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Electroorganic reactions. Part 53. The electrosynthesis of novel water-soluble poly-(*p*-xylylene) (PPX) and poly (*p*-phenylenevinylene) (PPV) polymers and co-polymers

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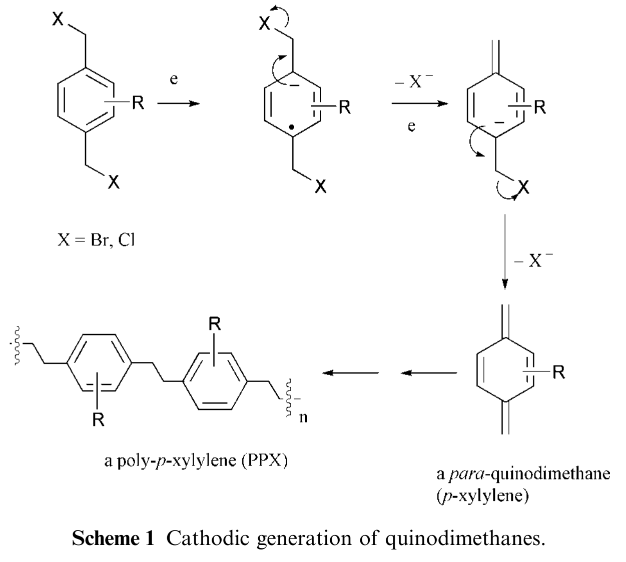
Controlled potential reduction at an Hg pool cathode of 2,5-bis(bromomethyl)benzenesulfonic acid, 2,5-bis(dibromomethyl)benzenesulfonic acid and the analogous benzoic acids, in aqueous solution with ammonium acetate or lithium nitrate electrolyte, is an efficient route to the corresponding water-soluble PPX and PPV polymers. Co-electrolyses of combinations of these precursors yield water-soluble random co-polymers. The polymers were primarily examined by gel-permeation chromatography, FTIR, ^{1}H and ^{13}C NMR (solution and solid state). The sulfonic acid substituted PPX forms insoluble complexes or salts with Ba^{2+}, Fe^{3+} and Cu^{2+}.

Water-soluble synthetic organic polymers are important as paint additives, polyelectrolytes, sequestering agents and in biomedical applications. Attention has also been drawn to their potential role in devising degradable products.[1] Water-solubility is usually conferred by polar functionality, as in poly(sodium styrene-4-sulfonate) and polyethylenesulfonic acid. Recent examples include the radical copolymerisation of maleic acid and sodium styrene-4-sulfonate[2] and the electro-oxidative polymerisation of carboxylate-substituted bithiophenes.[3] There is much current interest in innovative polymer synthesis and it has stimulated, among other examples, new syntheses of water-soluble polymers, notably the application of group transfer[4] and atom transfer radical polymerisation[5,6] to give novel and well-defined methacrylate-containing polymers and block co-polymers.

The versatility of electrosynthesis in DMF, applied to poly(*p*-xylylene) (PPX) and poly(*p*-phenylenevinylene) (PPV) polymers and co-polymers, has been demonstrated.[7,8] These polymerisations are tolerant of a wide range of functionality and have been shown[9] to proceed *via* quinodimethane (QDM) intermediates according to Scheme 1. Other examples of QDMs have been electrogenerated, characterised *in situ* and their reactivity studied.[9] Furthermore co-electrolysis of different bis(halomethyl) precursors leads to random co-polymers.[7–9] Because the QDMs are neutral they are not vulnerable to protonation in aqueous solution (as are radical-anions) and should therefore react in water as in DMF. We report here on the success of this approach as applied to the synthesis of novel water-soluble polymers.



Scheme 1 Cathodic generation of quinodimethanes.

Results and discussion

Preparation of precursors

The 1,4- bis(bromomethyl)- and 1,4-bis(dibromomethyl)arenes (**1a**, **1b**, **1d**) were prepared according to precedent[7,8] from 2,5-dimethylbenzoic or 2,5-dimethylsulfonic acid by treatment with bromine under UV irradiation. Details are given in the Experimental section.

