Synthesis and Characterization of Poly(1,4-anthrylenevinylene)

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ABSTRACT: The first anthracene-containing conjugated polymer, poly(1,4-anthrylenevinylene) (PAV), was synthesized. Its processability was accomplished by using the precursor polymer route. Consideration of the mechanism responsible for the polymerization reaction led to selection of the adequate monomer to achieve polymerizability. UV spectra of PAV films showed a band-gap energy 0.3 eV smaller compared to that of poly(phenylenevinylene) (PPV) as a result of the minimization of the energy difference between aromatic and quinoid resonance structures by the anthracene unit. Model compound **13** was synthesized to exclude structural defects of PAV as well as to clarify the role of the steric and electronic effects on the conformation of the main chain. The optical properties of PAV thin films drastically changed upon reaction with a dienophile in the solid state.

Introduction

Multiple potential applications of conjugated polymers have been foreseen based on the combination of its electrooptical properties with the advantage of the mechanical strength and easier fabrication of such materials in device structures. Poly(arylenevinylene)s of general formula $[-\mathrm{AR}-\mathrm{CH}=\mathrm{CH}-]_n$ are promising candidates among the conjugated polymers for use in all-optical signal processing or as the active layer in light-emitting diodes.[1-4] Although most of the studies have centered on poly(*p*-phenylenevinylene) (PPV, Ar = phenylene), the variation of the arylene building block offers the possibility of tailoring the electro-optical properties of these polymers. Attractive units for structural variations are anthracene,[5,6] due to the extension of the π-system, cyclooctatetraene,[7] due to its outstanding redox activity, or 2,2′-biphenyl,[8] due to its conformational mobility.

In particular, poly(anthrylenevinylene)s are of interest for the following reasons. According to experimental observations obtained from oligomers[6] and theoretical expectations,[9] the incorporation of the anthracene unit into the polymer main chain will minimize the energy difference between the aromatic and quinoid resonance structures when compared to the 1,4-phenylene unit, with the consequent decrease in the electronic band gap of the macromolecule. Furthermore, we have demonstrated that the electrophoric subunit anthracene in a series of oligo(anthrylenevinylene)s is able to accept two charges in a reduction process;[6] therefore, the charge-storage properties of poly(anthrylenevinylene)s should be remarkable. By selection of adequate topology, e.g., an anthracene moiety linked by the 1,4-position, an element of two-dimensionality could also be introduced in the monodimensional electronic structure of the polymer backbone. On the basis of previous results obtained from poly(*p*-naphthalenevinylene), this structural modification is expected to affect both the magnitude and the response time of the third-order nonlinear optical signal.[10] Finally, there is the attractive possibility of performing polymer analogous reactions in the reactive 9,10-positions of the anthracene unit to modify the optical properties of the material.

The present study focuses on the synthesis and characterization of poly(1,4-anthrylenevinylene) (PAV, **7**) (Scheme 1). The well-known precursor polyelectrolyte route[11] was selected because it is the only one available that provides processability for the unsubstituted high molecular weight poly(arylenevinylene)s. It should be noted, however, that monomer **2** could not be polymerized when this synthetic route was used in an attempt to obtain the yet unknown poly(9,10-anthrylenevinylene) (**8**).[6] An important feature of the mechanism of this polymerization reaction is that the true monomer is a quinodimethane sulfonium salt, which is formed *in situ* by reaction of the bis(sulfonium) salt with a base.[12] Thus, although the monomer **2** easily generates the corresponding 9,10-anthraquinodimethane (**4**), this intermediate does not polymerize as a consequence of its relatively stable quinodimethane structure. This is due to the electronic stabilization of the quinodimethane brought about by the fused benzene rings and due to the steric yielding of the exocyclic double bonds exerted by the peri-hydrogens.[13] These effects are expected to be less pronounced in the reactive intermediate **3**, which is generated from the bis(sulfonium) salt **1**. Therefore, we reasoned that **3** should be less stable than **4** and be able to polymerize to afford the polyelectrolyte **5**. This turns out to be the case.

Results and Discussion

A schematic summary of the synthesis of the monomer is shown in Figure 1. The main concern in the design of the synthetic pathway of **1** was the known reactivity of the 9,10-positions of the anthracene unit that limit the range of reactions to be used during the synthetic transformations. In the first steps these reactive positions were protected as being part of an anthraquinone moiety. Then, after the reduction to obtain compound **10**, a straightforward succession of transformations at the saturated carbons on positions 1 and 4 led to the sulfonium salt monomer. The chloride sulfonium salt **1** was selected instead of the bromide salt due to the lower solubility shown by diverse bromide sulfonium salts compared to that shown by the chloride ones.

