Polymer Chemistry

6-Oxoverdazyl Radical Polymers with Tunable Electrochemical Properties

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COMMUNICATION

6-Oxoverdazyl Radical Polymers with Tunable Electrochemical Properties

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6-Oxoverdazyl radical polymers were synthesized and their tunable redox properties studied in solution and the solid-state. The preservation of the pendant 6-oxoverdazyl moieties in the polymers produced was confirmed through spectroscopic studies and comparison to closely related model compounds. The results of Kelvin probe force microscopy experiments highlighted the potential utility of 6-oxoverdazyl polymers as functional redox-active thin films.

Organic radicals have fascinated scientists since the discovery of the persistent triphenyl methyl radical by Gomberg in 1900.[1] Since then, many families of stable radicals have been discovered and their properties widely explored across a number of applications.[2]

More recently, polymers containing stable radicals within or appended to a variety of polymer backbones have been prepared as part of efforts towards combining the processability of polymers with the functionality (*i.e.*, magnetic and redox properties) of stable organic radicals. Based on the combination of these traits, stable radical polymers have shown application as host materials in Li-ion batteries,[3] silica-grafted catalysts for the oxidation of alcohols,[4] ferromagnetic organic materials,[5] solid-state conductive materials,[6] redox mediators in transparent conducting materials,[7] the functional component of rewritable memory devices,[8] and electrode materials in stable radical polymer batteries.[9,10]

Although advances in the stable radical polymer field have been impressive, examples that exhibit readily tunable properties through substituent variation have remained elusive. 6-Oxoverdazyl radicals (**1**: X = CO) represent one of the only classes of stable radicals with stabilities rivaling nitroxide (**2**) and nitronyl nitroxide radicals (**3**). The ability to tune the properties of 6-oxoverdazyl radicals through structural variation (**1**: R, R', and X) has led to their use as mediators for controlled radical polymerization,[11] in model coordination complexes for molecule-based magnets,[12,13] as photoconductive liquid-crystalline materials,[14] and in tunable redox-active molecular materials.[15,16] However, the synthetic methodologies required to produce polymers containing 6-oxoverdazyls,[17] which have the potential to exhibit tunable redox properties,[15] have not been developed to date.

1
X = CO, CS, CR₂
R, R' = alkyl, aryl

2

3
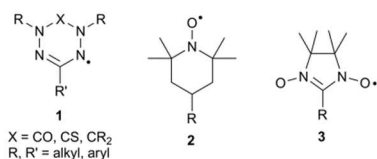
Herein we describe the synthesis and characterization of two side-chain 6-oxoverdazyl polymers and a series of model compounds designed to delineate the underlying properties of the isolated polymers. The poly(phenyl methacrylate) backbone employed was chosen as it was anticipated to have a stabilizing effect on the pendant 6-oxoverdazyl groups.[18]

The synthetic routes established during this study (Scheme 1) began with the free radical polymerization of phenyl methacrylate-substituted tetrazanes **4a,b** (Figs. S1–S4), which afforded tetrazane polymers **5a,b** as white powders in 83% and 76% yield respectively (Figs. S5 and S6). Oxidation of tetrazane polymers **5a,b** with *p*-benzoquinone gave 6-oxoverdazyl polymers **6a,b** in 78% and 81% yield after purification by column chromatography and repeated precipitation. A summary of characterization data for polymers **5a,b** and **6a,b** can be found in Table 1 and additional synthetic details can be found in the supplementary information (Figs. S7–S16).

4a, R = *i*Pr, 65%
4b, R = Ph, 64%

5a, 83%
5b, 76%

6a, 78%
6b, 81%
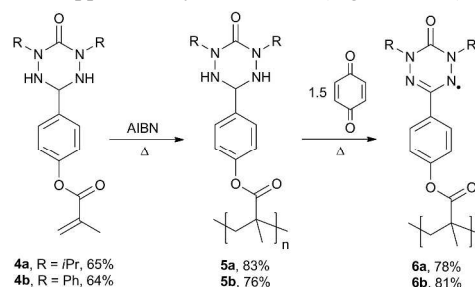
Scheme 1   Synthesis of 6-oxoverdazyl radical polymers **6a,b**.