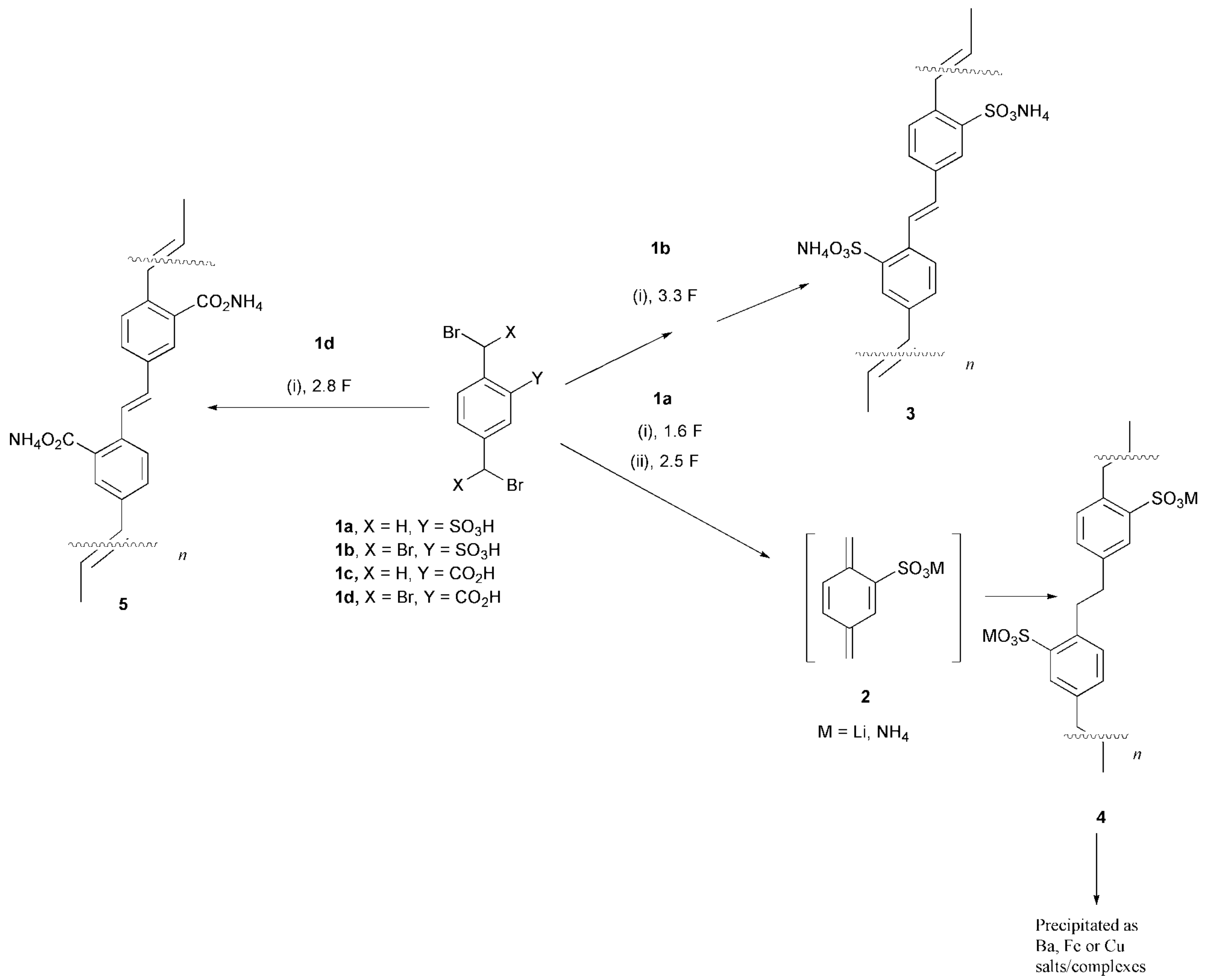
Cyclic voltammetry

Cyclic voltammetry was performed at $0.3\ V\ s^{-1}$ using a polished gold cathode in H_2O–NH_4OAc (0.1 M), with the pH adjusted with NH_4OH to *ca.* 9. Reduction of substrates **1a**–**1d** was observed as chemically irreversible shoulders on the electrolyte background cut-off curve. Potentials (V *vs.* SCE) were, for the 1,4-bis(bromomethyl)arenes, −1.25 (**1a**) and −1.40 (**1c**); for the 1,4-bis(dibromomethyl)arenes the values were −1.19 (**1b**) and −1.24 (**1d**).

