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Poly(phenylenevinylene) analogs with ring substituted polar side chains and their use in the formation of hydrogen bonding based self-assembled multilayers

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Poly(arylenevinylene) homopolymers and copolymers with polar hydroxy and carboxy moieties attached to the aromatic phenyl ring were prepared. The copolymers and the related homopolymers are copoly[5-(2-hydroxyethoxy)-2-methoxy-1,4-phenylenevinylene/1,4-phenylenevinylene], co(PHydroxyV-PV), and copoly(5-carboxymethoxy-2-methoxy-1,4-phenylenevinylene/1,4-phenylenevinylene), co(PCarboxyV-PV). For co(PHydroxyV-PV) the photoluminescence and electroluminescence spectra can be adjusted over a range of 100 nm as a function of the percentage of the hydroxy substituted phenyl ring. For co(PCarboxyV-PV) the observed spectral features are a function of the pH from which the final conjugated polymer was prepared. The optical density and photoluminescence of co(PCarboxyV-PV) films prepared from solutions at pH = 12 were significantly blue-shifted compared to polymers prepared from pH = 2 solutions at up to 30% substitution at the phenyl ring. The presence of the polar side chain was used to form self-assembled multilayer films, poly(ethyleneimine)/poly(styrenesulfonate)/co(PHydroxyV-PV), based on hydrogen bonding interactions rather than electrostatic forces. The luminescence spectra in the layered systems were blue-shifted compared to the spin coated films.

Electroluminescent conjugated polymers especially of the poly(arylenevinylene) family are leading candidates as active layers in light emitting diode devices based on organic compounds. The parent poly(1,4-phenylenevinylene) (PPV) has been the predominant polymer used for device application;[1] however, much research (both in homopolymers and copolymers) has been reported on PPV derivatives or analogs. Derivatisation has been based either on substitution at the aromatic nucleus or more occasionally at the vinylic carbons. Use of alternative aromatic moieties instead of phenyl units also leads to compounds analogous to PPV. The major intent in the preparation of PPV-like compounds has been to improve their performance in device operation. One direction of research has been to increase device efficiency or quantum yields by adjustment of the polymer electron affinity. This has been achieved by substitution with electron withdrawing groups[2] and introduction of electron deficient aromatic rings containing nitrogen into the polymer backbone.[3] The second research goal has been to tune the emission spectra by tailoring the π–π^* optical band gap. The strategies used to reach this goal have been substitution with electron withdrawing or donating groups,[4] variation of the polymer building blocks including incorporation of non-chromophoric segments[5] and introduction of sterically demanding substituents which affect planarity and the effective conjugation length.[6] These types of 'chemical tuning' have been realized in polymer blends, *e.g.* PPV and polyvinylcarbazole,[7] homopolymers and copolymers. Light emission ranging from the near infrared through the red, green and blue to the ultraviolet has been observed.

An easily accessible group of PPV analogs are those originating from 1,4-dialkoxybenzene.[8] These dialkoxy substituted homopolymers have absorption peaks at ~470 nm and emission peaks at 570–590 nm independent of the alkoxy chain length.[9] Building on the successful polymerization of dialkoxyphenyl monomers, we presently report on the synthesis of new PPV based polymers which contain reactive polar functional side chains. The functional units in this case are hydroxy groups as in copoly[5-(2-hydroxyethoxy)-2-methoxy-1,4-phenylenevinylene/1,4-phenylenevinylene], co(PHydroxyV-PV), and carboxy moieties as in copoly(5-carboxymethoxy-2-methoxy-1,4-phenylenevinylene/1,4-phenylenevinylene), co(PCarboxyV-PV), shown in Scheme 1. The photoluminescence (PL) and electroluminescence (EL) spectra of co(PHydroxyV-PV) showed fine tuning of the peak position as a function of the copolymer composition. Similar UV–VIS, PL and EL spectra of co(PCarboxyV-PV) showed a strong dependence of the spectral features as a function of the pH of the precursor polymer solution.

The self-assembly technique as related to conjugated polymers has recently emerged as an important technique for processing PPV into ultrathin multilayer films with controlled thickness and architecture.[10] These films have been shown to enable quantum confinement and blue-shifted spectra. In the past, however, the self-assembly method has been solely based on electrostatic forces between the insulating and conjugated pre-polymer used to build the layer structure. Now, the presence of the polar side chains on the herein newly described polymers can be used to fabricate self-assembled multilayer films based on strong hydrogen bonding between the amine group of an insulating poly(ethyleneimine) and the hydroxy group of the co(PHydroxyV-PV) conjugated polymer.

