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Electronic Conductivity of Benzoin Dianion Reduced Poly(tetrafluoroethylene)

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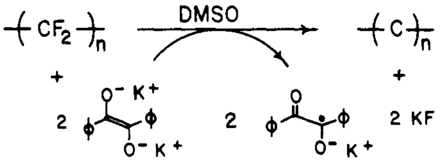
The discovery[1] that polyacetylene, upon appropriate oxidation, exhibits an electronic conductivity of 560 Ω^{-1} cm^{-1} prompted an enormous effort to prepare other electrically conducting organic polymers.[2] The limiting properties of these materials (infusibility and insolubility) have led to attempts at preparing conducting materials from processable precursors.[3] Of particular importance to the work reported here are the alkali metal and electrochemical reductions of poly(tetrafluoroethylene) (PTFE).[4-7] We recently reported[8] the reduction of PTFE with benzoin dianion (eq 1). This reaction converts the surface of PTFE to a metallic gold colored, air-sensitive carbonaceous material, the thickness of which can be determined by gravimetric analysis. In this note, we report the electronic conductivity of this material.



(1)

Treatment[9] of 0.5 cm × 1 cm PTFE samples with individual 30-mL $(CH_3)_2SO$ solutions of benzoin (0.27 g, 1.3 mmol) and potassium *tert*-butoxide (1.0 g, 8.75 mmol) for 1–144 h at 50 °C followed by successive washings with ten 25-mL portions of water and five 25-mL portions of THF and subsequent overnight evacuation (0.01 mm) rendered samples suitable for conductivity measurements.[10] Films prepared by this procedure exhibit very low conductivities ($\sigma < 10^{-10}$ Ω^{-1} cm^{-1}); oxidation (doping) with iodine[11] induces a dramatic increase to values of 0.3–40 Ω^{-1} cm^{-1}. Figure 1 shows a plot of conductivity vs. the thickness of the conductor for I_2-doped samples. Several points warrant discussion: the thickness is the average thickness of the reduced PTFE layer, calculated from the weight difference between the initial PTFE sample and the reduced and then oxidized $(KClO_3/H_2SO_4)$ sample.[8] The reduction is corrosive and the average thickness is much greater than the minimum thickness; hence the measured values are lower than the intrinsic conductivity of the material. The data are quite scattered, but a general trend implying an *inverse* thickness–conductivity relationship is apparent. Possible explanations for this result are that a competitive, deleterious (for conductivity) reaction occurs along with the reduction and/or the calculated thickness (average) increases faster than the conductivity-limiting thickness. That the conductivity is electronic in nature (not ionic) was verified by passing current at 1 V for 6 h and then reversing the probes of the multimeter: no change in resistance was observed. The I_2-doped material is quite air stable, unlike the undoped material: a sample that exhibited a maximum conductivity of 36 Ω^{-1} cm^{-1}, showed a conductivity of 14 Ω^{-1} cm^{-1} after 12 h in air. The temperature dependence of conductivity (Figure 2) indicates that the material is a semiconductor with an activation energy of 0.4–0.7 eV over the temperature range studied.[12] Treatment of reduced PTFE with sodium naphthalide did not impart conductivity.

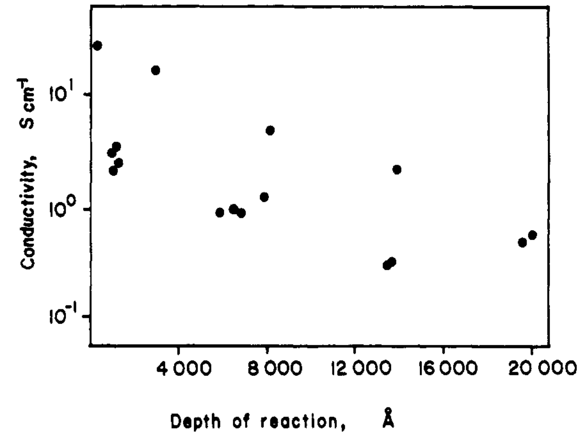


Figure 1. Conductivity vs. thickness of conductor.

