expected structures.

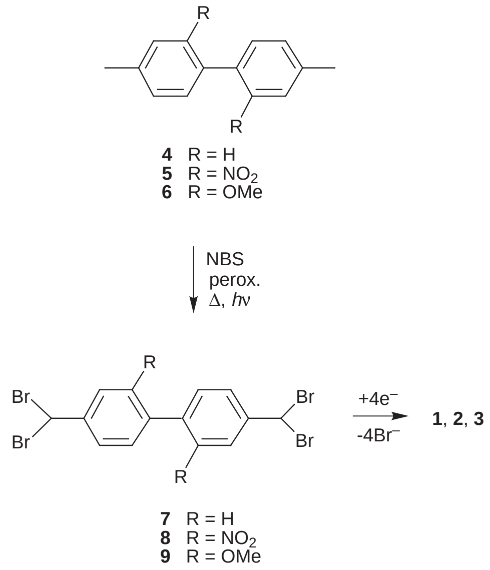
Cyclic voltammetry

Single-sweep voltammetry of compounds **7**, **8** and **9** at a mercury bead cathode in DMF–Et_4NBr ($0.1\ mol\ l^{-1}$) at $0.40\ V\ s^{-1}$ revealed several irreversible reduction peaks and with the data to hand it is not sensible to speculate on the origins of each peak. However, it was found that the most negative of the reduction peaks (E_{red} in Table 1) could be used successfully for the reduction potentials of controlled potential electrolysis.

Controlled potential electrolyses

These were carried out on a 1 g scale in a conventional cell equipped with a magnetically stirred mercury pool cathode, a Ag/AgBr reference electrode, a graphite anode and a microporous divider. The solvent was DMF containing $0.1\ mol\ l^{-1}$ Et_4NBr as supporting electrolyte. The cathode compartment was continually flushed with a slow stream of dry nitrogen.

The tetrabrominated precursors **7**, **8** and **9** were converted to the corresponding polymers **1**, **2** and **3** (Scheme 2) and the



Scheme 2 Synthesis of polymers **1**, **2** and **3**.

reactions were complete after the passage of ~4 F mol^{-1}, at which point the current had fallen to the background level. Part of the polymers precipitated during electrolyses as fibrous solids and part was obtained from the DMF filtrate after dilution with water, except polymer **3** which gave only soluble material (Table 1).

Spectroscopy studies

The methodology used to establish the key structural features of these electrosynthesised polymers was essentially that used for the analogous PPVs and it has been fully described.[3] Spectroscopic data are given in the Experimental section.

Important observations include the IR absorptions at ~960 cm^{-1} (Fig. 2) which confirm the *trans*-alkene structure. For soluble fractions it was possible to obtain ^{1}H NMR spectra and, although the peaks are somewhat broadened, the chemical shifts and integrations are as expected for these oligomers. The UV spectra of the soluble fractions (Fig. 3) show a similar pattern to the spectrum of PPV,[9] although with hypsochromic shifts, which may reflect some degree of non-coplanarity of the phenyl rings owing to the steric hindrance produced by the 2,2′-substituents. The observed values for the energy gaps are 3.3, 3.7 and 3.2 eV for polymers **1**, **2** and **3**, respectively.

Thermal analyses

Polymers **1**, **2** (insoluble fractions) and **3** were examined by differential scanning calorimetry (DSC) (Fig. 4), and thermogravimetry (TG), (Figs. 5 and 6). The main observations are: (i) the polymers are thermally stable up to 200 °C and the DSC curves do not show any enthalpic changes up to this temperature; (ii) they gradually decompose in air or nitrogen above 200 °C in exothermic processes; (iii) they do not show glass transition points.

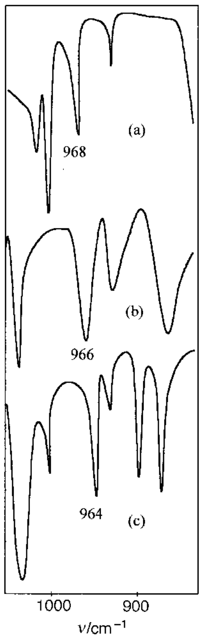


Fig. 2 IR absorptions at ~960 cm^{-1} of polymers **1** (a), **2** (b) and **3** (c).