Results and Discussion

Synthesis

The synthetic pathway for the synthesis of co(PHydroxyV-PV) and co(PCarboxyV-PV) is outlined in Scheme 1. Alkylation of 4-methoxyphenol by ethyl bromoacetate led to the dialkoxide **1** with a terminal ester group. This compound was then reduced either to the corresponding alcohol **2** or hydrolyzed to the corresponding carboxylic acid **3**. Bromomethylation of **2** and **3** was carried out using paraformaldehyde in a HBr–acetic acid solution. During the course of the bromomethylation reaction the hydroxy group of **2** was also converted to the corresponding bromide **4** as was proven by mass spectral analysis. The two bromomethylated products **4** and **5** were then reacted with tetrahydrothiophene (THT) in

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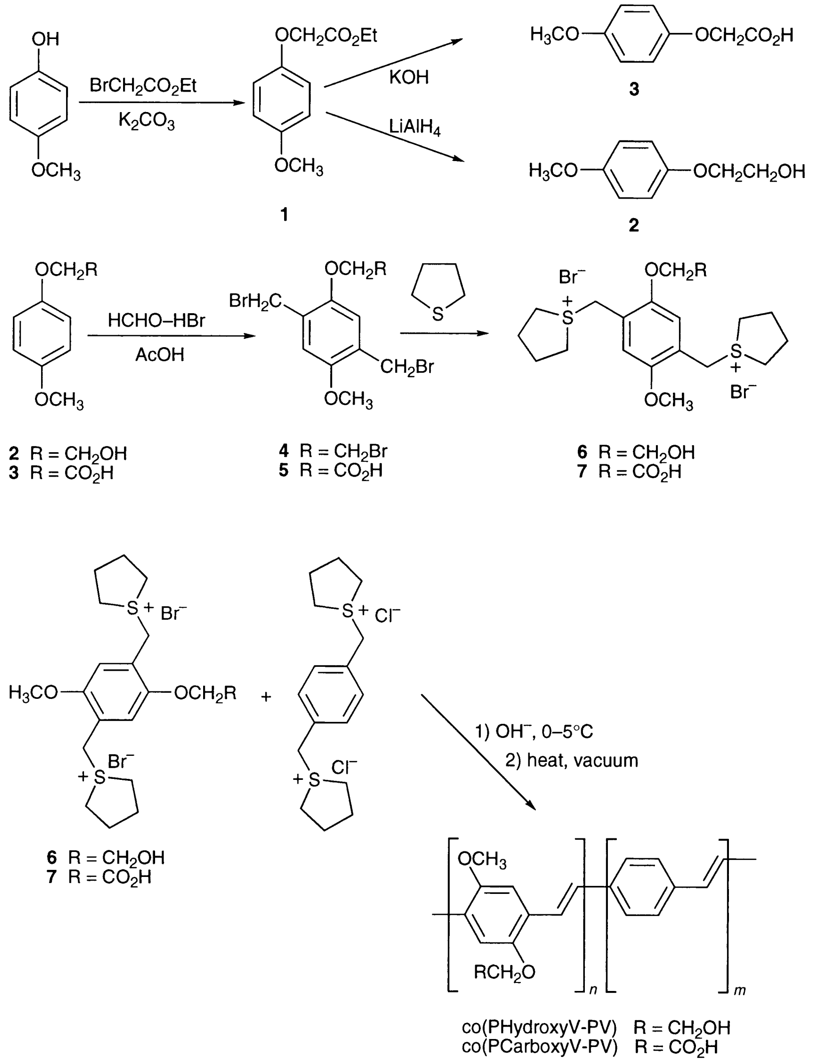

Scheme 1

methanol to form the required monomers, **6** and **7**. During reaction with THT the aliphatic bromide of **4** was reconverted to the corresponding hydroxy derivative as unequivocally shown in the mass spectral analysis.

Homopolymers and copolymers, PPV, PPHydroxyV, PPCarboxyV, co(PHydroxyV-PV) and co(PCarboxyV-PV) were prepared according to the standard Wessling[11] and Lenz[12] methods from the water soluble precursors. Conversion of monomers to polyelectrolyte and the final conjugated polymer yields were measured by titration and gravimetrically, respectively. The results are shown in Fig. 1. As the mole fraction of the carboxy monomer **7** was increased in the polymerization reaction, there was an initial decrease in the conversion, with a minimum at ~20 mol% of **7**, followed by a steady increase in conversion which was practically quantitative in the homopolymerization of carboxy monomer. For copolymerization of hydroxy monomer **6**, the conversion at up to ~30 mol% of **6** was constant at 45–50% and increased steadily, similar to what was found for **7**. Again the homopolymerization was quantitative. After dialysis to remove low molecular mass fractions using a cellulose membrane with a 12 000 molecular mass cutoff, the final polymer yield was measured after the thermal elimination reaction. It is clear from Fig. 1 that the final high molecular mass polymer yield decreased as the relative fraction of the functionalized monomer used increased. Apparently, the use of both the hydroxy and carboxy monomers led to the formation of lower molecular mass oligomers. The presence of the functionalized units in the conjugated polymer was verified with FTIR using the typical carbonyl and hydroxy group absorptions as reference. From the analysis of the optical densities it was concluded that there is a reasonable correlation, ±5%, between the initial feed ratio and the final composition of the copolymer.