Products of controlled potential electrolyses

Scheme 2 outlines the key materials used and the experiments relating to water-soluble homopolymers (**3**–**5**). In line with the voltammetric results, typical conditions for the conversions into QDMs were exhaustive electrolysis at controlled potential at *ca.* −1.3 to −1.5 V *vs.* SCE, and aqueous electrolyte [NH_4OAc (0.1 M), pH 9–10, adjusted with NH_4OH]. In all cases the charge consumed was less (by 20–25%) than the theoretical amount (2 F and 4 F for PPX and PPV formation, respectively), possibly a consequence of competing hydrolysis of the starting materials. By analogy with earlier experiments in DMF a stirred Hg pool cathode was used to minimise the possibility of passivation by electrode filming.

Additionally, cathodic polymerisation was attempted using



Scheme 2 Controlled potential preparative-scale electrolyses and co-electrolyses. Electrolysis conditions: (i) Hg cathode, −1.3 V (SCE), H_2O–NH_4OAc–NH_4OH; (ii) Hg cathode, −1.3 V (SCE), H_2O–$LiNO_3$–LiOH.

2,5-bis(bromomethyl)benzoic acid (**1c**) as precursor. In this case no polymeric product was obtained. With this exception efficient electropolymerisation was obtained, under the conditions described in Scheme 2, with apparently high yields of the homopolymers (**3**–**5**), see Table 1 and experimental section. Co-electrolysis of 1 : 1 mixtures of (**1a**+**1c**) and (**1b**+**1d**) gave the expected co-polymers (**6** and **7**) according to FTIR, ^{13}C NMR in D_2O and, for the solids (see below), elemental analysis. The homopolymers and copolymers were initially obtained as the ammonium salts; for the PPXs as beige or colourless, viscous solutions and for the PPVs as clear, fluorescent, viscous yellow solutions. Conversion into the acid form by treatment with ion-exchange resin, followed by freeze drying, allowed isolation of the PPXs as beige or white fibrous solids and the PPVs as fluorescent yellow filaments. Overall yields were high, according to NMR, although precise calculation of the yields of the solid samples was problematical because of sometimes-incomplete conversion into the acid form and uncertainty about the amount of residual water or inorganic salt. The solid polymers were stable at up to 300 °C and did not melt; progressive decomposition took place in the 300–600 °C range. The sulfonic acid polymers and co-polymers were hygroscopic and they readily redissolved in water to form viscous solutions. The carboxylate polymers and co-polymers similarly redissolved in water in their salt forms.

In one case (**1a**) electrolysis in $LiNO_3$–H_2O–LiOH gave a

Table 1 GPC analysis[a] of PPX and PPV polymers

Starting material	Polymer	Methyl ester			Sulfonamide[b]		
		M_n/g mol^{-1}	M_w/M_n	n	M_n/g mol^{-1}	M_w/M_n	n
1a	PPX (**4**)	4020	1.5	30	5455	2.0	60
1b	PPV (**3**)	115270	2.0	1153	121900	2.0	1320
1d	PPV (**5**)	72150	1.6	826			
1a+**1c**	PPX (**6**)	6260	1.4	50	6700	1.35	55
1b+**1d**	PPV (**7**)	74210	2.0	865	259000	2.3	1594
[**1e** (X=Br, Y=SO_3NEt_4), in DMF][10]	PPV (**8**)	7820	3.7	93			

[a]Mobile phase, DMF containing 0.1% LiBr at 73 °C. Polymer molecular weights calculated using Polymer Laboratories PL Caliber GPC System, version 4.01. Polymer Laboratories PL-gel (polystyrene–divinylbenzene copolymer gel) mixed C (5 μm two 300 × 7.5 mm and guard) columns, calibrated against narrow standard polystyrene (molecular weight range 580–3 × 10^6). [b]Sulfonic acid polymers treated with DMF at 100 °C until dissolution.[11,12]

solution of the lithium salt and on treatment with $Ba(NO_3)_2$ solution the totally insoluble barium salt of the PPX was precipitated and characterised by FTIR and solid-state ^{13}C NMR. Treatment of the PPX-sulfonic acid derived from **4** with aqueous $FeCl_3$ and with $Cu(NO_3)_2$ gave yellow and blue precipitates respectively. They were shown by atomic absorption spectroscopy to have iron and copper contents corresponding to (Fe, 41%) and (Cu, 34.5%) occupancy of available sites for salt formation or complexation assuming a ratio of $(-SO_3H):M$ of 3 ($M=Fe$) or 2 ($M=Cu$)