The precursor polymer was prepared from the bis(sulfonium) salt using the Wessling-Zimmermann process as shown in Scheme 1. Although this polymerization reaction is commonly carried out in aqueous media, a mixture of water and acetonitrile was used as solvent due to the limited solubility of the monomer in water. In addition to the increased monomer solubility, this solvent mixture was used because of the beneficial effects of acetonitrile on the generation of quinodimethanes, the

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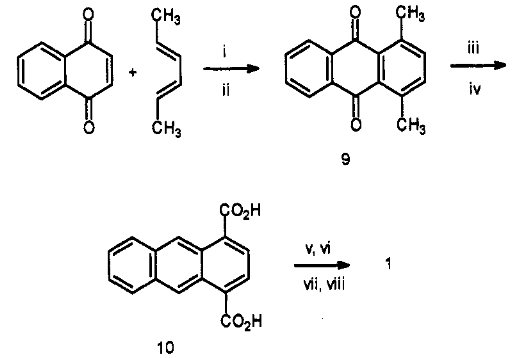
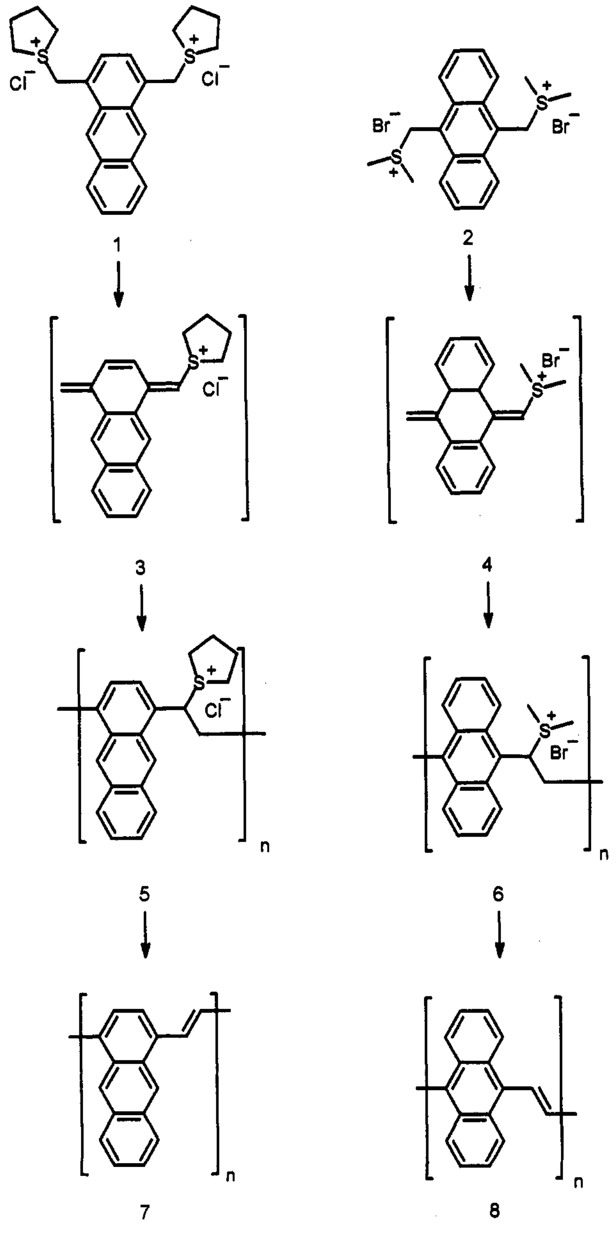


Figure 1. Synthesis of monomer **1**: (i) toluene/60 °C, 99%; (ii) O$_2$/KOH/ethanol, 71%; (iii) HNO$_{3(aq)}$/120 °C, 69%; (iv) NH$_{3(aq)}$/Zn/heat, 85%; (v) CH$_2$N$_2$/ether, 99%; (vi) HLiH$_4$/tetrahydrofuran, 86%; (vii) SOCl$_2$/methylene chloride/acetonitrile, 48%; (viii) tetrahydrothiophene/methanol/60 °C, 87%.

Scheme 1



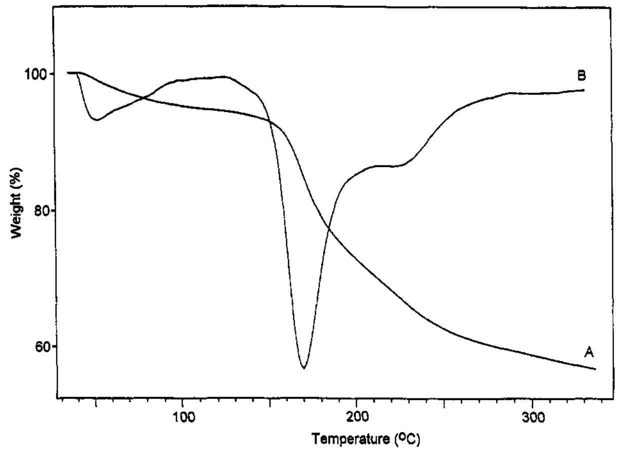


Figure 2. Thermogravimetric analysis of precursor polymer **5** at a heating rate of 20 °C min^{-1}.