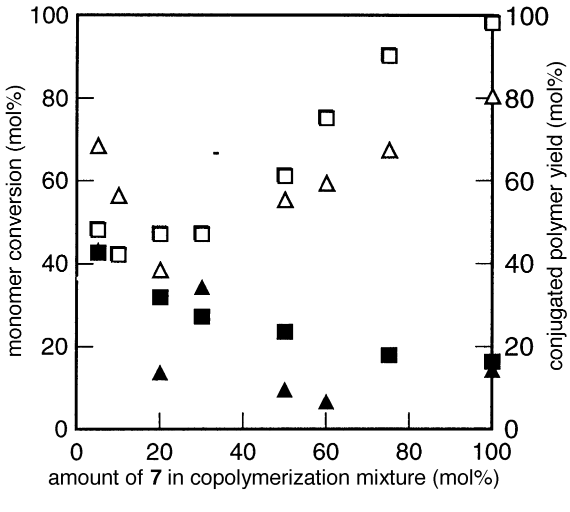

Fig. 1 Monomer conversion and final polymer yield for co(PHydroxyV-PV) and co(PCarboxyV-PV) as a function of the initial monomer ratio: (■) yield of co(PHydroxyV-PV), (□) conversion of co(PHydroxyV-PV), (▲) yield of co(PCarboxyV-PV) and (△) conversion of co(PCarboxyV-PV)

UV–VIS, PL and EL spectra in spin coated films

The PL and EL spectra of PPV and co(PHydroxyV-PV) are shown in Figs. 2 and 3, respectively. In both cases, there is a clear pattern of a bathochromic shift as the relative ratio, *n*/*m*, of the functionalized *vs.* non-functionalized moiety increases. This attests to a controllable method of chemical tuning of luminescence for these polymers as has been observed in other alkoxy substituted PPV type copolymers.[13] At low mol fractions (up ~10 mol%) of substituted units there is virtually no change in the wavelength of the luminescence peak. Above 10% co(PHydroxyV-PV) there is a continuously increasing red shift proportional to the content of the hydroxy moiety in the emission spectra for *both* PL and EL. The spectra of the homopolymer, PPHydroxyV, are identical to those of 75% co(PHydroxyV-PV). The internal quantum efficiency of an indium–tin oxide (ITO)/75% co(PHydroxyV-PV)/Al device was found to be 0.4% and the threshold voltage from the current–voltage curve (Fig. 4) was 10 V.

The absorption spectra of co(PHydroxyV-PV) are shown in Fig. 5. Here one can observe the broadening of the spectra of co(PHydroxyV-PV) compared to the parent PPV. In fact this broadening is also observable in both the PL and EL spectra. The broadening in both the absorption and emission spectra led us to conclude that the larger peak widths in co(PHydroxyV-PV) *vs.* PPV are attributable to vibronic sidebands and/or lack of homogeneity in the copolymers. Also noticeable is that at low, *i.e.* 5%, fractions of co(PHydroxyV-PV), the peak of the absorption spectra is blue shifted relative to PPV whereas this blue-shifted peak is not evident in the respective PL and EL spectra. A closer examination of the absorption spectra reveals that the absorption edge for 5 and 20% co(PHydroxyV-PV) are similar. Thus, since the emission spectra are influenced by the absorption edge rather than the absorption peak the absence of a blue-shifted emission spectrum for 5% co(PHydroxyV-PV) is explainable.

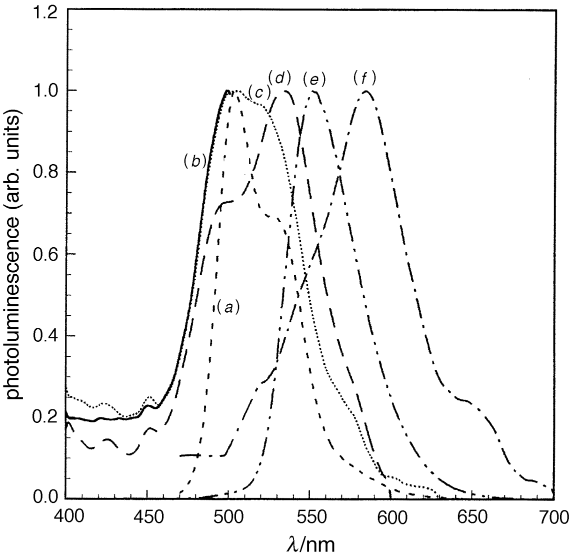

Fig. 2 PL spectra of thin films of co(PHydroxyV-PV): (*a*) PPV, (*b*) 5, (*c*) 10, (*d*) 20, (*e*) 50 and (*f*) 100%

