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Unusual Internal Electron Transfer in Conjugated Radical Polymers

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Abstract: Nitroxide-containing organic radical polymers (ORPs) have captured attention for their high power and fast redox kinetics. Yet a major challenge is the polymer's aliphatic backbone, resulting in a low electronic conductivity. Recent attempts that replace the aliphatic backbone with a conjugated one have not met with success. The reason for this is not understood until now. We examine a family of polythiophenes bearing nitroxide radical groups, showing that while both species are electrochemically active, there exists an internal electron transfer mechanism that interferes with stabilization of the polymer's fully oxidized form. This finding directs the future design of conjugated radical polymers energy storage and electronics, where careful attention to the redox potential of the backbone relative to the organic radical species is needed.

Redox active polymeric battery electrodes have attracted a great deal of attention due to their unique features in portable and flexible electronic devices over recent years.^[1-2] Organic radical polymer (ORP) batteries are especially interesting because of their exceptionally fast electron transfer kinetics.^[3-5] For example, PTMA (poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) has a theoretical capacity of 111 mAh/g^[6] (comparable to inorganic metal oxides such as LiCoO₂), redox potential of 3.6 V vs Li/Li⁺, nearly 100% Coulombic efficiency, and electrochemical stability beyond 500 cycles.^[7] However, success of PTMA and similar ORPs as cathode materials depends on improving its electronic conductivity. Otherwise, carbon additives are required, which dilutes the active material.^[8]

Recent approaches to improve the conductivity and capacity of ORPs have focused upon replacing the aliphatic backbone with conjugated units to form a conjugated radical polymer (CRP). The conjugated backbone adds a second site for redox activity and an electron-conducting pathway. However, polypyrrole^[9] and polythiophene^[10] with tethered nitroxide radicals did not show improved cathode performance or conductivity. The reason for this was not immediately clear at the time.

Here, we hypothesized that interactions between the radical unit and the conjugated backbone were responsible for the low capacity and modest conductivity of CRPs. This questions whether the radical unit and the conjugated backbone can be treated as separate entities or whether there is coupling and electron transfer between the two. This issue has not yet been examined in CRPs, and is of utmost importance to the future design of these promising materials.

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Polythiophenes bearing pendant TEMPO (2,2,6,6-Tetramethylpiperidine 1-Oxyl) radicals with varying alkyl spacer groups (CRP-4, CRP-6 and CRP-8) were synthesized according to our prior report.^[11] Poly(3-butylthiophene) (P3BT), a polythiophene bearing no pendant nitroxide radicals, was synthesized electrochemically and used as a control (Figure 1a and Figure S1).



Figure 1. (a) Chemical structures of polythiophene conjugated radical polymers (CRPs) with alkyl spacers (n=4, 6, 8) and control polymer P3BT. (b) Cyclic voltammograms (CVs) of CRPs and P3BT at 0.5 mV/s. (c) Peak current vs. [scan rate]^{1/2} for CVs of CRPs. (NO•: TEMPO radical; PT: polythiophene). Measurements were taken using a three-electrode cell with the polymer as the working electrode, lithium ribbons as counter and reference electrodes, and 0.5 M LiClO₄ in propylene carbonate as the electrolyte.

Cyclic voltammetry at a scan rate of 0.5 mV/s (Figure 1b) indicates little peak separation between the anodic and cathodic peaks for the CRPs (~ 65 mV), suggestive of a very reversible and facile reaction. The E1/2 for the CRPs was around 3.60 V vs. Li/Li⁺, consistent with that of PTMA, and is, therefore, assigned to the nitroxide radical.^[12] In contrast, P3BT exhibited a higher E1/2 of 3.88 V^[13] as well as broad and weak redox peaks, which is a typical feature of polythiophenes.^[14] It is noted that the CRP oxidation potential increased slightly with increasing alkyl spacer length, whereas the reduction potential remained constant. This is probably due to the fact that the longer alkyl chains are more electronically insulating, which impedes both electron transfer and ion diffusion.^[15-16] Higher oxidization potentials are required to go from the insulating to the conductive form, but the reverse is not required for the reduction process. As the scan rate increased, a linear relationship between the square root of the scan rate and the peak current was obtained for all polymers (Figure 1c and Figure S2), confirming diffusion-limited processes.