true monomers in this polymerization reaction, and on the molecular weight of the polyelectrolyte.[14] In a preliminary test, the quinodimethane intermediate **3** was detected as a transient absorption, which faded within an hour, at 312 nm in the UV spectrum of a basic water/acetonitrile (4:1) solution of monomer **1**. In a parallel experiment under the same conditions but using monomer **2**, a band corresponding to **4** was observed to grow at 292 nm and to remain at the maximum absorbance value reached for 4 h. Thus, observation of the growth and decay of the intermediate **3** was a strong indication of the ability of monomer **1** to polymerize while the test confirmed the behavior previously observed for **2**. Indeed, a yellow gel was formed in 1 min after the base addition to the reaction mixture under the conditions described under Experimental Section. The polyelectrolyte was readily dissolved in methanol after isolation by precipitation from acetone/2-propanol. Solutions of **5** were not stable, however, and a yellow precipitate that was insoluble in a variety of solvents appeared shortly after the polyelectrolyte dissolution. This behavior of the polyelectrolyte is most probably due to solvent substitution of the sulfonium groups that yields a neutral polymer. Nevertheless, solutions of **5** in methanol or DMF could be stabilized by addition of pyridine as cosolvent to allow processing according to the procedure developed for dialkoxy-substituted precursor polymers.[15,16] The light yellow free-standing precursor polymer films, which were cast from these solutions, were homogeneous in appearance, flexible, and showed good mechanical properties.

The precursor polymer films were converted into the conjugated polymer by thermal elimination at 290 °C. Free-standing films of PAV were dark green with a metallic luster and somewhat brittle, while the thin films (100 nm thick) cast on quartz plates showed a purple color. The result of the elemental analysis of the eliminated films showed that the content of sulfur was below the detection limit (0.05%), thus indicating a quantitative elimination of the sulfonium groups. The progress of elimination of a cast film was followed by thermogravimetry (TGA) as shown in Figure 2. After an initial weight loss due to solvent evaporation below 100 °C, the sample loses 34% of its weight between 100 and 300 °C, this value being very close to the theoretical weight loss. The prominent thermal transition maximum at 170 °C shown in Figure 1 corresponds to the elimination of hydrogen chloride and tetrahydrothiophene, while the shoulder that shows a maximum at 230 °C most probably corresponds to the elimination of hydrogen chloride from CH$_2$CHCl units generated by substitution of the sulfonium group by the chloride counterion. These temperature values are approximately 50 °C higher than those observed in poly(*p*-phenylenevinylene)[17] but are in the same range as the values (*ca.* 190 °C) corresponding to the more sterically congested poly(*p*-phenylenevinylene).[18] Undoubtedly, steric requirements play a role in the thermal elimination of the sulfonium salt polyelectrolytes that should be taken

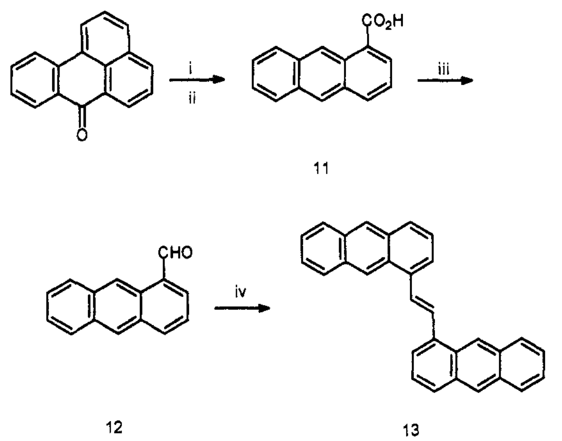


Figure 3. Synthesis of model compound 13: (i) $Na_2Cr_2O_7/H_2SO_{4(aq)}$, 68%; (ii) $NH_{3(aq)}$/Zn/heat, 88%; (iii) $BH_3{\cdot}Me_2S$, PCC/methylene chloride/heat, 65%; (iv) $TiCl_4$/Zn/tetrahydrofuran/heat, 90%.

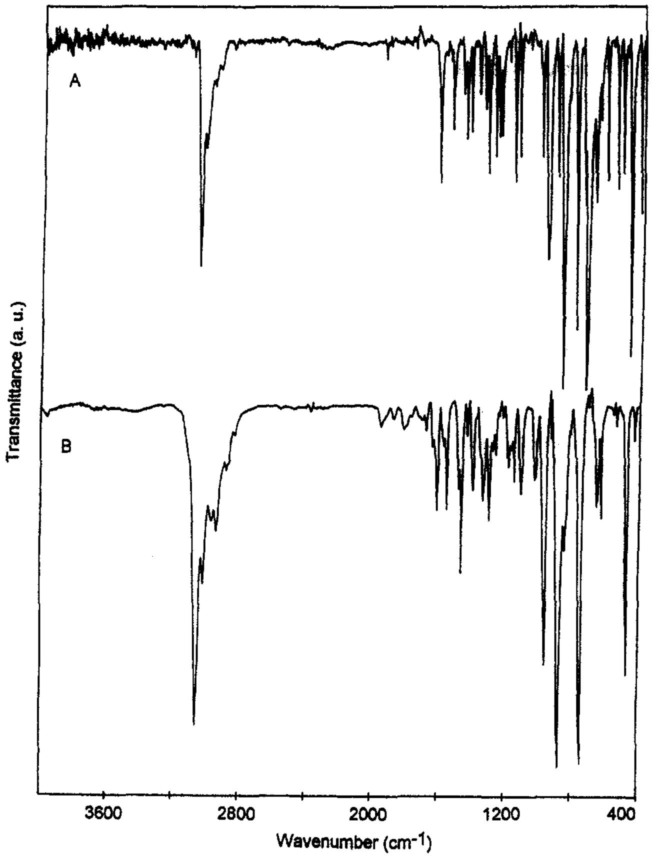


Figure 4. IR spectra of (A) model compound 13 (KBr pellet) and (B) polymer 7 (film).