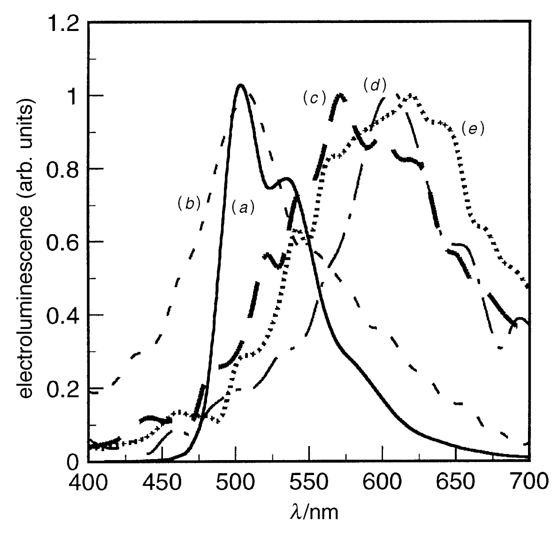

Fig. 3 EL spectra of thin films of co(PHydroxyV-PV): (*a*) PPV, (*b*) 5, (*c*) 30, (*d*) 50 and (*e*) 100%

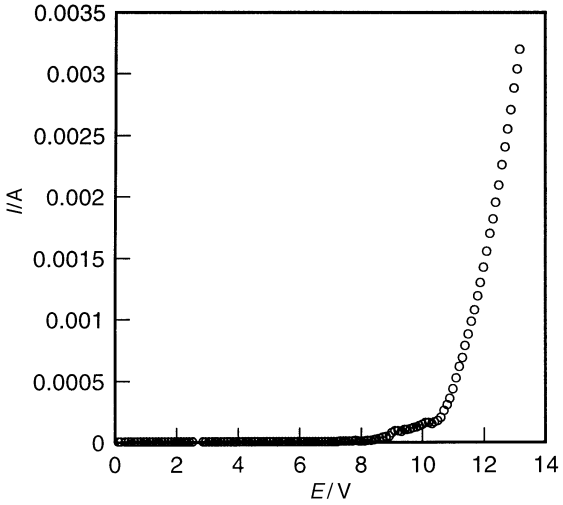

Fig. 4 Current *vs.* voltage curve for a ITO/20% co(PCarboxyV-PV)/Al LED

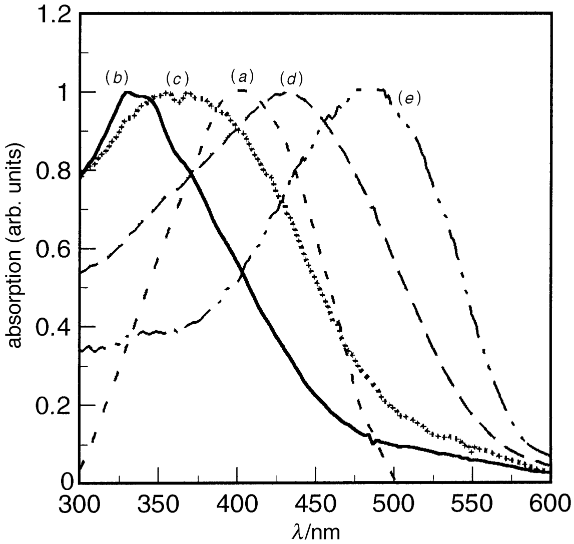

Fig. 5 UV–VIS spectra of thin films of co(PHydroxy V-PV): (*a*) PPV, (*b*) 5, (*c*) 20, (*d*) 50 and (*e*) 100%

The spectra of co(PCarboxyV-PV) were measured as a function of the pH of the solution of the precursor polyelectrolyte solution. It was hypothesized that the spectra of the final conjugated polymer would be affected by the ionic state of the carboxy unit. The result of such an experiment carried out on 20% co(PCarboxyV-PV) is presented in Fig. 6. Conjugated polymers prepared from solutions at pH 12 showed blue shifted UV–VIS, PL and EL spectra compared with similar spectra from solutions at pH 2. PPV spectra from solutions of different pH were unaffected. The ionization state of the carboxy unit was verified by FTIR with peaks at 1689 and 1715 $\mathrm{cm^{-1}}$ at pH 2 assignable to the COOH moiety and a peak at 1625 $\mathrm{cm^{-1}}$ at pH 12 assignable to the $\mathrm{COO^{-}Na^{+}}$ group. Therefore, clearly

