Communications to the Editor

Poly[3,5-di-*tert*-butyl-4-[(2,4,6-tri-*tert*-butylphenyl)oxalato]phenylacetylene]: A Photochemical Precursor to a Conjugated Polyradical

Frank C. Rossitto and Paul M. Lahti*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

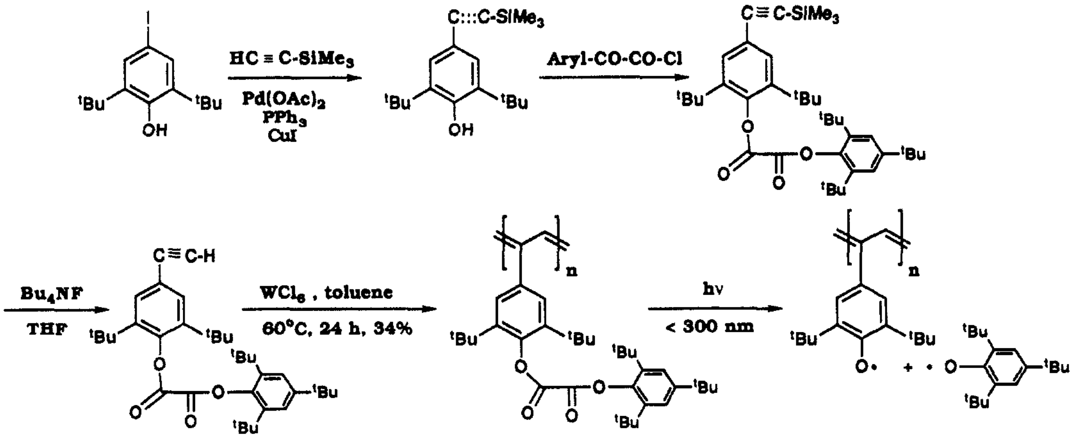
Received August 9, 1993
Revised Manuscript Received September 9, 1993

Recent interest in the design of organic and organometallic polymers with unusual magnetic properties has prompted the synthesis of a number of very high spin oligomers and polymers. High spin states may be created in conjugated polycarbene[1-3] and polynitrene[4-6] systems by using molecular design strategies based upon qualitative theoretical arguments[7-9] relating connectivity to ground-state spin multiplicity. Polycarbenes and polynitrenes are excellent model systems, but their instability makes them unsatisfactory choices for materials of potential practical utility. A number of polymers or large oligomers with stable pendant radical sites have been synthesized,[3,10-14] some with quite high percentages of spin sites per monomeric unit. Despite these successes in the synthesis of very high spin polymers, none of the materials made to date has shown bulk magnetic behavior other than that associated with isolated or weakly antiferromagnetically coupled behavior. This design drawback may be attributed in part to specific problems in the systems chosen to date for synthesis, particularly poly(phenylacetylene) analogues, in which conformational complexity may overcome a connectivity-based preference for ferromagnetic intrachain exchange coupling.[15] One strategy to overcome this problem is to devise polyradical precursors with sufficient stability to allow processing (and thus some conformational control of the precursor) and then generation of the polyradical sites. In this report, we describe the synthesis and photolysis of poly[3,5-di-*tert*-butyl-4-[(2,4,6-tri-*tert*-butylphenyl)oxalato]phenylacetylene] (1), a photochemical precursor to polyradical 2.

The monomer of 1, acetylene 3, was synthesized as shown in Figure 1. The order in which the steps were carried out was important, since the photoprecursor diaryl oxalate (DAO) group was partly cleaved under some reaction conditions. The monomer[16] was metathesis polymerized using WCl_6 to give highly soluble, deep-red, fluffy 1,[16] with a M_w (M_n) by gel permeation chromatography of 15 400 (2200) relative to polystyrene standards. Infrared spectroscopy showed the DAO group (1780 cm^{-1}) to be intact in the polymer, and UV–vis spectroscopy showed bands at about 220 nm (strong) and 490 nm, similar to the spectrum of the polyphenol precursor to polyradical 2.[10] In the absence of strong light, 1 appears to be indefinitely stable in air at room temperature, as was true for nonconjugated polyradical DAO precursors previously investigated by us.

Photolysis of neat 1 with quartz-filtered light from a 1000-W xenon arc lamp for 30–60 min at 77 K turns the red sample very dark colored and gives a strong peak in the 9.58-GHz electron spin resonance (ESR) spectrum, with $g = 2.0046$, an approximately Gaussian line shape, and a peak-to-peak line width (ΔH_{pp}) of about 10 G (Figure 2). This peak lost 39% of its doubly-integrated signal intensity upon being warmed to room temperature for 5 min. ESR spin count experiments[17] at 77 K show the yield of spin sites generated upon photolysis of 1 (0.9% w/w dispersed in a poly(methyl methacrylate) film by our previous method[18]) to be typically 20–33% of the possible number of radical spins, depending upon photolysis conditions and assuming that two radicals are generated per monomeric unit per photolytic cleavage, one pendant radical plus one leaving group radical.

