Conjugated Polymers

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Poly(anthrylenebutadiynylene)s: Precursor-Based Synthesis and Band-Gap Tuning**

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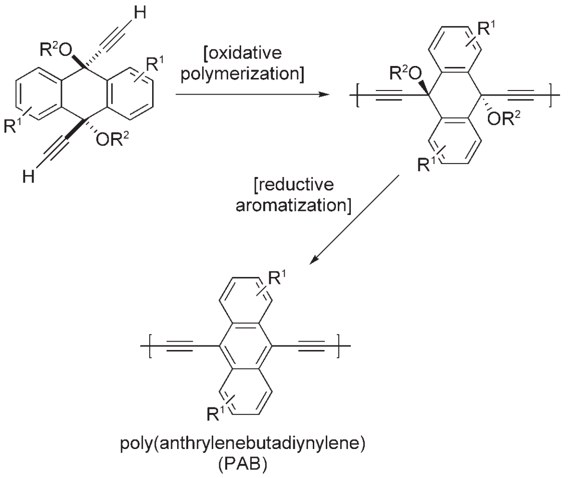
The utility of conjugated polymers in such diverse applications as sensors, photovoltaic devices, light-emitting diodes, field-effect transistors, and electrochromic devices stems in large part from the ability of chemists to systematically modify the properties of these materials through structural variation. A powerful strategy for varying the electronic structure of organic polymers involves modulating the degree of quinoid character of the conjugated backbone. Decreasing the energy difference between aromatic and quinoid resonance structures results in a decreased band gap, as demonstrated by Wudl and co-workers in the synthesis of poly(isothianaphthene), the first low-band-gap polymer to be prepared.[1] Since this report, poly(isothianaphthene) has served as the prototype for several low-band-gap polymers based upon fused heteroaromatic repeat units.[2] In contrast, low-band-gap polymers based upon acene repeat units are unknown, despite the documented proquinoid character of anthracene and the higher acenes.[3] We report herein the photophysical and electrochemical properties of high-molecular-weight, butadiyne-linked anthracene homopolymers prepared by a new synthetic route involving reductive aromatization of polymeric precursors.

The synthesis of anthracene-based polymers has been the subject of intensive research effort.[4] Significant advances include the preparation of poly(9,10-anthrylene)s,[5] poly(9,10-anthrylenevinylene)s,[6] and poly(9,10-anthrylene-ethynylene)s.[7] Despite their interesting properties, these materials display moderate band gaps (greater than 2.0 eV), which are a consequence of the sterically hindered nature of the 9- and 10-positions of the anthryl group. Müllen and co-workers have demonstrated that poly(9,10-anthrylene)s and oligo(9,10-anthrylenevinylene)s adopt twisted conformations, and this same group has shown that a substantial lowering of the band gap is effected by enforcing a coplanar conformation in ladder poly(*p*-phenylene-*alt*-9,10-anthrylene)s.[8]

We became interested in the possibility that poly(anthrylenebutadiynylene)s (PABs) could exhibit substantial delocalization owing to the ability of the butadiyne functional group to allow a coplanar arrangement of adjacent repeat units or arising from the rotationally symmetric nature of its electronic structure. These polymers also emerged as attractive targets in light of the utility of Eglinton-type oxidative couplings for homopolymerizations.[9] However, the requisite 9,10-bis(ethynyl)anthracenes are unstable compounds, which poses a stumbling block for the preparation of well-characterized, high-molecular-weight materials.[10]

To address this challenge, we explored a precursor-polymer-based approach using an established procedure for acene synthesis: the reductive aromatization of dihydroacenediols (Scheme 1).[11] This venerable method continues to be employed extensively for the preparation of acene hydrocarbons, including such challenging targets as hexacene and heptacene.[12] The preparation of oligo(9,10-anthrylenes), in which reductive aromatizations were employed as key steps, constitutes the most direct precedent for the proposed synthesis.[5] Apart from monomer stability, additional advantages could result from this approach. The mild aromatization conditions could minimize the decomposition of these electron-rich macromolecules, and the solubility of protected dihydroacenediol-based polymers might facilitate the preparation of high-molecular-weight materials.[13]



Scheme 1. Strategy for PAB synthesis.