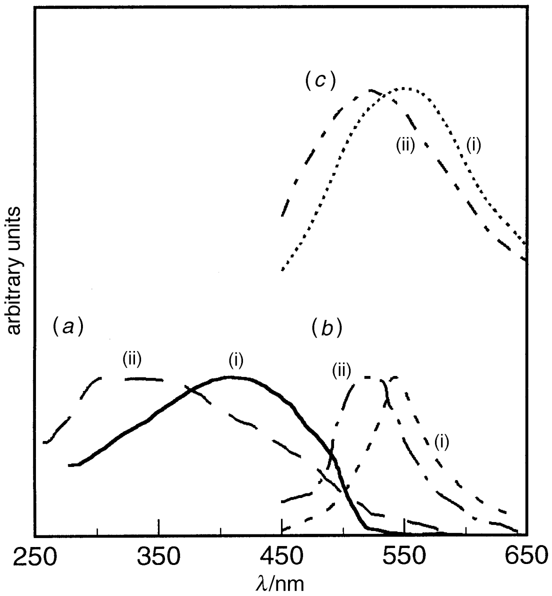

Fig. 6 (*a*) UV–VIS, (*b*) PL and (*c*) EL spectra of 20% co(PCarboxyV-PV) at (i) pH 2 and (ii) 12

the ionic state of the carboxy unit affects the spectra; the anionic carboxylate moiety leads to a blue shift compared to the non-ionized carboxylic acid form. This pH dependent method for control of the π–π* optical band gap is unique and could be due to conformational or more probably aggregation effects.[14]

Multilayer structures by hydrogen bonding

In the past, we have demonstrated that multiple bilayers of the type (SPS/conjugated polymer)$_n$ where SPS is poly(styrenesulfonic acid sodium salt) could be formed with a variety of conjugated polymers including PPV and poly(naphthylenevinylene). The bilayer formation was based on the electrostatic interaction between the sulfonate anion of the insulating polymer, SPS, and the sulfonium cation of the pre-PPV. Similar attempted bilayer formation with the precursors of co(PHydroxyV-PV) and co(PCarboxyV-PV) failed due to aggregration of the precursor polymer presumably because the polar side chains in these polymers interact by hydrogen bonding. This observation, however, has now enabled us to fabricate multiple trilayers based on PEI/SPS/co(PHydroxyV-PV) where PEI is poly(ethyleneimine). The amine moieties in PEI function to hydrogen bond the hydroxy polar side chain of co(PHydroxyV-PV), thus preventing aggregation. Direct evidence for hydrogen bonding was obtained by comparison of the FTIR spectrum of PEI alone and the multiple trilayers. For PEI the absorption was at 3366 cm^{-1} and was shifted to a lower energy peak at 3309 cm^{-1} in the multilayer system. This shift in the IR spectrum is very similar to what was observed in other conjugated polymer multilayers where hydrogen bonding interactions are proposed.[15] In Fig. 7, one may observe the typical specular X-ray reflectivity spectra of self-assembled PEI/SPS/100% co(PHydroxyV-PV) on float glass after thermal conversion to form the conjuaged polymer. Kiessig oscillations due to interference of beams reflected from the upper and lower interfaces are clearly observable and enable calculation of the total film thickness, *d*. The linear correlation between *d* and the number of trilayers, *n*, (Fig. 7 inset) yields a thickness per trilayer after annealing of ~55 Å for PEI/SPS/100% co(PHydroxyV-PV). Both PEI/SPS/20% co(PHydroxyV-PV) and PEI/SPS/50% co(PHydroxyV-PV) gave similar results. The photoluminescence spectrum (Fig. 8) of the multiple trilayers show peaks at 500, 525 and 540 nm for 20, 50 and 100% co(PHydroxyV-PV), respectively. The emission peak is independent of the number of trilayers. These

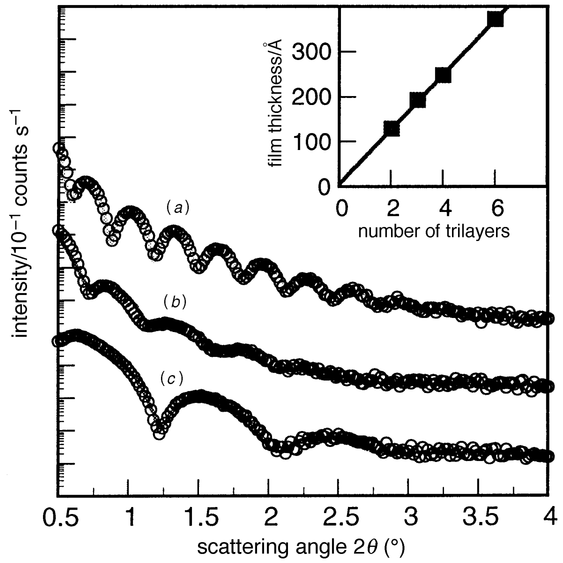

Fig. 7 Specular X-ray reflectivity spectra of self-assembled multilayer films based on PEI/SPS/100% co(PHydroxyV-PV): $d=(a)$ 370, (*b*) 245 and (*c*) 126 Å. Inset: film thickness as a function of the number of trilayers after annealing to form the conjugated polymer.