into account to choose the optimum conversion temperatures.

Model compound 13 was prepared to support the interpretation of the spectroscopic data as well as to assess the occurrence of structural defects in PAV. A schematic summary of the synthesis of 13 is shown in Figure 3. The structural regularity of the polymer is evidenced by comparison of the IR spectra of 7 with that of model compound 13 (Figure 4). Allowing for the slight differences in either the position or the intensities of the vibrations, both spectra show the same shape. The only significant difference between the two spectra arises from the different substitution pattern in the ring linked to the vinylic units. Thus, the bands at 682 and 795 cm^{-1}, which are present in 13 and absent in 7, correspond to CH out-of-plane bending mode of three adjacent hydrogens. No signals

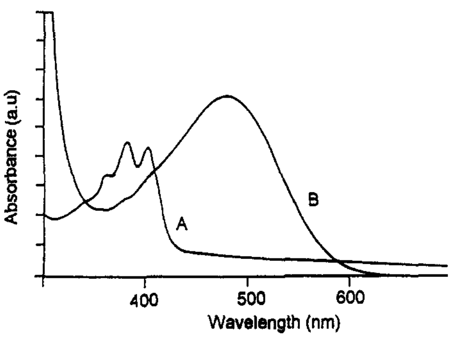
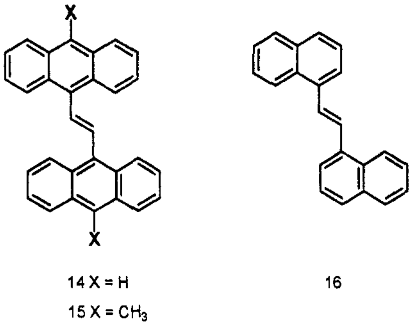


Figure 5. UV spectra of (A) precursor polymer 5 and (B) conjugated polymer 7.

Chart 1



corresponding to saturated units can be identified in the spectra of PAV, in agreement with the results from the elemental analysis. The most noticeable features common to both spectra are the bands shown by the polymer at 740, 871, 952, 3007, and 3053 cm^{-1} and also present in the model compound at 733, 874, 968, 3016, and 3051 cm^{-1}. The first three bands can be assigned to the CH out-of-plane bending modes of the four adjacent hydrogens in the anthracene unit, the 9,10 isolated hydrogens, and the *trans*-vinylene group, respectively. The last two bands correspond to *trans*-vinylene and aromatic CH stretch, respectively.

Figure 5 shows the UV spectra of a polyelectrolyte film before and after thermal treatment at 290 °C. The UV spectra for the clear, saturated films displayed a strong absorption band (not shown) with overlapping maxima associated with both the anthracene group (λ = 246, 252 nm) and the sulfonium group (λ = 265, 270, 276 nm) and a band with the characteristic vibrational pattern of the isolated anthracene group (λ = 344, 363, 382, 403 nm). When the sample was thermally eliminated, the UV spectrum shows a broad continuous absorption centered at 476 nm and an electronic band gap of 2.12 eV, calculated by measuring 10% of the maximum absorbance of the longest wavelength absorption. This band-gap energy is about 0.3 eV smaller compared to that of PPV and very close to the calculated value for polymer 8, which is expected to be lower than the value for 7 as a result of the different connectivity. Although in 8 the anthracene units are linked by the position of highest AO coefficients in the frontier orbitals, there is a significant steric interaction between the hydrogens in the 1,4,5,8-positions and the vinylic hydrogens that causes a torsion about the formal single bonds and thus decreases the conjugation along the main chain. As a matter of fact, crystallographic data of model compound 14 (Chart 1) show an interplanar angle of 69.8°.[19] It is reasonable to assume that part of this steric strain will be released in polymer 7, compensating then the less favorable electronic component. We were not able to obtain a single crystal of 13; however, compound 16, which presents the same steric requirements of 13 on