The polymers have been characterised by FTIR, ^{13}C NMR (solid and solution), elemental analysis (C,H,N,S), DSC and, after conversion into DMF-soluble methyl esters or sulfonamides,[2] by gel permeation chromatography (GPC). Major spectroscopic features (FTIR and ^{13}C NMR) were closely similar to those of PPXs and PPVs formed in DMF.[7,8] The elemental analysis results imply for the sulfonic acid polymers an associated molecule of water and a loss of *ca.* 20% of sulfur, possibly through cleavage during electrolysis. However, the measured C:H ratios were acceptably close to calculated values.

Doping and measurement of the electrical conductivities of the water-soluble PPVs has not been attempted. However, a sample of a water and DMF-soluble PPV, **8**, analogous to **3**, but as the Et_4N^+ salt, has been prepared[10] by reduction in DMF–Et_4NBr (0.1 M) of methyl 2,5-bis(dibromomethyl)benzenesulfonate; the methyl ester cleaves during reduction and the isolated product is the yellow, fluorescent, tetraethylammonium salt. Use of sodium bromide as electrolyte gave[10] the corresponding sodium sulfonate PPV. Doping of solid samples with BF_3 and measurement of conductivity according to reported[8] procedures, gave values of 0.01 and 0.05 S cm^{-1} for the sodium and tetraethylammonium salts respectively.

GPC analysis in aqueous solution is problematical and consequently the polymers were converted into DMF-soluble samples of the methyl esters and sulfonamides. Analysis of these derivatives, using polystyrene standards, gave in each case a bimodal distribution of molecular size, the lower mass species corresponding to oligomers. Conversion into the methyl esters is cleaner than conversion into the sulfonamides and in each case it is not possible to be certain that the molecular weight information has not been distorted in the process of obtaining DMF-soluble samples. We regard the results from the methyl esters as the more reliable. The broad conclusions are, however, likely to be reliable. The higher mass fractions are described in Table 1 and it is evident that the PPXs are formed with a lowish degree of polymerisation, in contrast to the PPVs. The extent of polymerisation in water is at least as high as found for comparable[8] reaction in DMF and the polydispersities better.

Summary and conclusions

The efficiency and versatility of the electrochemical method established for PPX and PPV synthesis in aprotic solvent is replicated in aqueous solution and examples of novel water-soluble polymers and co-polymers have been produced. The sulfonic acid polymers are easily converted into insoluble barium, iron and copper salts/complexes. The properties of the polymers, copolymers and salts/complexes, and possible applications, are under examination.

Experimental

Solvents, electrolytes and analytical procedures

Solvents and supporting electrolytes. Triply distilled water was used together with tetraethylammonium bromide (Aldrich, Et_4NBr, recrystallised from EtOAc) and ammonium acetate (Aldrich, Analar grade) as electrolytes. All other chemicals were used as purchased without further purification unless stated otherwise. Preparative column chromatographic separations were performed using Merck silica gel 60H (230–400 mesh), while precoated silica gel plates (Merck, $60F_{254}$) were used for analytical TLC.

Instruments. Melting points were obtained on a Reichert melting point apparatus and were uncorrected. Infrared spectra were recorded as liquid films or KBr discs on a Shimadzu FTIR-8300. Solution ^1H and ^{13}C NMR spectra were recorded using a Bruker AM250 and AMX600 spectrometers (University of London Intercollegiate services, ULIRS) in $CDCl_3$, D_2O, and DMF-d_7 as solvents with either TMS or TSP as internal standards, while solid spectra were obtained using an MSL300 spectrometer (ULIRS). Differential scanning calorimetry (DSC) was performed on a Perkin Elmer PC series DSC7 calorimeter. EI mass spectra were measured using a Kratos MS50RF/KratosDS90 data system, and FAB mass spectra were obtained on the same spectrometer using *m*-nitrobenzyl alcohol as a matrix.