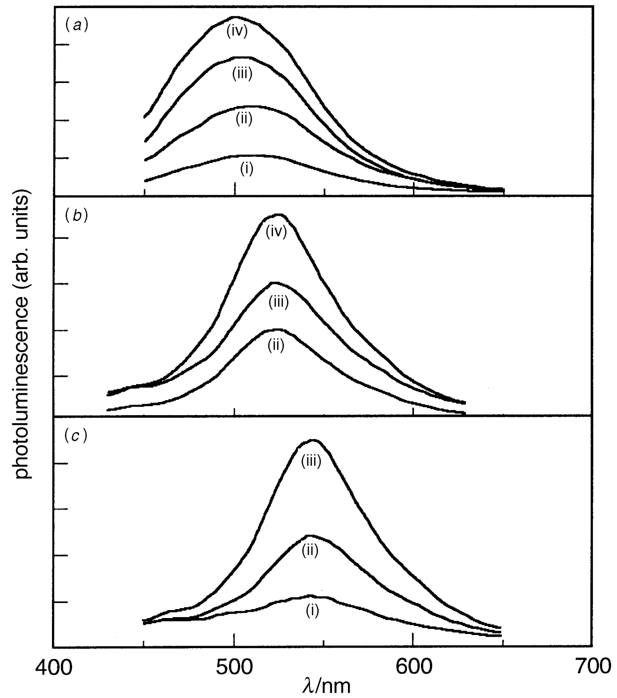

Fig. 8 Photoluminescence spectra of [PEI/SPS/co(PHydroxyV-PV)]$_n$: (*a*) 20, (*b*) 50 and (*c*) 100% co(PHydroxy-PV); (i) 2, (ii) 3, (iii) 4 and (iv) 5 trilayers

peaks are blue-shifted by 30–45 nm relative to the peaks at 535, 555 and 585 nm, observed in the spin coated films (Fig. 2). These blue-shifted peaks are best explained by the confinement of the electron-hole pair in the conjugated polymer layer between the insulating PEI+SPS layer having a thickness of 35–40 Å.[10] Very similar spectra (Fig. 9) are observable for electroluminescence in the case of seven trilayers of PEI/SPS/20% co(PHydroxyV-PV) and PEI/SPS/100% co(PHydroxyV-PV) in a ITO/multilayer/Al configuration.

Experimental section

Materials and instrumentation

Chemicals were obtained from commercial sources of the highest purity available and used without further purification.

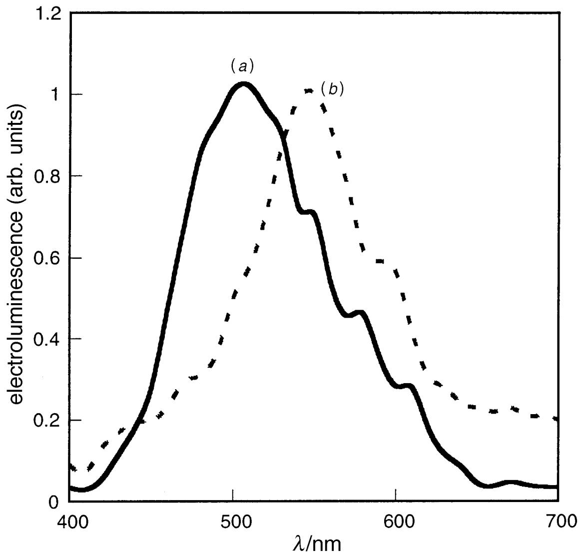

Fig. 9 Electroluminescence spectra of [PEI/SPS/co(PHydroxyV-PV)]$_n$: (*a*) 20 and (*b*) 100% co(PHydroxyV-PV)

Solvents were dried when so noted using the common methods. ^{1}H NMR spectra were measured using a Bruker AMP 300 spectrometer. Mass spectra were measured on a TSQ 70 FinniganMat triple quadrupole spectrometer. UV–VIS spectra were measured on a Hewlett Packard HP8452A diode array spectrophotometer. PL spectra were obtained using a JASCO spectrofluorimeter (FP-770) or a Perkin-Elmer LS-5 spectrometer using an excitation wavelength of 375 nm, although measurements showed PL spectra independent of the excitation wavelength in the range of 300–400 nm. The EL spectra were measured using an ITO/polymer/Al configuration and a computer controlled Oriel monochromator in a setup described previously.[16] IR spectra were measured using a Nicolet 510M instrument. The specular X-ray reflectivity measurements were carried out using a Cu-Kα ($\lambda = 1.54$ Å) beam from a narrow line source of a 12 kW Rigaku rotating anode generator.

Ethyl 4-methoxyphenoxyacetate 1

The compound was prepared by a modification of the procedure of Neu *et al.*[17] Thus, 4-methoxyphenol (20 g, 0.16 mol) was dissolved in dry acetone (500 ml), potassium carbonate (33 g, 0.24 mol) was added and the solution was refluxed for 15 min. After 15 min, ethyl bromoacetate (36 ml, 0.32 mol) was added in one portion and the reflux was continued for another 4 d. The potassium carbonate and bromide were then filtered off, and the acetone and the excess ethyl bromoacetate were removed by evaporation and vacuum distillation, respectively. The product was obtained in 95% yield (32 g). δ_H ($CDCl_3$): 1.28 (3H, t, CH_3); 3.77 (3H, s, OCH_3); 4.22 (2H, q, CH_2); 4.55 (2H, s, OCH_2); 6.82 (2H, d, Ar); 6.84 (2H, d, Ar).