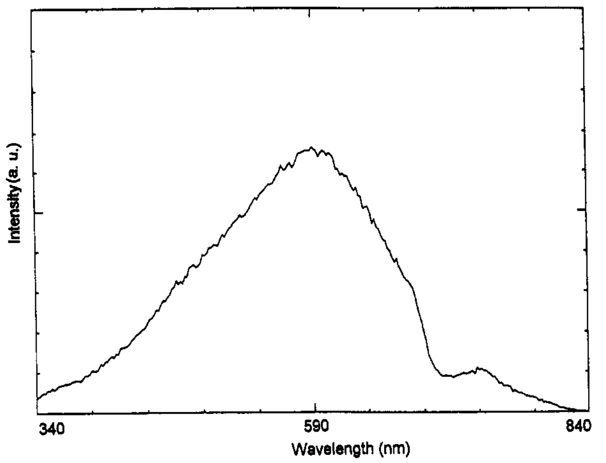


Figure 6. Fluorescence spectrum of polymer 7.

the vinyl group, shows an angle of 18.3° in the crystalline state.[20]

Further insight into the stereoelectronic effects was obtained from cyclic voltammetry and fluorescence studies of the model compounds. The successive reduction of each anthracene unit with one electron in cyclic voltammetry experiments is a useful method to probe the electrostatic interactions between the anthracene units because the potential difference for the first and second electron transfers, $E_2 - E_1$, reflects the degree of interaction of the electrophores. It is anticipated that this mutual influence will depend on the extent of the π-conjugation. No interaction has been detected for the dianthryl compound **15**; that is, the first and second electron transfers occurred at more or less the same potential, and $E_2 - E_1 = 0$.[21] On the contrary, for model compound **13** we observed a finite value for the potential difference, $E_2 - E_1 = -0.21$ V, thus indicating a greater interaction between the anthracene units. Likewise, it has been shown that the magnitude of the Stokes shift in anthrylenes indicates the degree of twisting in the ground state of the anthracene units around the "single" bond linking it to the ethylene unit.[22,23] Thus, the large Stokes shift (*ca.* 10 000 cm^{-1}) reported for **14** is in agreement with its crystallographic data,[24] while the relatively small shift we observed for **13** in methylene chloride solution (4300 cm^{-1}) points to a more planar structure. The fluorescence spectrum of a thin film of PAV is shown in Figure 6. The broad structureless band shows a $\lambda_{\max}{}^{\mathrm{em}} = 590$ nm, and the Stokes shift for PAV (4300 cm^{-1}) is similar to the one observed for its model compound despite the different physical states in which the measurements were made.

The absence of the vibrational structure in both the absorption and the emission spectra of PAV deserves a comment. While in PPV the presence of the vibrational structure has been associated with intrachain order,[25,26] it is difficult to apply the same reasoning to PAV. The loss of the vibrational structure and the band broadening are common features in the absorption as well as in the emission spectra of dianthrylenevinylenes. So although it is conceivable that the presence of the protruding anthrylene groups would introduce additional conformational defects in the polymer main chain as compared to PPV, it would be difficult to estimate the degree of order of the material with optical methods. The wide-angle X-ray diffraction analysis on a PAV film revealed only diffuse rings consistent with an amorphous structure.

A remarkable blue shift to 400 nm in the absorption maxima of a film of PAV was observed when it was placed in contact with a chloroformic solution of *N*-phenyl-3,5-triazolindione, a reactive dienophile. Regrettably, the nature of the product of the solid-state reaction could not be determined. In a control experiment, the reaction between the same dienophile and model compound **13** was shown not to be regiospecific even at −30 °C. Despite this result, this reaction remains of interest for the photonic applications of PAV since it provides a way of structuring films of the conjugated polymer. Further investigation of the physical properties of this novel conjugated polymer is under way.

Conclusions

The generation from the 1,4-bis(sulfonium) salt **1** of the quinodimethane intermediate **3** afforded the polyelectrolyte **5**, which possesses film-forming capabilities. The elimination of the sulfonium group proceeded in high yield, as could be judged from the IR, elemental analysis, and TGA data. Despite a less favorable electronic topology, the release of steric strain owing to the 1,4-substitution, compared with the 9,10-substitution, permitted the polymer **5** to minimize the energy difference between the aromatic and quinoid resonance structures and to thus decrease the electronic band gap. The high conjugation and structural purity make this polymer amenable for further physical studies. Subjects to be pursued with this polymer are luminescent properties, third-order nonlinear optical properties, and solid-state reactions.

Experimental Section

General Procedures. Melting points, Büchi Dr. Tottoli apparatus (uncorrected), commercial solvents purified according to standard procedures; IR spectra, Beckmann IR 4220 spectrometer; UV spectra, Perkin-Elmer Lambda 15 spectrometer; fluorescence spectra, Spex Fluorolog (450-W xenon lamp); ^{1}H NMR spectra, Varian Gemini (200 MHz) spectrometer; ^{13}C NMR spectra, Varian Gemini (50 MHz) and Bruker AM 400 (100 MHz) spectrometers; MS (EI), Varian MAT CH 7 A; TGA, Mettler TG 50 (under N_2 flow); cyclic voltammetry was performed in THF using the instrumentation already described.[27] A gold wire sealed in glass served as a working electrode with a platinum wire as counter electrode. A silver wire was used as a quasi-reference, and calibration was done with the ferrocene/ferrocene$^+$ redox couple: $E_{1/2} = 310$ mV vs SCE. Experiments were performed at −15 °C with a scan rate of 100 mV/s if not otherwise stated.