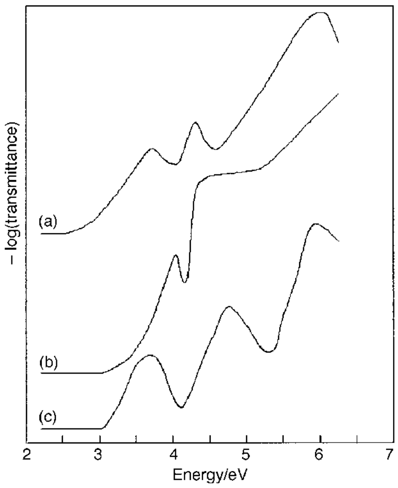


Fig. 3 Optical absorption spectra of: (a) polymer **1**; (b) polymer **2**; (c) polymer **3**.

Doping and conductivity

Pressed discs of the polymers were exposed in closed vessels to iodine vapour, for 24 h, and conductivities measured immediately after removal from the vessels using the four-probe and the two-probe methods.[10] The measured values, represented in Table 1, are of the same magnitude as those observed for other PPVs,[3] in the case of polymers **1** and **3**. Polymer **2** has a much lower conductivity probably due to the strong electron-withdrawing effect of the nitro groups.

Table 1 Some experimental data for precursors **7**–**9** and polymers **1**–**3**

Precursor	Polymer	$-E_{red}$/V *vs.* Ag/AgBr	Yield (%)	Soluble fraction (%)	Conductivity/S cm^{-1} Two-probe	Conductivity/S cm^{-1} Four-probe
7	**1**	1.6	85	47	4×10^{-5}	1×10^{-5}
8	**2**	1.5	77	31	3×10^{-7}	1×10^{-7}
9	**3**	1.8	60	60	2×10^{-5}	9×10^{-6}

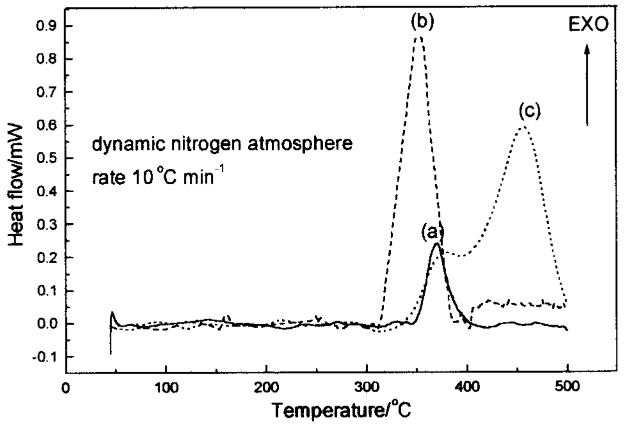


Fig. 4 DSC curves (a) polymer **1**, sample weight 1.61 mg; (b) polymer **2**, sample weight 0.410 mg; (c) polymer **3**, sample weight 0.893 mg.

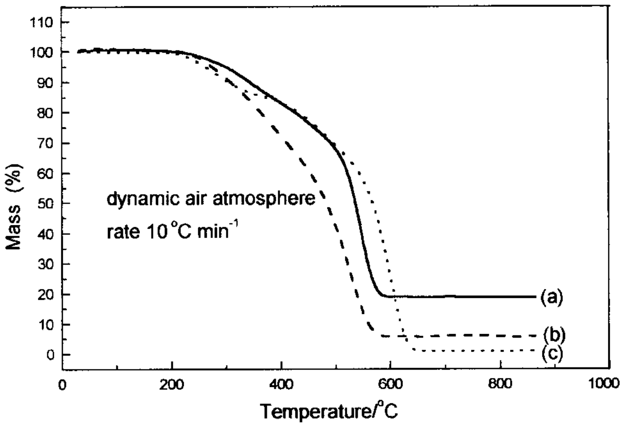


Fig. 5 TG curves (a) polymer **1**, sample weight 2.44 mg; (b) polymer **2**, sample weight 0.577 mg; (c) polymer **3**, sample weight 2.79 mg.