2-(4-Methoxyphenoxy)ethanol 2

A 500 ml three-necked flask was equipped with a dropping funnel and thermometer. The flask was cooled to 0–5 °C, charged with 200 ml of dry tetrahydrofuran (THF) and $LiAlH_4$ (5.4 g, 0.14 mol) under a nitrogen atmosphere. Then **1** (20 g, (0.095 mol) dissolved in 200 ml of dry THF was added dropwise over a period of 1 h and the reaction was continued for another 6 h. The excess $LiAlH_4$ was carefully quenched with water and the THF was evaporated at the pump. The product was isolated by extraction with diethyl ether giving 80% of **2** (12.8 g). δ_H ($CDCl_3$): 2.65 (1H, br s, OH); 3.75 (3H, s, OCH_3); 3.90 (2H, t, OCH_2); 4.00 (2H, t, CH_2O); 6.83 (4H, s, Ar).

4-Methoxyphenoxyacetic acid 3

A sample of **1** (10 g, 0.015 mol) was refluxed in 100 ml of a 2 M KOH solution for 12 h. Upon cooling a white precipitate was formed which was filtered, washed with diethyl ether and added to a solution of 200 ml of water and 300 ml diethyl ether. A 5 M HCl solution was added slowly until an aqueous phase pH of 2 was obtained. The organic layer was separated and the aqueous layer was extracted twice with diethyl ether. The organic extracts were combined, dried with magnesium sulfate and solvent removed by evaporation. The yield was 80% (7.25 g). δ_H ($[^2H_6]$DMSO): 3.70 (3H, s, OCH_3); 4.60 (2H, s, OCH_2); 6.86 (4H, s, Ar); 12.96 (1H, s, COOH).

1,4-Bis(bromomethyl)-2-(2-bromoethoxy)-5-methoxybenzene 4

Compound **2** (15 g, 0.096 mol), paraformaldehyde (14.4 g, 0.48 mol) and 136 ml of 5.4 M HBr in acetic acid were reacted in 250 ml of acetic acid for 18 h.[18] After formation of a white precipitate water (300 ml) was added to the reaction mixture. The solution was filtered and the precipitate was washed with water until the pH of the filtrate was 6. After drying the product under vacuum the yield was 73% (23.7 g), mp 102–103 °C. δ_H ($CDCl_3$): 3.85 (3H, s, OCH_3); 4.20 (2H, t, OCH_2); 4.44 (2H, t, CH_2Br); 4.50 (2H, s, CH_2Br); 4.52 (2H, s, CH_2Br); 6.86 (2H, s, Ar); 6.87 (2H, s, Ar). The chemical ionization mass spectrum (CI-MS) using isobutane showed the molecular ion peak at *m*/*z* 472, 474, 476, 478 for [M + isobutane] at the required peak ratio of 1 : 3 : 3 : 1. The base peak at *m*/*z* 314, 316 (1 : 1) was attributed to [M + isobutane − 2Br] and smaller peaks at *m*/*z* 393, 395, 397 (1 : 2 : 1) were assigned to [M + isobutane − Br].

2,5-Bis(bromomethyl)-4-methoxyphenoxyacetic acid 5

Compound **2** (15 g, 0.082 mol), paraformaldehyde (5.19 g, 0.164 mol) and 40.15 ml of 5.4 M HBr in acetic acid were reacted in 150 ml of acetic acid for 8 h at 65 °C. After formation of a white precipitate water (300 ml) was added to the reaction mixture and the solution was filtered and the precipitate was washed with water until the pH of the filtrate was 6. After drying the product under vacuum the final yield was 63% (19.0 g), Mp 134 °C. δ_H ($[^2H_6]$DMSO): 3.81 (3H, s, OCH_3); 4.58 (2H, s, OCH_2); 4.65 (2H, s, CH_2Br); 4.68 (2H, s, CH_2Br); 7.08 (1H, s, Ar); 7.13 (1H, s, Ar). Elemental analysis for $C_{11}H_{12}Br_2O_4$): calc. (found) C, 35.90 (36.43); H, 3.29 (3.33); Br, 43.42% (42.29).