The IR spectra of tetrazanes and 6-oxoverdazyls were found to be highly diagnostic (Figs. S17–S22). In each case the spectra of model compounds (*i.e.*, **7a,b** and **8a,b**) were in very close agreement with those collected for the corresponding polymers. Further comparison

Table 1   Characterization data for polymers **5a,b** and **6a,b**.

|	M_n (Da)[a]	PDI[a]	T_g (°C)	Onset of Decomp. (°C)[b]
5a	25,260	1.83	204	288
6a	25,750	1.89	203	188
5b	20,280	1.48	180	246
6b	12,000	1.46	174	236

[a]Conventional calibration GPC vs. polystyrene standards in DMF (10 mM LiBr and 1% (v/v) NEt₃) at 85 °C. See supplementary information for additional discussion of GPC experiments. [b]Calculated at 2% mass loss.

of the IR spectra qualitatively confirmed the complete conversion of tetrazane polymers **5a,b** to 6-oxoverdazyl polymers **6a,b** as the NH stretches of **5a,b** disappeared completely and CO stretches shifted to higher energies (Figs. S19 and S22). The radical content within the verdazyl polymer backbones was studied qualitatively using electron paramagnetic resonance (EPR) spectroscopy. Broad, isotropic signals were observed for radical polymers **6a,b** (g = 2.0050 and 2.0043) and complex signals were observed for model 6-oxoverdazyl radicals **8a,b** (g = 2.0043 and 2.0038) (Scheme 2, Figs. S23–S30). The broadening of the EPR spectra obtained for polymers **6a,b** is consistent with their proposed structures and macromolecular nature. Quantitative analysis of the radical content in 6-oxoverdazyl polymers **6a,b** was performed using UV-vis spectroscopy. The complex spectra obtained were in close agreement with model compounds **8a,b** indicating that >95% of the repeating units within the polymer backbone contained a pendant radical unit (Figs. S31 and S32).

The electrochemical properties of 6-oxoverdazyl polymer **6a,b** and the model 6-oxoverdazyls **8a,b** were studied using cyclic voltammetry in THF (Figs. 1, S33, and Table 2). Consistent with reports of similar compounds,[15] 6-oxoverdazyls **8a,b** were reversibly oxidized and reduced. Polymers **6a,b** exhibited *pseudo* reversible oxidation and reduction waves under similar conditions. It should be noted that, as a result of the loss of control associated with the slow diffusion of polymers in solution, sharp, asymmetric waves were observed in the CVs of **6a,b**.[19] Crucially, switching from *iso*propyl to phenyl *N*-substituents caused a shift in the half wave oxidation ($E_{ox}°$) and reduction ($E_{red}°$) potentials by 220 mV and 530 mV respectively. Although the redox properties of verdazyl polymers **6a,b** are very similar to those of the model complexes studied, the incorporation of the radicals into polymers will allow them to be used in applications where film-forming properties are essential.

The ability of stable radical polymers to undergo redox reactions without significant structural change is advantageous for their use in organic electronics where changes in volume accompanying electron transfer are highly undesirable. In order to study potential structural changes accompanying oxidation, we chemically oxidized 6-oxoverdazyls **8a,c** with nitrosonium tetrafluoroborate (Scheme 2). Oxidation resulted in a red shift in the wavelength of their maximum absorption (*e.g.*, from λ_{max} = 414 nm in **8c** to λ_{max} = 510 nm for **9c**). The crude residues were washed with diethyl ether to afford

analytically pure samples of **9a,c** (Figs. S34–37), which exhibited qualitatively similar electrochemical behaviour to the corresponding neutral radicals (Figs. S38 and S39), in 96% and 79% yield.[20]
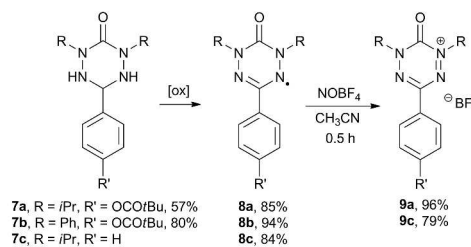
Scheme 2   Synthesis and oxidation of 6-oxoverdazyl radicals **8a,b**. [ox] = 1.5 equivalents of *p*-benzoquinone for **8a,c** and Ag₂CO₃/celite for **8b**.