Elemental analyses were done inhouse and by Analytische Laboratorien in Gummersbach 1 Elbach, Germany.

1,4-Dimethylanthraquinone (9). This compound was obtained in two steps. First, a solution of 1,4-naphthoquinone (18.7 g, 0.118 mol) and 2,4-hexadiene (10.0 g, 0.121 mol) in toluene (70 mL) was heated at 65 °C for 4 days. Then the solvent was evaporated, and the remaining oily 1,4-dimethyl-1,4-dihydro-9,10-anthraquinone (28.1 g, 99%) was used in the next step without further purification. ^{1}H NMR (CDCl$_3$) δ 7.93 (m, 2H), 7.65 (m, 2H), 5,57 (s, 2H), 3.40 (d, 2H, J = 5.8 and 3.2 Hz), 2.59 (m, 2H), 0.99 (d, 6H, J = 7.4 Hz); ^{13}C NMR (CDCl$_3$) δ 198.7, 136.6, 133.8, 130.0, 126.1, 51.4, 31.6, 18.2; MS (70 eV), *m/z* (%), 240 (M$^+$, 20), 225 (39), 223 (50), 158 (77), 104 (100).

A solution of 1,4-dimethyl-1,4-dihydro-9,10-anthraquinone (28.0 g, 0.117 mol) in absolute ethanol (500 mL) was added to a solution of KOH (60 g) in ethanol (2.5 L) cooled at 10 °C. Then a current of oxygen was bubbled through the solution for 1 h while the temperature was maintained at 10 °C. After the solvent was evaporated the semisolid residue was treated with water (600 mL) and extracted with benzene. Removal of the aromatic solvent and recrystallization of the residue from ethanol at 4 °C afforded 19.5 g (71%) of pure **9**: mp 141–142 °C; ^{1}H NMR (CDCl$_3$) δ 8.16 (dd, 2H, J = 5.8 and 3.5 Hz), 7.55 (dd, 2H, J = 5.8 and 3.5 Hz), 7.39 (s, 2H), 2.78 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 185.7, 140.1, 137.2, 133.9, 133.3, 132.6, 126.4, 23.7; MS (70 eV), *m/z* (%), 237, 236, 235 (M$^+$, 12, 100, 48), 178 (60), 165 (31), 76 (17). Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.21; H, 5.25.

1,4-Dicarboxyanthracene (10). A suspension of **9** (19.0 g, 0.080 mol) in 60% nitric acid (190 mL) was heated under reflux for 1 week. Then, the volume of the suspension was reduced to *ca.* 100 mL and 500 mL of water was added. The yellowish solid was isolated by filtration and digested with acetic acid (300 mL). The suspension was filtered, and the white solid was washed with water and dried at 120 °C under reduced pressure. The yield of 1,4-dicarboxyanthraquinone was 16.4 g (69%): mp >340 °C; ^{1}H NMR (DMSO-d_6) δ 12.63 (s, 2H), 8.16 (m, 2H), 7.93 (m, 2H), 7.85 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 181.4, 169.5, 136.5, 134.7, 132.6, 132.2, 129.9, 126.7; MS (70 eV), m/z (%), 296 (M$^+$, 4), 252 (41), 208 (87), 178 (100), 152 (41).

The dicarboxylic anthraquinone was reduced according to the method of Elbs.[28] The anthracene derivative was obtained in a yield of 85% as an orange solid: mp 315 °C (dcpn) (lit.[28] mp 320 °C); ^{1}H NMR (CDCl$_3$) δ 13.5 (br s, 1H), 9.46 (s, 1H), 8.16 (m, 2H), 8.14 (s, 2H), 7.60 (dd, 2H, J = 6.5 and 3.1 Hz); ^{13}C NMR (DMSO-d_6) δ 168.5, 132.4, 131.6, 128.6, 128.3, 128.0, 126.9, 125.3; MS (70 eV), m/z (%), 266 (M$^+$, 100), 221 (6), 176 (8), 164 (26), 110 (6), 88 (7).

[1,4-Anthranylenebis(methylene)]bis(thioanylium chloride) (1). This compound was obtained in four consecutive steps. At first, **10** (7.8 g) was treated with an ethereal solution of diazomethane. The solid dimethyl 1,4-anthracenedicarboxylate (8.6 g, 99%) obtained after removal of the solvent under reduced pressure was used in the next synthetic step without further purification: mp 112–115 °C (lit.[29] mp 115 °C); ^{1}H NMR (CDCl$_3$) δ 9.46 (s, 2H), 8.09 (s, 2H), 8.05 (m, 2H), 7.52 (m, 2H), 4.06 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 167.5, 132.2, 131.6, 128.7, 128.6, 128.0, 126.6, 125.5, 52.4; MS (70 eV), m/z (%), 294 (M$^+$, 59), 236 (68), 177 (47), 149 (77), 88 (64), 83 (100).