2-[4-Methoxy-2,5-bis(tetrahydrothiophen-1-ium-1-ylmethyl)-phenoxy]ethanol dibromide 6

Compound **4** (25 g, 0.06 mol) and tetrahydrothiophene (16 ml, 0.18 mol) in 350 ml of methanol were stirred at 50 °C for 48 h. The solution was concentrated by evaporation at room temp. and the residue was poured into 250 ml of acetone. The suspension formed was stirred at 0–5 °C for 1 h and the product was filtered off. The yield was 63% (20 g). δ_H (D_2O): 2.40 (8H, m, $\mathrm{SCH_2C}\mathit{H}_2$); 3.55 (8H, m, $\mathrm{SC}\mathit{H}_2\mathrm{CH_2}$); 3.96 (3H, s, OCH_3); 4.15 (2H, t, OCH_2); 4.35 (2H, t, CH_2OH); 4.57 (2H, s, Ar-CH_2); 4.62 (2H, s, Ar-CH_2); 7.26 (2H, s, Ar). Elemental analysis for $C_{19}H_{30}Br_2O_3S_2$): calc. (found) C, 43.19 (43.33); H, 5.34 (5.62); S, 12.14 (11.78); Br, 30.24% (30.02). The negative ion EI–MS of **6** showed a molecular ion peak at *m*/*z* 408, 410, 412 (1 : 2 : 1). The base peak was at *m*/*z* 273, 275 from M − [(2THT) + Br], (THT = tetrahydrothiophene) and another peak at *m*/*z* 352, 354, 356 (24) from M-(2THT).

4-Methoxy-2,5-bis(tetrahydrothiophen-1-ium-1-ylmethyl)-phenoxyacetic acid dibromide 7

Compound **5** (10 g, 0.027 mol) and tetrahydrothiophene (7.18 ml, 0.081 mol) in 150 ml of methanol were stirred at

50 °C for 48 h. The solution was concentrated by evaporation at room temp. and the residue was poured into 250 ml of acetone. The suspension formed was stirred at 0–5 °C for 1 h and the product was filtered off. The yield was 95% (14 g). δ_H (D_2O) 2.27–2.37 (8H, m, SCH_2CH_2); 3.47–3.58 (8H, m, SCH_2CH_2); 3.98 (3H, s, OCH_3); 4.53 (2H, s, OCH_2); 4.62 (2H, s, $ArCH_2$); 4.96 (2H, s, Ar-CH_2); 7.16 (1H, s, Ar); 7.27 (1H, s, Ar). Elemental analysis for ($C_{19}H_{28}Br_2O_4S_2 \cdot CH_3OH$): calc. (found). C, 42.86 (42.71); H, 5.71 (5.38); S, 11.44 (11.03).

Polymerization

The homopolymerization and copolymerization reactions were carried out according to Wessling.[11,12] Thus, a combined amount of the sulfonium salt monomer (0.015 mol) was dissolved in 200 ml of water under nitrogen at 0–5 °C. 1 M NaOH (1 equiv.) was injected into the solution per non-functionalized monomer and for **6**, and 2 equiv. for monomer **7**. The mixture was stirred vigorously for 1 h and the excess of base was titrated by 1 M HCl. Monomer conversion was calculated from the titration data. The viscous precursor polymer solutions were dialyzed in water for 10 d using a dialysis tube with a molecular mass cut-off of 12 000. The free-standing film technique was used to cast the polyelectrolytes on quartz substrate for UV–VIS and PL measurements. Indium tin oxide (ITO) coated glass was spin cast with the required polyelectrolyte for EL measurements. The final conjugated polymer was obtained in all cases by heating the film at 220 °C and 10^{-6} Torr for 12 h. The yields of the conjugated polymers were determined by weighing the films.

Multilayer structures

The fabrication of multilayer films *via* self-assembly for the X-ray reflectivity and photoluminescence studies was carried out on a smooth float glass substrate cleaned for 1 h in an ultrasonic cleaner using a 7:3 solution of H_2SO_4–H_2O. For electroluminescence studies an ITO coated glass was used. The multilayer films were prepared by sequential treatment of the substrate with aqueous solutions (using Millipore water) of poly(ethyleneimine), PEI, poly(styrenesulfonic acid) sodium salt, SPS, and co(PHydroxyV-PV). Thus, the substrate was first dipped into a solution of 0.1 vol% PEI in water at pH 7–8 for 10 min, followed by dipping into an aqueous 0.01 M solution of SPS, also for 10 min, and finally dipped into a solution of precursor co(PHydroxyV-PV). This sequence was repeated until the desired number of trilayers were built up. The conjugated co(PHydroxyV-PV) was formed in the assembled structure by heating at 250 °C at 10^{-6} Torr for 10 h.

Conclusion

The synthesis and characterization of new poly(phenylenevinylene) type conjugated copolymers with polar side chains has been presented. The luminescence spectra can be tuned by control of the copolymer composition. Furthermore, in the case of the carboxylated copolymer the luminescence spectra were found to be a function of the pH of the precursor solution. The copolymer with the hydroxy containing moiety can be used to self-assemble multiple trilayers based for the first time on hydrogen bonding rather than electrostatic interactions. Luminescence spectra of such multiple trilayers are considerably blue shifted due to an electron-hole confinement within the conjugated copolymer layer.

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