Monomers **2a**–**2d**, each bearing four substituents to maximize polymer solubility, were prepared from anthraquinones **1a**–**1d** (Scheme 2; see the Supporting Information). Alkoxy-substituted compounds **2c** and **2d** were prepared in order to investigate the possibility of decreasing the band gap by raising the energy of the highest occupied molecular orbital (HOMO). This sort of substituent effect has precedent

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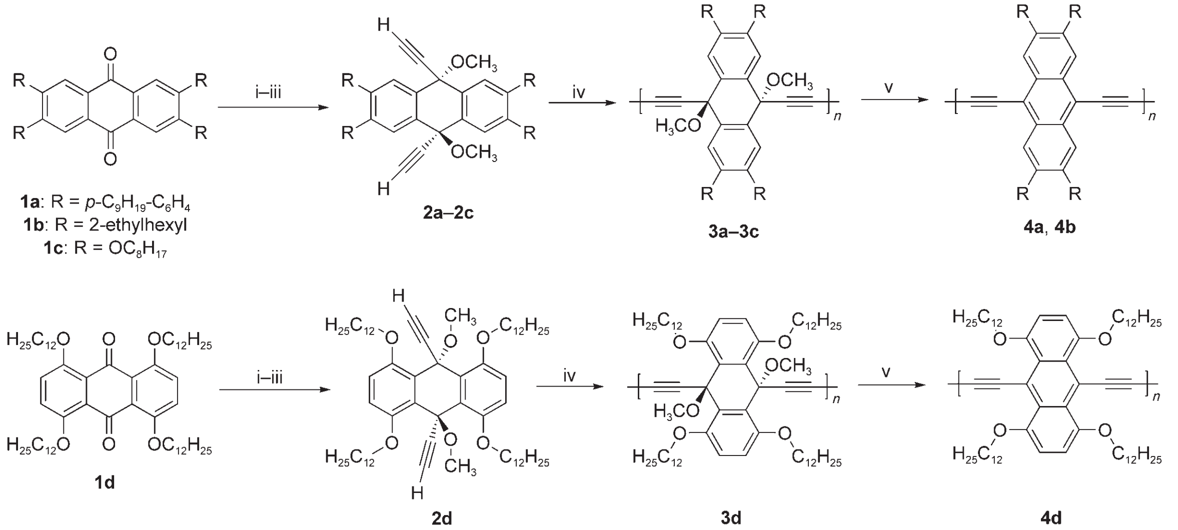

Scheme 2. Synthesis of substituted PABs. i) (Triethylsilyl)acetylene, *n*BuLi, THF, 0→23 °C. ii) CH_3I, *n*BuLi, THF, 0→23 °C. iii) Tetra-*n*-butylammonium fluoride (TBAF), THF, 0→23 °C. **2a** 64%, three steps. **2b** 56%. **2c** 22%. **2d** 22%. iv) *p*-benzoquinone, $[Pd(PPh_3)_4]$, CuI, *i*Pr_2NH, toluene, 60 °C. v) $SnCl_2$, 1 M HCl, CH_2Cl_2, 23 °C (see Table 1).

for several classes of conjugated polymers. Homocoupling cocatalyzed by palladium and copper with benzoquinone as oxidant yielded colorless, high-molecular-weight polymers **3a**–**3d** (Table 1).

Table 1: Yield and GPC data for polymers **3a**–**3d** and **4a**–**4d**.

Polymer	Yield	M_n[a]	M_w/M_n[a]
3a	89%	8.7×10^4	3.0
3b	96%	1.2×10^5	2.7
3c	32%	3.3×10^4	2.6
3d	87%	1.6×10^5	2.9
4a	>95%	8.7×10^4	5.3
4b	>95%	6.6×10^4	4.6
4c	decomp	–	–
4d	>95%	5.5×10^4	2.3

[a] Determined by gel permeation chromatography (GPC) relative to polystyrene standards. M_n = number-average molecular weight; M_w = weight-average molecular weight.