Gel permeation chromatography. A Hewlett-Packard HP1100 series liquid chromatograph, operated by HP ChemStation software, was employed with a quaternary gradient pump and UV (270 nm) detector. Polymer molecular weights were calculated using Polymer Laboratories PL caliber GPC system, version 4.01. Polymer Laboratories PL-gel (polystyrene–divinylbenzene copolymer gel) Mixed C 5 μm, two 300 × 7.5 mm and guard columns, enclosed in a constant temperature oven, were used. A calibration curve was constructed using narrow standard polystyrene (molecular weight range 500 to 3×10^6). The mobile phase was DMF (Aldrich, HPLC grade) containing 0.1% LiBr at 73 °C and at the elution rate of 1.0 ml min^{-1}

Atomic absorption measurements. About 20 mg of the metal-containing polymer sample was accurately weighed and fused with sodium hydroxide with subsequent extraction with nitric acid (AR). The extract was diluted to 100 ml using distilled water, to give a final acid concentration of about 10% v/v. A blank was also prepared using the same reagents. Immediately prior to analysis the samples were filtered through a Whatman 541 filter paper to remove particulate carbon. The metals were determined by Atomic Absorption Spectroscopy using a Unicam 939 AAS with an air–acetylene flame. Standards were prepared by diluting Spectrosol (BDH) 1000 ppm standard solutions of iron and copper with subsequent dilution. Iron was measured at 248.3 nm with background correction and copper at 324.8 nm (no background correction required). No copper or iron was found in the blank samples.

Electrochemical experiments

Cyclic voltammetric experiments were performed using either an Princeton Applied Research (PAR) VersaStat or Model263A potentiostat with controlling PAR software (Model 270/250 Research Electrochemistry Software v 4.00). Glass cells for cyclic voltammetry were undivided and equipped with a gold disc (1.0 mm) working electrode (cathode), saturated calomel reference electrode (SCE) and platinum coil counter electrode (anode). The experiments were carried out in 0.1 M NH_4OAc–H_2O solutions with the pH adjusted to *ca.* 9 0 (NH_4OH).

Preparative scale electrochemical reductions were carried out using a DT 2101 Hi Tek potentiostat with an electronic charge integrator constructed in the Department's electronic workshop. Conventional glass cells were used, typically with the cathode compartment (*ca.* 40 ml capacity with a stirred mercury pool, 16 cm^2 area) and anode (graphite) separated by a medium porosity glass sinter. The reference electrode was saturated calomel electrode (SCE). The reaction was kept in an inert atmosphere by the slow bubbling of nitrogen through the solution. The compounds were added to an efficiently stirred solution of aqueous NH_4OAc (0.1 M) in the working compartment and pH adjusted to *ca.* 9.0 with NH_4OH and maintained at this value for the duration of the experiment. The solution was electrolysed at the appropriate potential (as determined by CV, *vs.* SCE). Electrolysis was stopped when the current returned to a low background value. The catholyte was evaporated carefully (avoiding excessive foaming) using a rotary evaporator at *ca.* 60 °C. The residue was dissolved in distilled water (40 ml) and to the solution was added Amberlite IR 120 (30 ml, H^+-preactivated). The resin was decanted and the supernatant was evaporated to dryness. Acetic acid was removed by azeotropic distillation with toluene and water to give a solid material, which was washed with ethanol to remove soluble impurities. The solid product was dried under reduced pressure (0.5 mmHg, 24 h) and stored in a desiccator. Methylation of the polymers, when required, was accomplished by heating (under reflux condition) the suspension of the desired polymers in anhydrous MeOH for 4–5 days. Conversion into sulfonamides required treatment with DMF at 100 °C until dissolution.[11,12]

Starting materials

Bromination of 1,4-dimethylarenes: general method. 2,5-Dimethylbenzenesulfonic acid or 2,5-dimethylbenzoic acid (0.04 mol) was added, under nitrogen to dry $CHCl_3$ (300 ml). The well-stirred suspension was heated under gentle reflux and irradiated at close range with a 300 W UV lamp. Bromine (0.082 or 0.164 mol, for dibromo or tetrabromo derivatives, respectively), in dry $CHCl_3$ (50 or 80 ml), was added dropwise with vigorous reflux. During this period (*ca.* 2 h), HBr was evolved copiously and when this ceased the solution was cooled and the solvent removed. The solid product was recrystallised from $CHCl_3$–petroleum ether (60–80 °C).

