Electrochemical Oxidation of Double-Stranded Bis-Polynorbornenes Containing Linearly Aligned Ferrocene Linkers

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Experimental

Cyclic voltammetry and differential pulse voltammetry. A conventional three-electrode system with a potentiostat/galvanostat (Eco Chemie, microAutolabIII) was employed for cyclic voltammetric and differential pulse voltammetric experiments. A Pt disk electrode (diameter 2 mm), a Pt wire, and an Ag/Ag⁺ (10 mM AgNO₃) were used as the working, the counter and the reference electrodes, respectively. Sample was dissolved in dry CH₂Cl₂ containing 0.1 M nBu₄NPF₆, and the electrolyte was purged with Ar for at least 10 min before electrochemical experiments. All the potentials reported in the text were referred to the ferrocene/ferrocnium (Fc/Fc⁺) redox couple, which potential was measured after every electrochemical experiments.

Chronoamperometric bulk electrolysis. A tube-shaped Pt web working electrode (52 mesh, diameter 5 mm, height 5 mm) surround by a coaxial tub-shaped Pt foil counter electrode (diameter 8 mm, height 5 mm) with an Ag/Ag⁺ (10 mM AgNO₃) reference electrode placed at 1 mm above the center of the working electrode was employed for bulk-electrolysis experiments. A CH₂Cl₂ solution containing 0.1 M Bu₄NPF₆ and specified amount of sample was stirred by a magnetic stir bar at 5 mm below the working electrode throughout the entire electrolysis process. A constant potential was applied to carry out the electrochemical oxidation, and the electrolysis process was stopped when a steady-state current response around zero was reached. The charge consumption was calculated by integrating the area under the i-t curve.

The experiment details are summarized in Table 3.
Table 3. The experiment details of bulk-electrolysis of the ferrocene containing polymers.

<table>
<thead>
<tr>
<th></th>
<th>Amount taken (mg)</th>
<th>Monomer molecular weight</th>
<th>Ferrocene units (μmole)</th>
<th>Applying potential (V)</th>
<th>Total charge consumed (C/μmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>13700</td>
<td>13.1</td>
<td>721</td>
<td>18.2</td>
<td>0.35</td>
</tr>
<tr>
<td>3b</td>
<td>31100</td>
<td>4.7</td>
<td>777</td>
<td>6.0</td>
<td>0.35</td>
</tr>
<tr>
<td>3c</td>
<td>31200</td>
<td>5.0</td>
<td>873</td>
<td>5.7</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>1700</td>
<td>10.2</td>
<td>212</td>
<td>48.1</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>11900</td>
<td>7.2</td>
<td>597</td>
<td>12.1</td>
<td>0.40</td>
</tr>
</tbody>
</table>

The amount of ferrocene units employed in the bulk-electrolysis was estimated by dividing the molecular weight of polymer used over the molecular weight of its corresponding monomer.

**Chronoamperometric experiment at microelectrode.** A microdisk working electrode (diameter 10 μm), a Pt wire counter electrode and an Ag/Ag⁺ (10 mM AgNO₃) reference electrode with a potentiostat/galvanostat (EG&E, PAR 273A) were employed for potential-step experiments. The sample was dissolved in CH₂Cl₂ containing 0.1 M Bu₄NPF₆, and purged with Ar for at least 10 min before each experiment. The applying potential was firstly maintained at the open-circuit voltage (-0.15 V) for 5 sec then step to a desired potential (0.25 V for 3b and 3c, 0.35 V for 4) for 35 sec, and the i-t response was recorded. The diffusion coefficients were estimated to be 1.19 × 10⁻⁶, 1.04 × 10⁻⁶, and 2.05 × 10⁻⁶ cm²/sec for 3b, 3c, and 4, respectively. The electrochemically oxidized 3a and 4 were seriously deposited onto the microelectrode surface, therefore the electron transfer numbers and diffusion coefficients could not be estimated.

**Polymer radical cation.** Compound 3a was electrolyzed according to the method mentioned above. The oxidized 3a, insoluble in CH₂Cl₂, was filtered and washed three times by CH₂Cl₂, and then dried under vacuum.

**Magnetic Measurements.** The magnetization data were recorded on a SQUID magnetometer (MPMS7 Quantum Design company) with an external magnetic field of 1.0 Tesla in the temperature range of 2K to 295K. The diamagnetic background of sample holder was measured at the same experimental condition before the sample was measured. The magnetic susceptibility data were corrected for diamagnetism by the tabulated Pascal’s constants.
Figure S1. $(i_d(t) / i_{d,ss})$ vs. $(t^{1/2})$ plots of (a) 3b, (b) 3c, and (c) 4 in CH$_2$Cl$_2$ containing 0.1 M Bu$_4$NPF$_6$. $i_d(t)$: chronoamperometric current response at a microdisk electrode. $i_{d,ss}$: stead-state current response at a microdisk electrode.
\[ E(\text{HOMO-5}) = -4.3283 \text{ eV} \]

\[ E(\text{HOMO-4}) = -4.3107 \text{ eV} \]

\[ E(\text{HOMO-3}) = -4.2877 \text{ eV} \]

\[ E(\text{HOMO-2}) = -4.2877 \text{ eV} \]

\[ E(\text{HOMO-1}) = -4.2782 \text{ eV} \]

\[ E(\text{HOMO}) = -4.2773 \text{ eV} \]

\[ E(\text{LUMO}) = -1.6021 \text{ eV} \]

\[ E(\text{LUMO+1}) = -1.5551 \text{ eV} \]

Figure S2. Selected frontier orbitals of 5.