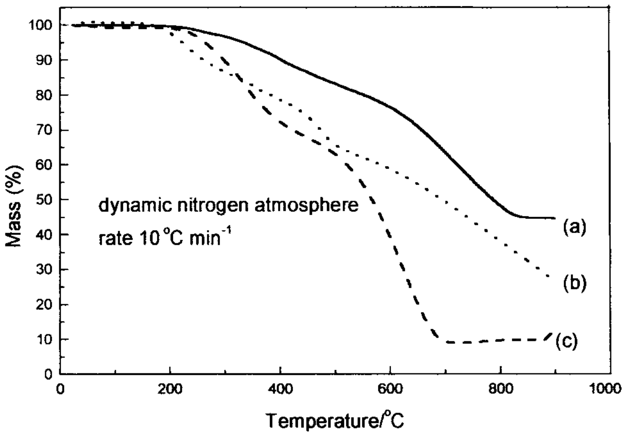


Fig. 6 TG curves (a) polymer **1**, sample weight 2.07 mg; (b) polymer **2**, sample weight 0.723 mg; (c) polymer **3**, sample weight 2.93 mg.

Conclusions

The cathodic elimination reaction of 4,4′-bis(dibromomethyl)-biphenyl **7**, 2,2′-dinitro-4,4′-bis(dibromomethyl)biphenyl **8** and 2,2′-dimethoxy-4,4′-bis(dibromomethyl)biphenyl **9** yields the corresponding polymers, PBPV **1**, PBPV-NO_2 **2** and PBPV-OMe **3** in good yields. At the stirred mercury pool cathode reaction proceeds to completion because any insulating film is continuously broken up and the electrochemical route has the advantage of its inherent smooth conditions.

Experimental

Melting points

Melting point data are uncorrected and were measured with an Electrothermal 9100 melting point apparatus or a Dynamic Optics AHT microscope melting point apparatus.

Solvents, electrolyte and reagents

***N,N*-Dimethylformamide (DMF).** For the CV experiments and the preparative electrolyses, commercial DMF (Aldrich GPR) was dried over anhydrous $CuSO_4$ for 2 days and then distilled at 44–45 °C (25 mmHg) through a 40 cm Vigreux column and stored over freshly baked 4 Å molecular sieves.

Tetraethylammonium bromide (Et_4NBr). Commercial grade Et_4NBr (Aldrich) was baked at 150 °C overnight before use.

Carbon tetrachloride. Commercial grade CCl_4 (Merck) was heated under reflux over phosphorous pentoxide for 10 h before distillation. It was stored over freshly baked 4 Å molecular sieves.

***N*-Bromosuccinimide (NBS).** Commercial grade NBS (Aldrich) was recrystallized from ten times its weight of hot water and dried in a vacuum desiccator over phosphorous pentoxide.

Electrochemical experiments

Cyclic voltammetric experiments were carried out using a USP electronics workshop-constructed triangular wave generator/potentiostat with a PAR RE0074 XY recorder. Controlled potential electrolysis experiments were carried out using a potentiostat with an electronic charge integrator constructed in our laboratory.[11,12]

Conventional glass cells were used, as described further on.

Spectroscopic studies

^1H NMR FT spectra (200 MHz) were recorded on a Bruker AC-200 spectrometer using deuteriated chloroform and TMS (Aldrich) as solvent and reference, respectively.

FTIR spectra were recorded as a KBr disc, on a Perkin-Elmer 1750 series grating. Only major or important absorptions are given.

UV spectra were recorded on a Beckman DU 70 scanning spectrophotometer using acetonitrile as solvent.

Thermal analyses

DSC experiments were carried out on a Shimadzu DSC50 calorimeter with nitrogen as the purge gas, and TG experiments on a Shimadzu TGA50 thermogravimeter with nitrogen or air as the purge gases. The heating rate was 10 °C min^{-1} in all cases.

Conductivity measurements

Polymer discs were prepared using a hydraulic press to a pressure of 1 tonne cm^{-2}. The conductivity of the polymer disc was measured using either a Signatone SP4–62.5–8.5-osmium tipped four-probe head or a two-probe head connected to an electrometer constructed in our laboratory.[10]

Elemental analyses

These were carried out on a Perkin Elmer Elemental Analyser 2400 CHN.

Starting materials

Compounds **4**, **5** and **6** were obtained following methods described in the literature.[6–8]