The galvanostatic charging response for each CRP (Figure 2 a-c, Figure S3) exhibited contributions from both the nitroxide

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radical unit and the polythiophene backbone at low current (e.g., 2 μ A cm⁻²). Upon charging, a flat plateau around 3.5 – 3.7 V appeared, which is a typical feature of the nitroxide radical.^[6] As charging proceeded further, the potential increased and then plateaued around 4.1 V, which originates from the oxidation of the polythiophene backbone.^[14] This second plateau disappeared at higher rates, which indicates sluggish electron transfer kinetics for the polythiophene unit relative to the more reversible nitroxide radical group. The P3BT control, on the other hand, exhibited pseudocapacitive behavior with no distinguishable plateaus (Figure 2d).



Figure 2. Galvanostatic charge-discharge response of polymers at different currents. (a) CRP-4 (b) CRP-6, (c) CPR-8 and (d) P3BT; The arrows in panel (a) apply to panels (b), (c), and (d). Dashed lines in panel (b) mark typical respective charging plateaus for NO• and PT in CRPs.

From the discharge curve, the capacities were calculated and compared to theoretical values. At the lowest rate of 2 μ A cm⁻², the areal capacities for CRP-4, CRP-6, and CRP-8 were 1.70, 1.26 and 0.77 μ Ah cm⁻², respectively, corresponding to specific capacities of 68.0, 44.0, 21.5 mAh g⁻¹; these are 38.2%, 27.7%, and 14.6% of their corresponding theoretical capacities. In comparison, the P3BT control had a capacity of 40.5 mAh g⁻¹, which was 21.1% of its theoretical value. This result is also on par with earlier investigations.^[17] Each of these capacities are lower than that of PTMA (77-110 mAh g⁻¹). This indicates that the CRP's polythiophene backbone either suppresses or does not enhance redox activity.

Figure S4 shows the areal capacity of the CRPs and P3BT at various current densities. It is noted polymer that CRP-6 had a better rate capability than that of the other three polymers as shown in Figure S4, although CRP-4 generally had the highest capacity. CRP-8 and P3BT, on the other hand, had the poorest rate capability and capacities. This suggests that the alkyl spacer influences charge transfer, but the exact mechanism is beyond the scope of this study. We speculate that the alkyl spacer affects chain packing, radical-radical and radical-backbone proximity, and dopant accessibility.

To isolate the contributions of the nitroxide radical group and polythiophene backbone to the charging capacity, we carried out galvanostatic charging to varying potential cut-offs at a current density of 5 μ A cm⁻². For CRP-4, it is clearly seen in Figure 3a that the nitroxide radical plateau around 3.5-3.6 V dominated the charge storage process, where 86% of total charging capacity was stored in this step. Further charging from 3.7 V to 4.2 V accounted for only 16% of the overall capacity, indicating minimal participation of the polythiophene backbone. Figure 3b shows the normalized specific capacity, where it is noted that the longer octyl spacer required a higher potential to initiate the charging process, similar to the P3BT control. This shows that the nitroxide radical dominates charge storage, and that the longer spacer group indeed impacts charge transfer between the nitroxide radicals and polythiophene backbone, as the charge/discharge curves of CRP-8 partially resembles that of P3BT.



Figure 3. (a) CRP-4 charged to different cutoff voltages, (b) Normalized specific capacity of the CRPs and P3BT vs cut-off voltages. The current density was 5 μ A cm⁻² (c) Illustration of charging process of CRP-4 at 5 μ A cm⁻². The green and the purple portions indicate contributions from the nitroxide radicals, polythiophene backbones, respectively.

Open circuit potential (OCP) monitoring was conducted to explain the charge transfer equilibrium and the previously observed low capacity (Figure 4a and Figure S5-S6). After equilibrating the CRPs at 4.2 V, the bias was removed and the potential was allowed to drift. All CRPs displayed a sharp voltage drop within the first 1000s, whereas P3BT displayed only a gradual voltage drop. With further time (6 h), the OCP gradually plateaued to around 3.6 - 3.7 V for the CRPs; this value is consistent with that of the nitroxide radical's potential. P3BT exhibited an OCP decay to around 3.8 V, indicative of the higher oxidation potential of the polythiophene.