*2,5-Bis(bromomethyl)benzenesulfonic acid (**1a**).* 2,5-Dimethylbenzenesulfonic acid (5.58 g, 0.03 mol) was brominated using the general procedure to give a white crystalline product (4.1 g, 40%). Mp 96–98 °C; IR (KBr), ν/cm^{-1}: 1218, 1132 (SO_3H), 634 (C–Br); ^1H NMR (250 MHz, D_2O/TSP, δ_{ppm}): 7.94 (1H, d, $J=2.5$ Hz, Ar, H-6), 7.62 (2H, m, Ar, H-3,4), 4.98 (2H, s, Ar-CH_2-Br), 4.62 (2H, s, Ar-CH_2-Br).

*2,5-Bis(dibromomethyl)benzenesulfonic acid (**1b**).* 2,5-Dimethylbenzenesulfonic acid (7.4 g, 0.04 mol) was brominated using the general procedure to give a white crystalline product (14.2 g, 71%). This material was extracted with dichloromethane (soxhlet) to remove remaining impurities. Mp 146–147 °C (lit.[13] 146.5–147.5 °C; IR (KBr), ν/cm^{-1}: 2925 (SO_3H) 1218, 1132 (SO_3H), 678 (C–Br); ^1H NMR (600 MHz, D_2O/TSP, δ_{ppm}): 8.18 (1H, d, $J=8.1$ Hz, Ar, H-3), 7.96 (1H, d, $J=2.1$ Hz, Ar, H-6), 7.85 (1H, d, $J=8.1$, 2.1 Hz, Ar, H-4), 7.68 (1H, s, CH–Br_2), 6.92 (1H, s, CH-Br_2).

*2,5-Bis(bromomethyl)benzoic acid (**1c**).* 2,5-Dimethylbenzoic acid (7.4 g, 0.04 mol) was reacted with bromine (14 g, 0.082 mol) following the above general procedure to give white crystalline 2,5-bis(bromomethyl)benzoic acid (**1c**) (3.6 g, 26%). A second crop (3 g) was also isolated. Mp 115–116 °C (lit.[13] 116 °C); IR (KBr), ν/cm^{-1}: 2970–2500 (CO_2H), 1693 (C=O), 1298–1200 (CO_2H), 634 (C–Br); ^1H NMR (250 MHz, $CDCl_3$, δ_{ppm}): 7.99 (1H, d, $J=1.2$ Hz, Ar, H-6), 7.47 (1H, dd, $J=8.4$, 1.2 Hz, Ar, H-4), 7.40 (1H, d, $J=8.4$ Hz, Ar, H-3), 4.98 (2H, s, Ar–CH_2–Br), 4.49 (2H, s, Ar–CH_2–Br).

*2,5-Bis(dibromomethyl)benzoic acid (**1d**).* 2,4-Dimethylbenzoic acid (3 g, 0.02 mol) was brominated using the general procedure to give a white crystalline product (7.6 g, 81%) that was recrystallised from chloroform–petroleum ether (60–80 °C). Mp 167–168 °C (lit.[10] 167–168 °C); IR ν/cm^{-1}: 3200–2500 (CO_2H), 1689 (C=O), 661 (C–Br); ^1H NMR (250 MHz, $CDCl_3$, δ_{ppm}): 8.19 (1H, d, $J=8.3$ Hz, Ar, H-3), 8.16 (1H, d, $J=2.3$ Hz, Ar, H-6), 8.12 (1H, s, Ar-CH-Br_2), 8.00 (1H, dd, $J=8.3$, 2.3 Hz, Ar, H-4), 7.25 (1H, s, Ar-CH-Br_2).