The solid-state structures of 6-oxoverdazyls **8a, 8c** and tetrazinium cation **9c** were determined by single crystal X-ray diffraction (Figs. 2, S40 and Tables 3, S2). In the solid-state structures of **8c** and **9c**, the N1-N2-C1-N4-N3-C2 heterocycle is planar, and twisted with respect to the phenyl substituents by 21.5° and 24.7° respectively. Despite these similarities, a shortening of the N-N bonds in the nitrogen-rich heterocycle was observed upon oxidation. The average N-N bond distance decreased from 1.369(2) Å in **8c** to 1.299(2) Å in **9c**, while the average C-N bond lengths increased slightly upon removal of an electron from the antibonding singly occupied molecular orbital (π-SOMO) of 6-oxoverdazyl **8c**. The structural metrics of 6-oxoverdazyl **8a** were found to be very similar to those of **8c**. The reversible nature of the electrochemical oxidation of 6-oxoverdazyl polymers **6a** and **6b** along with the structural similarities of model compounds **8c** and **9c** further illustrates the potential utility of the polymers produced in this study for use as redox-active thin films for organic electronics.

Kelvin probe force microscopy (KPFM),[21] a scanning probe technique able to image the work function (*i.e.*, the energy of the highest occupied molecular orbital) of materials at the nanoscale was employed in order to study thin films of 6-oxoverdazyl polymer **6a**. In this context, the KPFM measurements provide an estimate of the energy (relative to ITO, work function: 4.7 eV[22]) of the π-SOMO of the 6-oxoverdazyl polymer studied. A 166 ± 10 nm thick film of **6a**
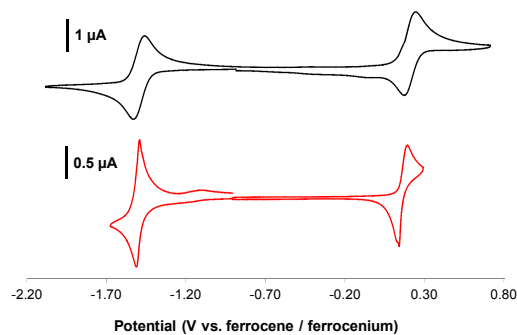

Fig. 1   Cyclic voltammograms of 6-oxoverdazyl polymer **6a** (red) and model 6-oxoverdazyl **8a** (black) recorded at scan rate 50 mV s⁻¹ in THF solutions containing 1 mM analyte and 0.1 M tetrabutylammonium hexafluorophosphate.
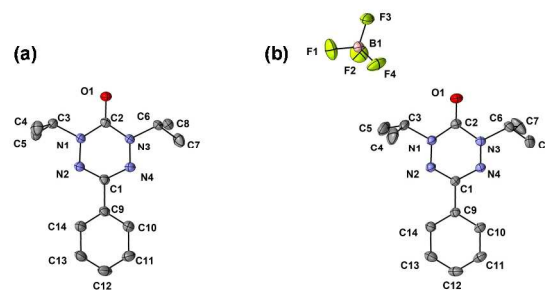

Fig. 2   Solid-state structures of (a) 6-oxoverdazyl **8c** and (b) tetrazinium cation **9c**. Thermal ellipsoids are shown at 50% probability level and hydrogen atoms have been omitted for clarity.

Table 2   Electrochemical data for verdazyl polymers **6a,b** and model verdazyl radicals **8a,b**.