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The rapid initial drop in OCP for the CRPs implies a possible internal electron transfer from the nitroxide radical to the polythiophene backbone (Figure 4b). At 4.2 V there exists both oxidized nitroxide radicals and thiophene units, with some minority not oxidized. This is because of the overlap of the redox activity of the nitroxide radical and the polythiophene backbone (Figure 1b). Once the bias is removed, any un-oxidized nitroxide radicals transfer an electron to the oxidized thiophene unit, thus reducing and dedoping the polythiophene backbone and oxidizing the nitroxide radical. In this relaxed state, the OCP will reflect that of the nitroxide radical, with little contribution from the polythiophene backbone (Figure 4a inset). These results explain the previously observed lower than theoretical capacities and moderate conductivities.^[9-10, 18] Conductivities of CRP-4, CRP-6, and CRP-8 were 8.1 x 10⁻⁷, 3.6 x 10⁻⁷, and 6.2 x 10⁻⁹ S cm⁻¹,^[11] respectively; whereas P3BT had a measured conductivity of 1.6 x 10⁻⁴ S cm⁻¹. The conductivity differences between the CRPs and P3BT is a consequence from the internal electron transfer process. The lower conductivity in CRP-8 is possibly due to the longer alkyl spacer that impacted the packing of the polymer chains. After charging the electrode, the CRP potential decays as the polythiophene backbone is reduced, leading to a dedoping of the backbone and a reduction in conductivity.



Figure 4. (a) OCP monitoring for 6 h. The electrodes were first charged by linear sweep voltammetry to 4.2 V and held at constant potential for 50 s (inset: schematic illustration of CRPs before and after open circuit potential decay); (b) Schematic illustration of the internal electron transfer process occurring for the CRPs.

To further reveal changes in the electronic structure of the CRPs, we conducted *in-situ* spectroelectrochemical measurements on CRP-6 and P3BT during the OCP decay process (Figure 5). As the OCP decayed from its initial value of 4.2 V for CRP-6, the UV-vis absorption intensity at 384 nm increased from 0.36 to 0.43 (a.u.) during the first 1000 s and reached a plateau thereafter (Figure 5a and Figure 5c); this band is attributed to the undoped form of polythiophene^[19], and

indicates dedoping of the backbone during OCP decay. Similarly, the intensity of the polythiophene cation (polarons) at 721 nm^{[19-} ^{20]} also increased from 0.49 to 0.58, which suggests conversion of bications (bipolarons) (> 1100 nm) to cations^[21-22] (Figure 5d) further supporting reduction of the polythiophene backbone. In comparison, P3BT showed a similar trend (Figure 5b), with more pronounced polymer cation conversion as compared to CRP-6. However, the intensity of the peak associated with polythiophene's neutral state for P3BT increased less than that of CRP-6, indicative of a spontaneous reduction of polythiophene cations by nitroxide radicals (Figure 4b). This is thermodynamically favored because polythiophene (3.88 V) has a higher oxidation potential than the nitroxide radical (3.60 V). Such internal electron transfer is also suggested for PTMA/LiFePO4 hybrid electrodes.^[23]



Figure 5. *In-situ* spectroelectrochemistry of (a) CRP-6 and (b) P3BT. Absorption for CRP-6 and P3BT at different wavelengths: (c) Neutral, de-doped polythiophene (384 and 401 nm); (d) polythiophene cation (721 nm).

In conclusion, the low capacity and conductivity of CRPs consisting of nitroxide radicals tethered to a polythiophene backbone is caused by internal electron transfer occurring between the two moieties. This is supported by evidence of a twostep charging process, in which the nitroxide radicals contributed to over 80% of the capacity. In situ spectroelectrochemistry during open circuit potential decay revealed evidence of a rapid dedoping of the polythiophene backbone caused by internal transfer of an electron from the nitroxide group to the polythiophene backbone. These results explain why conjugated radical polymers to date have exhibited such poor capacity, yet these results also bring to light interesting directions for future research in their design. To achieve a stable conjugated radical polymer, it will be essential to manipulate the redox potential of both the radical unit in reference to the conjugated backbone. In this study, the radical unit's redox potential was below that of the conjugated backbone; reversing or equalizing these potentials might provide alternative handles to adjust the stability and capacity of these materials. Alternatively, conjugated radical polymers are potentially interesting as protective materials in which they prevent overcharging by internally regulating an

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electrode's potential. More broadly speaking, conjugated radical polymers have been proposed in thermoelectrics and organic electronics applications, so these findings bear direct impact in the future design of these materials in general.

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