Products

Polymer 3. 2,5-Bis(dibromomethyl)benzenesulfonic acid (**1b**) (763 mg, 1.5 mmol) suspended in aqueous 0.1 M NH_4OAc (35 ml) was electrolysed at −1.3 V *vs.* SCE following the general procedure described above. A viscous fluorescent yellow solution was obtained after 3.3 F. Subsequent work-up and drying gave a yellow solid (600 mg, 211%). IR (KBr), ν/cm^{-1}: 3500–2350 (NH_4^+, SO_3H), 1680 (NH_4^+), 1627, 1604 (Ar, C=C), 1400 (NH_4^+), 1250–1100 (SO_3^-, salt); ^{13}C NMR (75 MHz, solid, δ_{ppm}): 140.4 (Ar, quaternary), 132.3 (Ar, tertiary, CH=CH), 40.0 (CH_2–CH_2, weak signal), 21.2 (Me, weak signal); (150 MHz, solution-D_2O, δ_{ppm}): 141–146 (Ar, quaternary), 127–136 (Ar, tertiary, CH=CH), 75–80 (Ar–CH–O), 45–47 (Ar–CH–$(C)_2$ [crosslinking]), 35–40 (CH_2–CH_2, weak signals), 22, 24 (Me, weak signals); ^1H NMR (600 MHz, solution-D_2O, δ_{ppm}): 6.7–8.3 (br s, Ar–H, CH=CH), 5.6–6.1 (br s, CH=CH), 4.8–5.25 (ArCH–O), 2.90–3.60 (CH_2–CH_2, weak signals), 2.1–2.7 (Me, weak signals); elemental analysis: ideal formula, $(C_8H_6SO_3)_n$, found, $(C_8H_{5.7}S_{0.9}\cdot H_2O\cdot N_{0.32}H_{1.28})_n$ (O not analysed); molecular weight distribution, see Table 1.

Polymer 4. 2,5-Bis(bromomethyl)benzenesulfonic acid (**1a**) (688 mg, 2 mmol) suspended in 0.1 M NH_4OAc (40 ml) was electrolysed at −1.3 V *vs.* SCE as described in the general procedure. When the current was returned to the background level, electrolysis was stopped (1.6 F) and the viscous catholyte solution was worked-up to give a beige solid (391 mg, 106%). IR (KBr), ν/cm^{-1}: 3413, 3161 (br, NH_4^+, SO_3H), 1618 (Ar, C=C), 1489, 1400 (NH_4^+), 1182, 1085, 1026 (SO_3^-, salt); ^{13}C NMR (75 MHz, solid, δ_{ppm}): NH_4^+ salts, 140.8–138.4 (Ar, quaternary), 132.5 (Ar, tertiary), 37.1 (CH_2–CH_2), 22 (Me); ^{13}C NMR (150 MHz, solution-D_2O, δ_{ppm}): 180 (CO_2H), 147–138 and 138–132 (Ar, quaternary), 132–128 (Ar, tertiary), 41–33 (CH_2–CH_2), 24, 23 (Me); ^1H NMR (600 MHz, solution-D_2O, δ_{ppm}): 7.81–7.60 (Ar-H), 7.60–7.20 (Ar-H), 3.80–3.10 (CH_2–CH_2), 2.3, 2.2 (Me); elemental analysis: ideal formula, $(C_8H_8SO_3)_n$, found, $C_8H_8S_{0.87}\cdot 2H_2O\cdot N_{0.14}H_{0.55}$ (O not analysed); molecular weight distribution, see Table 1.

Polymer 5. 2,5-Bis(dibromomethyl)benzoic acid (**1d**) (936 mg, 2 mmol) in aqueous 0.1 M NH_4OAc (40 ml) was electrolysed at –1.3 V *vs.* SCE as described in the general procedure. After 2.8 F was consumed, the fluorescent viscous solution was worked-up to give a yellow solid (305 mg, 104%). IR (KBr), ν/cm^{-1}: 3402 (CO_2H), 1716 (CO_2H), 1616 (Ar, CH=CH); ^{13}C NMR (150 MHz, solution-DMSO-d_6, δ_{ppm}): 168.6, 163.0 (CO_2H), 120.0 ± 137.0 (Ar, CH=CH), 68.8–82.4 (ArCH-O), 45–60 (Ar–CH–$(C)_2$ [crosslinking]), 37.7–40.0 (CH_2–CH_2, weak signals), 21.99 (Me, weak signal); ^1H NMR (600 MHz, solution-DMSO-d_6, δ_{ppm}): 7.0–8.5 (Ar-H), 5.80–6.65 (CH=CH), 2.4–2.7 (Me); elemental analysis: ideal formula, $(C_{36}H_{23}\cdot NH_4)_n$, found, $(C_{36.8}H_{23}\cdot NH_4)_n$ (O not analysed); molecular weight distribution, see Table 1.

