Conjugated Polymers

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).[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 Eglington-type oxidative couplings for homopolymerizations.[9] However, the requisite 9,10-bis(ethyl)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.[13] 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]

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...
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.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>M_n [g/mol]</th>
<th>M_w/M_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>89</td>
<td>8.7 x 10^5</td>
<td>3.0</td>
</tr>
<tr>
<td>3b</td>
<td>96</td>
<td>2.1 x 10^3</td>
<td>5.7</td>
</tr>
<tr>
<td>3c</td>
<td>32</td>
<td>3.3 x 10^4</td>
<td>4.5</td>
</tr>
<tr>
<td>3d</td>
<td>87</td>
<td>1.6 x 10^4</td>
<td>2.6</td>
</tr>
<tr>
<td>4a</td>
<td>&gt;95</td>
<td>8.7 x 10^4</td>
<td>5.3</td>
</tr>
<tr>
<td>4b</td>
<td>&gt;95</td>
<td>6.6 x 10^4</td>
<td>4.6</td>
</tr>
<tr>
<td>4c</td>
<td>&gt;95</td>
<td>5.5 x 10^4</td>
<td>2.3</td>
</tr>
<tr>
<td>4d</td>
<td>&gt;95</td>
<td>5.5 x 10^4</td>
<td>2.3</td>
</tr>
</tbody>
</table>

[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 1x hydrochloric acid. The reaction was monitored by 1H 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, alkyloxy-substituted 3c decomposed under the aromatization conditions, likely because of the Bronsted acidic conditions employed. In contrast, the other alkyloxy-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) or poly(arylenebutadiynylene). 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 alkyloxy 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) display comparable HOMO–LUMO gaps (LUMO = lowest unoccupied MO).[1] 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.

Alkylx-substituted 4d also displays unique redox behavior. Whereas 4a and 4b underwent irreversible oxidation at 0.7 and 0.8 V, respectively (referred 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-

Scheme 2. Synthesis of substituted PABs. i) (Triethylsilyl)acetylene, nBuLi, THF, 0–23 °C. ii) CH₃I, nBuLi, THF, 0–23 °C. iii) Tetra-n-butylammonium fluoride (TBAF), THF, 0–23 °C. 2a 64%, three steps. 2c 22%. iv) p-benzoquinone, [Pd(PPh₃)₄], Cul, iPr₂NH, toluene, 60 °C. v) SnCl₂, 1 M HCl, CH₂Cl₂, 23 °C (see Table 1).

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λ_max [nm]</th>
<th>Φ</th>
<th>τ</th>
<th>[ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>590</td>
<td>0.84</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>615</td>
<td>0.84</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>4d</td>
<td>709</td>
<td>0.84</td>
<td>1.0</td>
<td></td>
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</table>

[a] CHCl₃. [b] Film. [c] Band gap, estimated by onset of absorption spectrum. [d] Quantum yield relative to cresyl violet perchlorate. [e] See the Supporting Information.

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.

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