Aromatization of polymer **3a** to PAB **4a** was accomplished by treatment with tin(II) chloride and 1 M hydrochloric acid. The reaction was monitored by ^{1}H NMR spectroscopy (see the Supporting Information) and was accompanied by a gradual change in color, resulting in a purple solution at full conversion. While the synthesis of alkyl-substituted **4b** proceeded smoothly, alkoxy-substituted **3c** decomposed under the aromatization conditions, likely because of the Brønsted acidic conditions employed. In contrast, the other alkoxy-substituted polymer **3d** underwent clean aromatization to furnish polymer **4d** as a dark blue solid. Analysis of the aromatized polymers by GPC indicated a slight decrease in M_n relative to the precursor polymers, although high-molecular-weight products were obtained in each case (Table 1). This result may reflect the moderate solubility of the aromatized polymers or may stem from undefined side reactions that lead to polymer-chain cleavage.

The absorption and emission spectra of **4a**, **4b**, and **4d** (Table 2 and Figure 1) are red-shifted relative to conventional poly(aryleneethynylene)s or poly(arylenebutadiynylene)s. The band gap of both **4a** and **4b**, as estimated by the onset of the absorption spectra, is 1.9 eV. This value is in relatively good agreement with the estimated 1.7-eV band gap of unsubstituted PAB determined by DFT calculations on a series of oligomers (B3LYP/6-31G(d), see the Supporting Information). The alkoxy substituents of **4d** have a dramatic effect, resulting in a band gap of 1.5 eV. This is a remarkably low band gap for a polymer with an all-hydrocarbon backbone; of such polymers, only the poly(indenofluorene)s display comparable HOMO–LUMO gaps (LUMO = lowest unoccupied MO).[14] Polymer **4d** is nonfluorescent, whereas **4a** and **4b** are weakly emissive in chloroform solution and non-emissive in the solid state. The red-shifted solid-state absorption spectra of **4b** and **4d** are likely a result of aggregation of the polymer backbones through relatively strong π interactions between acene repeat units.

Table 2: Photophysical properties of **4a**, **4b**, and **4d**.

Polymer	abs λ_{max}[a] [nm]	abs λ_{max}[b] [nm]	$E_{g,optical}$[c] [eV]	em λ_{max}[a] [nm]	Φ_F[d]	τ_F[e] [ns]
4a	590	548	1.9	639	0.08	0.4
4b	615	639	1.9	649	0.02	0.2
4d	709	813	1.5	–	–	–

[a] $CHCl_3$. [b] Film. [c] Band gap, estimated by onset of absorption spectrum. [d] Quantum yield relative to cresyl violet perchlorate. [e] See the Supporting Information.

Alkoxy-substituted **4d** also displays unique redox behavior. Whereas **4a** and **4b** underwent irreversible oxidation at 0.7 and 0.8 V, respectively (referenced to ferrocene/ferrocenium (Fc/Fc^+); see the Supporting Information), **4d** was oxidized reversibly (onset at 0.25 V, Figure 2). The in situ conductivity of **4d** was measured using interdigitated micro-