Compound	$E_{ox}°$ (V vs. Fc/Fc⁺)	$E_{red}°$ (V vs. Fc/Fc⁺)
6a (R = *i*Pr)	0.17	−1.50
8a (R = *i*Pr)	0.20	−1.49
6b (R = Ph)	0.39	−0.97
8b (R = Ph)	0.38	−1.01

Table 3   Selected bond lengths (Å) and angles (°) for 6-oxoverdazyl **8c** and cation **9c**, determined by X-ray crystallography.

bonds and angles	**8c**	**9c**
N1-N2, N3-N4	1.372(2), 1.366(2)	1.307(2), 1.291(2)
C1-N2, C1-N4	1.327(2), 1.334(2)	1.340(2), 1.344(2)
N1-C2, N3-C2	1.381(2), 1.372(2)	1.398(2), 1.414(2)
N1-N2-C1, N3-N4-C1	115.0(1), 115.1(1)	117.4(1), 117.7(1)
N2-C1-N4	126.9(2)	123.2(1)
N2-C2-N3	114.1(1)	111.4(1)

was spin coated onto ITO glass from a 15 mg mL^{-1} solution in chlorobenzene. The topography image shown in Fig. 3 revealed a very smooth and uniform layer of polymer **6a** on ITO. The KPFM image of the polymer film (Fig. 3) was also very uniform, suggesting the presence of few defects, and corroborating a very high radical content of polymer **6a**. The work function of the π-SOMO orbital was measured to be 4.9 ± 0.1 eV, which corresponds to an oxidation potential of *ca.* 0.20 V against ferrocene, which has a work function of 5.1 eV.[23] This number agrees well with the solution-phase electrochemical data collected for 6-oxoverdazyl polymer **6a** and 6-oxoverdazyl radical **8a**.
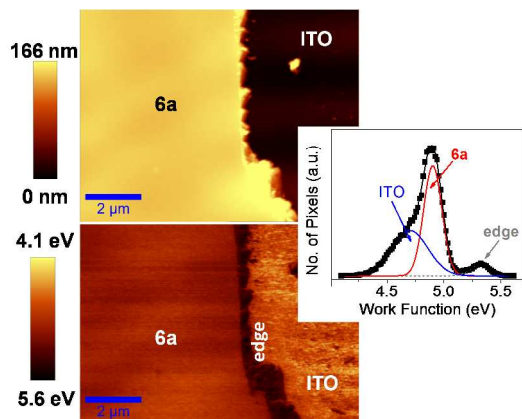

Fig. 3   AFM topography (top) and KPFM image (bottom) of 6-oxoverdazyl polymer **6a** referenced to ITO (work function: 4.7 eV[22]). The inset is a histogram of the KPFM image showing a work function of 4.9 ± 0.1 eV for **6a**. The small peak on the right is a KPFM artifact due to lateral contact of the tip with the film edge.

The synthetic routes described in this paper have allowed for the first examples of 6-oxoverdazyl polymers to be realized. The polymers exhibited substituent-dependent, tunable, and reversible oxidation and reduction events in solution. Their oxidation was also studied in thin films using KPFM, confirming that the redox properties of the 6-oxoverdazyl polymers are retained. Structural characterization of model compounds further demonstrated the potential of 6-oxoverdazyl polymers as functional redox-active materials as several structural features, including planarity, of the neutral radical were retained upon oxidation. Future work in this area will aim to exploit the structural versatility of the 6-oxoverdazyl scaffold and to evaluate the utility of the polymers reported as functional redox-active thin films.
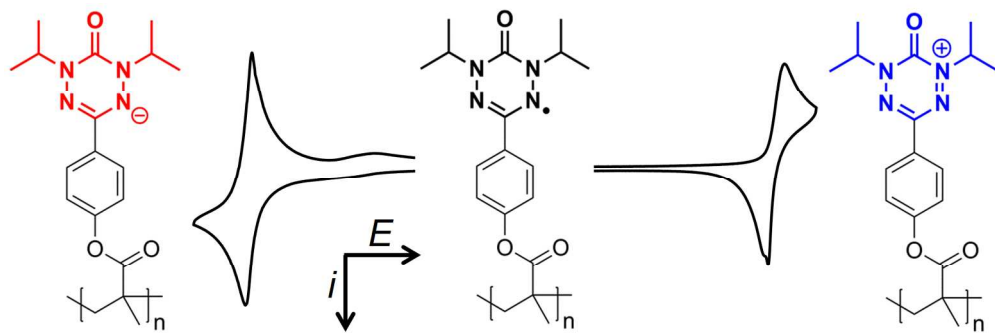
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