Copolymer 6. 2,5-Bis(bromomethyl)benzenesulfonic acid (**1a**) (344 mg, 1.0 mmol) and 2,5-bis(bromomethyl)benzoic acid (**1c**) (276 mg, 1.0 mmol) suspended in aqueous 0.1 M NH_4OAc (40 ml) were co-electrolysed at −1.3 V *vs.* SCE. The pH of the catholyte was adjusted to *ca.* 9–10 before electrolysis and maintained at this value throughout. Electrolysis was stopped when the cell current went back to background level and after a charge of 1.7 F was consumed. A beige coloured solid film (327 mg, 98%) was isolated after drying under reduced pressure (0.5 mmHg, 24 h). IR (KBr), ν/cm^{-1}: 3550–2700 (NH_4^+, SO_3H, CO_2H), 1637, 1618 (CO_2^- salt), 1400 (NH_4^+), 1250, 1100 (SO_3^-, salt); ^{13}C NMR (150 MHz, solution-D_2O, δ_{ppm}): 175.3 (CO_2H), 130.0–145.0 (Ar), 71.8 (Ar–CH–O [partial hydrolysis of C–Br?]), 32.2–39.0 (CH_2–CH_2), 20.8, 20.0 (Me); ^1H NMR (600 MHz, solution-D_2O, δ_{ppm}): 6.7–8.1 (Ar-H), 5.36 (ArCH–O), 3.1–3.5, 3.1–2.5 (CH_2–CH_2), 2.3, 2.6 (Me); elemental analysis: ideal formula, $(C_{17}H_{15}SO_5 \cdot NH_4)_n$, found, $(C_{17}H_{15.5}S_{0.76} \cdot H_2O \cdot N_{0.84}H_{3.36})_n$ (O not analysed); molecular weight distribution, see Table 1.

Copolymer 7. 2,5-Bis(dibromomethyl)benzenesulfonic acid (**1b**) (508 mg, 1.0 mmol) and 2,5-bis(dibromomethyl)benzoic acid (**1d**) (478 mg, 1.0 mmol) suspended in aqueous 0.1 M NH_4OAc (40 ml) were co-electrolysed at -1.5 V *vs.* SCE following the general procedure outlined above. When the cell current returned to low background level (after 2.8 F), the fluorescent viscous solution was worked-up to give a yellow solid (781 mg, 118%). IR (KBr) ν/cm^{-1}: 3413, 3172 (NH_4^+), 1701 (CO_2H), 1604 (Ar, CH=CH), 1490, 1400 (NH_4^+), 1182 (SO_3^- salt); ^{13}C NMR (150 MHz, solution-D_2O, δ_{ppm}): 167–171, 162–164 (CO_2H), 145–149 (Ar, quaternary), 122–140 (Ar, tertiary, CH=CH), 71–85 (ArCH–O, weak signal), 50–62, 47 (Ar–CH–$(C)_2$ [crosslinking]), 34–37 (CH_2–CH_2, weak signals), 22 (Me, weak signal); elemental analysis: ideal formula, $(C_{17}H_{11}SO_4 \cdot NH_4)_n$, found, $(C_{16.8}H_{11}S \cdot \frac{1}{2}H_2O \cdot NH_4)_n$, (O not analysed); molecular weight distribution, see Table 1.

Barium salt of polymer 4. This was prepared in 52% yield by precipitation from an aqueous solution of the lithium salt with an excess of $Ba(NO_3)_2$. ^{13}C NMR (75 MHz, solid, δ_{ppm}): Ba salts, 1140.8 (Ar, quaternary), 131.2 (Ar, tertiary), 37.7 (CH_2–CH_2),

Ferric salt of polymer 4. Ferric chloride ($FeCl_3 \cdot 6H_2O$, 810.9 mg, 3.0 mmol) was dissolved in 15 ml of degassed H_2O (N_2) and to the resulting solution was added polymer **4** (326 mg, 1.8 mmol). The suspension was stirred under N_2 at room temperature overnight. The precipitate formed was filtered and dried under reduced pressure over P_2O_5 to give an orange–brown precipitate (130 mg) containing 3.82% Fe (41% of expected), as determined by atomic absorption.

Cupric salt of polymer 4. Polymer **4** (269 mg, 1.5 mmol) was dissolved in 15 ml distilled water and treated with copper nitrate [$Cu(NO_3)_2 \cdot H_2O$, 725 mg, 3.0 mmol] and the greenish-blue solution was stirred overnight at room temperature. The resulting suspension was centrifuged and washed with water to give a bluish precipitate (86 mg after drying). Atomic absorption experiments showed the presence of 5.08% Cu (34.5% of expected).

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