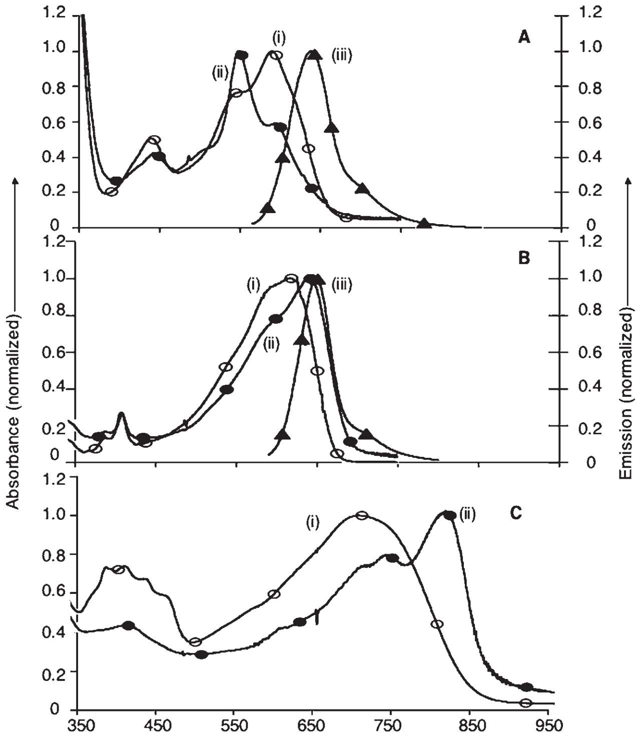

Figure 1. Normalized absorbance (i $CHCl_3$, ii thin film) and emission spectra (iii) of **4a** (A), **4b** (B), and **4d** (C).

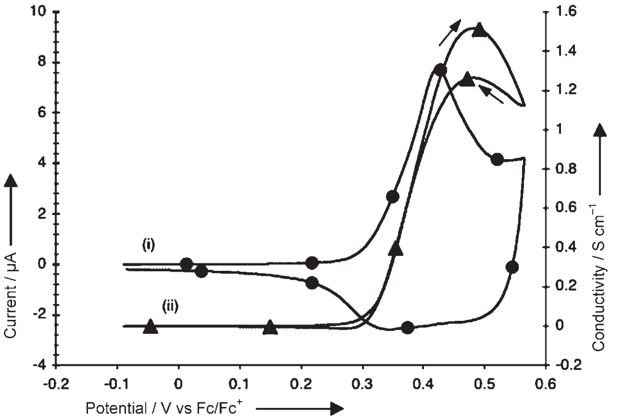

Figure 2. Cyclic voltammogram (i, 100 mVs^{-1}) and in situ conductivity (ii, 10 mVs^{-1}) of **4b**.

electrodes with the conductivity-potential profile reaching approximately 1.5 Scm^{-1} at +0.5 V. The spectral changes accompanying the oxidation of **4d** were studied by spectroelectrochemistry and by chemical oxidation of a thin film of **4d** with iodine vapor (see the Supporting Information).

Poly(anthrylenebutadiynylene)s are thus a new class of anthracene-based polymers that are readily accessed through reductive aromatization. In particular, *peri*-alkoxy-substituted **4d** is a structurally unique low-band-gap polymer that is soluble in organic solvents and stable to storage under ambient conditions. Such polymers remain rare despite intensive research efforts in this area and could fill an unmet need for applications in optoelectronic devices.[15] The low band gap of **4d** does not arise from a planar arrangement of backbone atoms, which is prevented by the *peri* substitution pattern (Figure 3). It remains to be determined whether the dramatic influence of the alkoxy substituents is a simple substituent effect or if the through-space interaction between the alkyne π system and the nonbonding electrons of the oxygen atoms plays a role in the low band gap of **4d**. The fact that *peri*-substituted anthracenes have served as a scaffold for the study of electronic interactions between adjacent π electron systems would appear to support the latter proposal.[16] To the extent that the *peri* substituents may also play a role in the steric stabilization of electron-rich **4d** and its derived radical cation (as demonstrated by cyclic voltammetry), the enforced proximity of π systems to a conjugated backbone could prove to be a general strategy for the design of stable, low-band-gap materials.

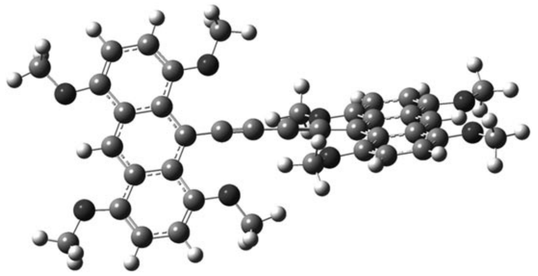

Figure 3. Energy-minimized geometry of dimer **5** ($(MeO)_4(C_{14}H_5)C{\equiv}C(C_{14}H_5)(MeO)_4$, B3LYP/6-31g(d), see the Supporting Information).

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