The temperature dependence[17] of the ESR signal intensity of the neat irradiated sample as a function of reciprocal absolute temperature (Curie–Weiss plot) showed only slight curvature, indicating nearly paramagnetic behavior for the sample (Figure 2, inset). ΔH_{pp} was 11.7, 10.1, and 9.6 at 10, 75, and 220 K, respectively, but the line shape remained approximately unchanged. Line broadening with decreased temperature is also observed in 2 produced by solution oxidation methods[10] and is attrib-



3 1 2

Figure 1. Synthesis of polymer 1.

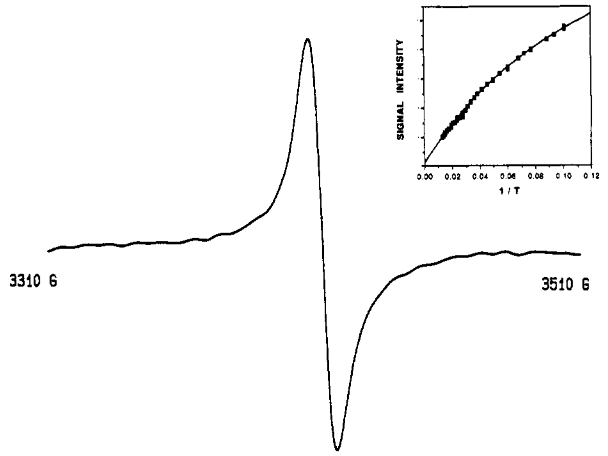


Figure 2. ESR spectrum over a 3310–3510-G range (9.58 GHz) from photolysis of polymer 1 at 77 K. The inset is a plot of the ESR signal intensity as a function of $1/T$ (K^{-1}) for the peak in the $g = 2$ region.

utable to interradical interactions.

Polyradical 2 exhibited antiferromagnetic behavior when generated by a solution oxidative route[10] to yield about 10% of the theoretically available spin sites. Although our spin yield is fairly high on the photolyzed surface of neat 1, little if any cooperative behavior is evidenced by the Curie–Weiss behavior of our material. We tentatively ascribe the difference between polyradical 2 generated by solution oxidation and solid-state photooxidation methods to conformational and/or morphological differences between 1 and 2. During precipitation from solution oxidation, 2 may adopt a conformation or morphology substantially different from that of 1, especially if a number of spin sites are altered by side reactions such as quinone formation.[10] When 2 is generated in the solid state from 1, it should be largely constrained to a morphology enforced by the original structure of precursor 1. Since photochemically-generated 2 still has many reactive radical sites—as shown by the loss of ESR signal intensity during the warming of the 77 K irradiated sample—there is a clear difference by comparison to the relative stability of the smaller number of radical sites isolated in solution-generated 2.[10] Given this evidence in favor of physical differences in samples of 2 generated by the two different methods, it is not surprising that solution oxidized and photooxidized samples of 2 have somewhat different magnetic behavior.

We aim in future work to use the poly-DAO and related precursor routes in efforts to generate other conjugated polyphenoxyl radicals and to control the bulk magnetic behavior of polyradicals through prephotolytic processing of such precursor polymers.

Acknowledgment. This work was supported by the University of Massachusetts Materials Research Laboratory and in part by the National Science Foundation (Grant CHE 9204695).

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(16) 3: mp 157–159 °C. IR (KBr, cm^{-1}): 3260 (acetylene C–H str), 2300–2800 (strong, aliphatic CH str), 2090 (C≡C), 1750 (C=O). Anal. Calcd for $C_{36}H_{50}O_4$: C, 79.08; H, 9.22; O, 11.70. Found: C, 78.59; H, 8.95. 1. IR (KBr, cm^{-1}): 2400–2850 (aliphatic CH str), 1780 (oxalate C=O str). UV–vis (THF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 220 (20 000), 250 (7280), 488 (4150).

(17) All ESR experiments were carried out on a Bruker ESP-300 spectrometer at a ≤100-μW power level, to avoid signal saturation effects. Temperature-dependent studies were carried out using an APD Cryogenics CS-101 Displex closed-cycle circulating helium cryostat with a copper sample spindle, using our previously described[18] procedures.

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