Second, following the technique described by Gundermann and Roeker,[29] a solution of the diester (8.6 g) in THF (46 mL) was added dropwise to a stirred suspension of LAH (7.68 g) in ether (310 mL) heated under reflux. After the addition was complete, the mixture was stirred under reflux overnight. A saturated aqueous solution of Na$_2$SO$_4$ (50 mL) was added, and the solid was filtered. Removal of the solvent gave 5.86 g (86%) of 1,4-bis(hydroxymethyl)anthracene as a yellow solid: mp 159–161 °C (lit.[29] 160 °C); ^{1}H NMR (acetone-d_6) δ 8.78 (s, 2H), 8.08 (m, 2H), 7.56 (s, 2H), 7.51 (m, 2H), 5.25 (d, 4H, J = 5.3 Hz), 4.31 (t, 2H, J = 5.3 Hz); ^{13}C NMR (CDCl$_3$) δ 137.0, 130.6, 129.3, 128.1, 125.5, 123.0, 122.6, 61.5; MS (70 eV), m/z (%), 238 (M$^+$, 100), 191 (68), 179 (63), 178 (78).

Then, a solution of SOCl$_2$ (6.4 mL, 53.7 mmol) in CH$_2$Cl$_2$ was added dropwise to a solution of 1,4-bis(hydroxymethyl)anthracene (5.8 g, 24.4 mmol) and pyridine (2.4 mL) in acetonitrile (75 mL) at room temperature. After that, the mixture was heated at 60 °C for 2 h. The reaction mixture was washed first with 2 M aqueous HCl, then with water, and dried. Purification by column chromatography of the crude product [silica gel, cyclohexane/ether (4:1)] afforded 3.2 g (48%) of 1,4-bis(chloromethyl)anthracene: mp 201–202 °C; ^{1}H NMR (CDCl$_3$) δ 8.71 (s, 2H), 8.07 (m, 2H), 7.54 (m, 2H), 7.46 (s, 2H), 5.13 (s, 4H); ^{13}C NMR (CDCl$_3$) δ 134.8, 131.1, 128.8, 128.2, 126.9, 126.3, 123.6, 44.6; MS (70 eV), m/z (%), 278, 276, 274 (M$^+$, 6, 38, 57), 239 (100), 204 (61), 203 (53), 202 (60). Anal. Calcd for $C_{26}H_{34}O_6$: C, 69.84; H, 4.40; Cl, 25.77. Found: C, 69.73; H, 4.38; Cl, 25.59.

Finally, a solution of the dichloride (1.2 g, 6.6 mmol) and tetrahydrothiophene (2.5 mL) in methanol (12 mL) was stirred at 60 °C for 15 h. The solvent was evaporated, the solid was dissolved in MeOH (*ca.* 3.0 mL), and 30 mL of THF was added to the viscous solution. The solid was isolated by filtration, redissolved in MeOH, and precipitated again in THF; 1.7 g (87% yield) of **1** as a yellow solid was obtained after drying *in vacuo* for 1 h: ^{1}H NMR (D$_2$O) δ 8.66 (s, 2H), 8.14 (m, 4H), 7.74 (m, 4H), 7.66 (s, 2H), 4.97 (s, 4H), 3.70–3.40 (m, 8H), 2.70–2.30 (m, 8H); ^{13}C NMR (CD$_3$OD) δ 124.7, 121.8, 121.1, 120.5, 120.4, 119.4, 116.2, 36.7, 35.9, 20.7. Anal. Calcd for $C_{24}H_{28}Cl_2S_2$: C, 63.84; H, 6.25; Cl, 15.70; S, 14.20. Found: C, 63.81; H, 6.30; Cl, 15.61; S, 14.04.

1-Carboxyanthracene (11). This compound was obtained in two steps. First, 1-carboxyanthraquinone was prepared by oxidation of benzanthrone according to a reported procedure:[30] mp 285–286 °C; ^{1}H NMR (DMSO-d_6) δ 8.29 (dd, 1H, J = 7.7 and 1.3 Hz), 8.2–812 (m, 2H), 8.0–7.88 (m, 3H), 7.84 (dd, 1H, J = 7.7 and 1.3 Hz); ^{13}C NMR (DMSO-d_6) δ 182.2, 182.1, 170.4, 136.2, 135.0, 134.9, 134.6, 133.6, 133.3, 132.9, 132.7, 129.7, 127.8, 127.1, 127.0; MS (70 eV), m/z (%), 253, 252 (M$^+$, 2, 1) 235 (6), 208 (100), 180 (81), 152 (56). Then, the anthraquinone was reduced to 1-carboxyanthracene in aqueous ammonia by addition of zinc dust: mp 245–246 °C (lit.[31] mp 245 °C); ^{1}H NMR (DMSO-d_6) δ 9.54 (s, 1H), 8.68 (s, 1H), 8.32 (d, 1H, J = 8.1 Hz), 8.21 (d, 1H, J = 7.1 Hz), 8.12 (m, 2H), 7.57 (m, 3H); ^{13}C NMR (DMSO-d_6) δ 168.7, 133.5, 132.0, 131.5, 130.9, 130.5, 128.7, 128.3, 127.8, 127.7, 127.1, 126.3, 126.2, 124.8, 124.2; MS (70 eV), m/z (%), 222 (M$^+$, 100), 205 (15), 177 (30), 176 (28), 88 (30).