Preparation of 4,4′-bis(dibromomethyl)biphenyl (7). 4,4′-Dimethylbiphenyl **4** (1.00 g; 5.49 mmol), NBS (4.52 g; 25.4 mmol) and dibenzoyl peroxide (10.0 mg) were added to dry carbon tetrachloride (18 ml) and heated to reflux for 4 hours under VIS illumination (300 W halogen bulb), then cooled to room temperature. The insoluble succinimide was filtered off then washed with chloroform. The combined filtrate was shaken with aqueous sodium chloride and then with water. After drying over anhydrous magnesium sulfate and solvent evaporation, the solid was recrystallized (hexane–$CHCl_3$) to give yellow crystals, yield 1.84 g (3.69 mmol; 67%). Mp 142–144 °C. FTIR: 3030 and 3007 ($\nu_{\text{arom.}}$ C–H), 2836 ($\nu_{\text{sat.}}$ C–H), 1603, 1557 and 1492 (benzene ring), 1396 ($\delta_{\text{sat.}}$ C–H); 823 (*p*-disubst. benzene ring), 637 and 605 (ν C–Br). NMR δ_H: 6.70 (2H, s, 2 × $CHBr_2$), 7.45–7.68 (8H, m, 2,3,5,6-Ar-H). Elemental analysis, found: C, 33.71; H, 2.00%. $C_{14}H_{10}Br_4$ requires: C, 33.78; H, 2.02%. CV: −1.6 V *vs.* Ag/AgBr.

Preparation of 2,2′-dinitro-4,4′-bis(dibromomethyl)biphenyl (8). 2,2′-Dinitro-4,4′-dimethylbiphenyl **5** (1.00 g; 3.68 mmol), NBS (3.27 g; 18.4 mmol) and dibenzoyl peroxide (6.7 mg) were added to dry carbon tetrachloride (11 ml) and were treated as above and the obtained solid was recrystallized ($CHCl_3$–CCl_4) to give yellow crystals, yield 1.17 g (1.99 mmol; 54%). Mp 100–104 °C. FTIR: 3078 and 3006 ($\nu_{\text{arom.}}$ C–H), 2856 ($\nu_{\text{sat.}}$ C–H), 1615 and 1561 (benzene ring), 1530 and 1344 (ν N=O), 846 (ν C–N); 815 (1,2,4-trisubst. benzene ring), 636 (ν C–Br). NMR δ_H: 6.74 (2H, s, 2 × $CHBr_2$), 7.35 (2H, d, 2 × 6-Ar-H, J = 8 Hz), 7.91–7.96 (2H, m, 2 × 5-Ar-H), 8.41–8.44 (2H, m, 2 × 3-Ar-H). Elemental analysis, found: C, 28.64; H, 1.57; N, 4.68%. $C_{14}H_8Br_4N_2O_4$ requires: C, 28.60; H, 1.37; N, 4.76%. CV: −1.5 V *vs.* Ag/AgBr.

Preparation of 2,2′-dimethoxy-4,4′-bis(dibromomethyl)biphenyl (9). 2,2′-Dimethoxy-4,4′-dimethylbiphenyl **6** (0.351 g; 1.45 mmol), NBS (1.19 g; 6.69 mmol) and dibenzoyl peroxide (2.5 mg) were added to dry carbon tetrachloride (5 ml) and were treated as described for compound **7** and the obtained solid was recrystallized ($CHCl_3$–CCl_4) to give yellow crystals, yield 0.497 g (0.891 mmol; 61%). Mp 179–181 °C. FTIR: 3034 ($\nu_{\text{arom.}}$ C–H), 2968, 2939, 2913 and 2870 ($\nu_{\text{sat.}}$ C–H); 1601 (benzene ring), 1463 ($\delta_{\text{sat.}}$ C–H), 1254 and 1032 (ν C–O–C), 877 and 818 (1,2,4-trisubst. benzene ring), 681 (ν C–Br). NMR δ_H: 3.83 (6H, s, 2 × OCH_3), 6.68 (2H, s, 2 × $CHBr_2$), 7.13 and 7.15 (2H, dd, 2 × 5-Ar-H, J = 5 Hz, J = 1 Hz), 7.19 (2H, d, 2 × 6-Ar-H, J = 5 Hz), 7.22 (2H, d, 2 × 3-Ar-H, J = 1 Hz). Elemental analysis, found: C, 34.31; H, 2.53%. $C_{16}H_{14}Br_4O_2$ requires: C, 34.41; H, 2.51%. CV: −1.8 V *vs.* Ag/AgBr.

Electrolyses

Controlled potential electrolysis of 4,4′-bis(dibromomethyl)biphenyl (7). Compound **7** (1.02 g; 2.05 mmol) was electrolysed at a mercury pool cathode in Et_4NBr (0.1 mol l^{-1})–DMF solution (50 ml) at −1.6 V (*vs.* Ag/AgBr) in a divided cell. A yellow precipitate formed during electrolysis. After *ca.* 4.2 F mol^{-1} had passed, the cell current dropped close to the background value. The precipitate was filtered and washed several times with water to remove DMF and Et_4NBr, and dried *in vacuo*. Water was added to the filtrate and another crop of polymer was obtained (DMF-soluble fraction), which was also washed and dried. Yield: 140 mg (0.777 mmol; 38%) of insoluble fraction and 173 mg (0.962 mmol; 47%) of soluble fraction. The soluble material gave FTIR: 3120 and 3024 ($\nu_{\text{arom.}}$ C–H), 2919 and 2856 ($\nu_{\text{sat.}}$ C–H), 1604 (benzene ring), 1399 ($\delta_{\text{sat.}}$ C–H), 968 ($\delta_{\text{trans.}}$ H–C=C–H), 807 (*p*-disubst. benzene ring). NMR δ_H: 7.21–7.64 (m, Ar-H and vinylic hydrogens). The insoluble material gave FTIR: 3117 and 3020 ($\nu_{\text{arom.}}$ C–H), 2920 and 2853 ($\nu_{\text{sat.}}$ C–H), 1606 (benzene ring), 1400 ($\delta_{\text{sat.}}$ C–H), 965 ($\delta_{\text{trans.}}$ H–C=C–H), 810 (*p*-disubst. benzene ring). Elemental analysis, found: C, 85.12; H, 5.12; Br, 9.53%. $(C_{14}H_{10})_n$ requires: C, 94.34; H, 5.66%. The low results for C and H and the presence of bromine are due to unreduced end groups (−$CHBr_2$) and point towards a degree of polymerization of *ca.* 17 and an average molar mass of 3350.

Controlled potential electrolysis of 2,2′-dinitro-4,4′-bis(dibromomethyl)biphenyl (8). Compound **8** (0.602 g; 1.02 mmol) was electrolysed as above at −1.5 V (*vs.* Ag/AgBr). Yield: 127 mg (0.470 mmol; 46%) of insoluble fraction and 84.8 mg (0.314 mmol; 31%) of DMF-soluble fraction. The soluble fraction gave FTIR: 2922 and 2853 ($\nu_{\text{sat.}}$ C–H), 1656 (benzene ring), 1528 and 1389 (ν N=O), 966 ($\delta_{\text{trans.}}$ H–C=C–H), 836 (1,2,4-trisubst. benzene ring). NMR δ_H: 7.24–8.13 (m, Ar-H and vinylic hydrogens). The insoluble fraction gave FTIR: 2925 and 2854 ($\nu_{\text{sat.}}$ C–H), 1657 (benzene ring), 1530 and 1386 (ν N=O), 965 ($\delta_{\text{trans.}}$ H–C=C–H), 839 (1,2,4-trisubst. benzene ring). Elemental analysis, found: C, 59.41; H, 2.86; N, 9.92; Br, 5.12%. $(C_{14}H_8N_2O_4)_n$ requires: C, 62.69; H, 3.00; N, 10.44%. The low results for C, H and N and the presence of bromine are due to unreduced end groups (−$CHBr_2$) and point towards a degree of polymerization of *ca.* 22 and an average molar mass of 6200.

Controlled potential electrolysis of 2,2′-dimethoxy-4,4′-bis(dibromomethyl)biphenyl (9). Compound **9** (0.789 g; 1.41 mmol) was electrolysed as described for compound **7** at −1.8 V (*vs.* Ag/AgBr). Yield: 0.201 mg (0.843 mmol; 60%) of DMF-soluble fraction, which gave FTIR: 2997, 2934 and 2856 ($\nu_{\text{sat.}}$ C–H), 1605 and 1492 (benzene ring), 1462 ($\delta_{\text{sat.}}$ C–H), 1252 and 1039 (ν C–O), 964 ($\delta_{\text{trans.}}$ H–C=C–H), 853 and 813 (1,2,4-trisubst. benzene ring). NMR δ_H: 3.76 (6H, s, 2 × OCH_3); 6.79 (2H, m, 2 × 3-Ar-H); 7.11–7.21 (6H, m, Ar-H and vinylic hydrogens). Elemental analysis, found: C, 76.59; H, 5.63; Br, 5.11%. $(C_{16}H_{14}O_2)_n$ requires: C, 80.65; H, 5.92%. The low results for C and H and the presence of bromine are due to unreduced end groups (−$CHBr_2$) and point towards a degree of polymerization of *ca.* 25 and an average molar mass of 6275.

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