1-Anthracenecarbaldehyde (12). A 2 M solution of borane/dimethyl sulfide complex in THF (1.84 mL) was added dropwise from a syringe under argon to a suspension of **11** (4.0 g, 19.4 mmol) in THF (24 mL). Then the mixture was heated under gentle reflux for 1 h. The solvent and dimethyl sulfide were removed under reduced pressure, and CH$_2$Cl$_2$ (40 mL) was added to the remaining white solid. Pyridinium chlorochromate (4.32 g, 15.9 mmol) was added in small portions to the well-stirred suspension of the aryloxyboroxine. The mixture was heated under reflux for 1 h, then diluted with ether (40 mL), and filtered through Florisil. A yellow solid was obtained after the solvent was evaporated. Purification by column cromatography of the crude product (silica gel, CCl$_4$) afforded **12**: mp 130–131 °C (lit.[32] mp 131–134 °C); yield, 2.4 g (65%); ^{1}H NMR (DMSO-d_6) δ 10.40 (s, 1H), 9.84 (s, 1H), 8.75 (s, 1H), 8.46 (d, 1H, J = 8.7 Hz), 8.24 (d, 1H, J = 6.6 Hz), 8.17 (m, 2H), 7.74 (dd, 1H, J = 8.7 and 6.6 Hz), 7.61 (m, 2H); ^{13}C NMR (DMSO-d_6) δ 194.1, 139.2, 136.0, 132.8, 131.2, 131.0, 128.7, 128.1, 127.5, 126.8, 126.5, 124.6, 123.7; MS (70 eV), m/z (%), 206 (M$^+$, 63), 178 (100), 88 (29).

1,2-(1-Anthryl)ethene (13). Zn powder (1.7 g, 26.1 mmol) was added to a solution of TiCl$_4$ (2.4 g, 12.7 mmol) in THF (35 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C and then heated to reflux for another 30 min. The 1-anthracenecarbaldehyde (2.4 g, 11.6 mmol) in THF (35 mL) was added dropwise, and refluxing was continued for 10 h. The reaction mixture was quenched with 1 N aqueous HCl. The yellow precipitate was collected by filtration, thoroughly washed with water, and dried at 100 °C under reduced pressure: yield, 2.0 g (90%); mp 267 °C (lit.[33] 267–269 °C); ^{1}H NMR (C$_2$Cl$_4$D$_2$) δ 8.84 (s, 2H), 8.51 (s, 2H), 8.13 (s, 2H), 8.10–7.99 (m, 6H), 7.94 (d, 2H, J = 7.0 Hz), 7.65–7.42 (m, 4H); ^{13}C NMR (C$_2$Cl$_4$D$_2$) δ 135.7, 132.2, 132.0, 131.8, 130.2, 129.5, 129.0, 128.9, 128.5, 128.2, 127.4, 126.14, 126.09, 125.7, 123.9, 123.0; MS (70 eV), m/z (%), 380 (M$^+$, 100), 202 (29), 191 (33), 178 (31); UV (THF) 403 (4.25) [lit.[33] 406 (4.31)].

Polymer Synthesis. The polymerization reaction was started by the additon of an argon-purged aqueous solution of tetraethylammonium hydroxide (1.72 mL, 2.33 mmol) (20% solution from Aldrich) to an argon-purged solution of the bis(sulfonium) salt **1** (0.956 g, 2.14 mmol) in a mixture of water (10.0 mL) and acetonitrile (5 mL). The reaction mixture was stirred with an amount of pentane such that the volume ratio of the aqueous reacting mixture to pentane was 1:2. A yellow gel was formed in 1 min after the base addition. Both solutions were first cooled in an ice–water bath, and the reaction was carried out at the same temperature under argon atmosphere for 30 min. Then, most of the pentane was decanted; the gel and some yellow precipitate formed in the latter stage of the reaction were dissolved with a minimum amount of methanol, and the mixture was neutralized with aqueous 0.1 N HCl solution. The polyelectrolyte **5** was isolated by precipitation in an acetone/2-propanol (1:1) mixture. All of the manipulations were performed below 5 °C and without delays. The yellow polyelectrolyte was dissolved in a mixture of methanol/pyridine (4:1). To measure the polymer yield, a known volume of the solution was cast into a film, which was transformed into a film of **7** by heating in vacuo (10^{-2} Torr) at 290 °C for 8 h. From the weight of the resulting film and the volume of the polymer solution, the yield (57%) of the polymerization was calculated. Anal. Calcd for $C_{16}H_{10}$: C, 90.51; H, 9.49. Found: C, 89.22; H, 9.64; Cl, 0.44; N, 0.20; S, <0.05. Free-standing precursor polymer films were obtained by casting *in vacuo* on flat polypropylene Nalgene dishes and thin films by spin-coating techniques. The film thickness was determined with a step profiler.

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