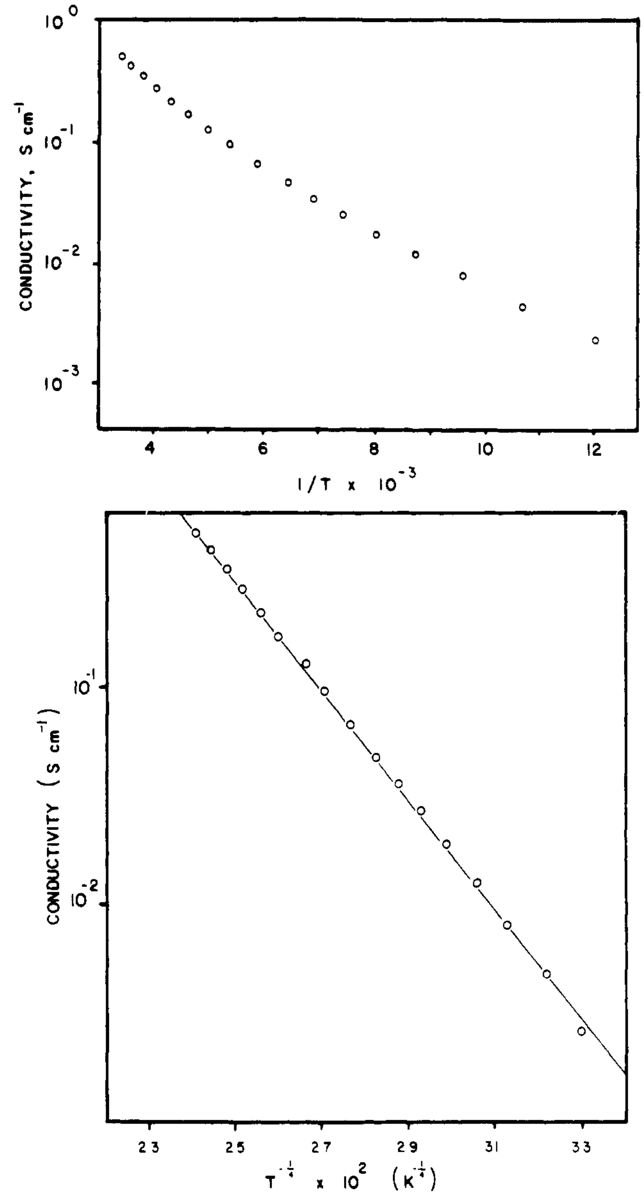


Figure 2. Temperature dependence of conductivity.

Drawing comparisons between this material and other reduced and doped PTFE materials[4-7] is difficult. The structures of the reduced materials are different[8] and the conductivity data of alkali metal and electrochemically reduced samples are incomplete and inconsistent: Yoshino et al.[4] report that the electrical conductivity of lithium naphthalide reduced PTFE is 10^{-5}–10^{-4} Ω^{-1} cm^{-1}. Nelson[5] and Brewis,[6] however, found no conductivity for sodium naphthalide and electrochemically prepared naphthalide

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reduced PTFE. Barker et al.[7] report that freshly formed films from electrochemical reduction exhibit resistances of 10^{-1}–10^{-2} Ω cm but that this value increases by several orders of magnitude when the film is exposed to air, water, or methanol and slowly increases when exposed to nitrogen or vacuum. We believe that these data are inconsistent because (1) the salts from the reductions were not removed and ionic contributions to conductivity were not addressed and (2) the reactions were not consistently run in inert environments.

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Registry No. PTFE (homopolymer), 9002-84-0; dipotassium benzoin, 16152-63-9.

References and Notes

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(9) Total exclusion of oxygen is necessary. The PTFE film (5 mil, Commercial Plastics/Du Pont Teflon) was extracted with THF for 24 h in a Soxhlet extractor and dried under vacuum at 60 °C to constant weight. Benzoin (Aldrich) was recrystallized twice from ethanol and stored in a vacuum desiccator. Potassium *tert*-butoxide (Aldrich) was sublimed. Doubly distilled water (Gilmont still) was degassed by purging with nitrogen. Tetrahydrofuran was distilled from sodium benzophenone dianion; dimethyl sulfoxide was distilled from calcium hydride at reduced pressure.

(10) Sample resistance was measured with a Fluka multimeter. The samples were mounted on two platinum electrodes with Electrodag under nitrogen. The smallest resistance obtained was 6000 Ω; thus contact resistance could be ignored and four probe measurements were unnecessary. The minimum resistance was used in the formula $\sigma = l/wt\Omega$, where l is the distance between electrodes, w is the width of the sample, and t is the conducting layer thickness.

(11) Iodine doping entailed exposure of the electrode-mounted sample to dry solid iodine at room temperature (initial pressure 0.005 mm). Conductivity normally reached a maximum after 30 min. Quantitative dopant uptake experiments indicated that 0.1–0.19 mol of I_2 per monomer equivalent of reduced PTFE was incorporated.

(12) For a discussion of the significance of these data, see: Chien, J. C. W. "Polyacetylene: Chemistry, Physics and Material Science"; Academic Press: New York, 1984.

Conjugated Polyenes: A Modified Equation To Relate $n_{C=C}$ and $\nu_{C=C}$

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Maddams et al.[1] have recently proposed an exponential equation to establish the accurate relationship between ν_2 (the C=C stretching frequency) and the number of conjugated C=C units, $n_{C=C}$, in polyenes. The aim of this Note is to propose a modification of such an equation that fits experimental data much better than the previously reported equation.

Table I
ν_2 and $n_{C=C}$ Values for Some Conjugated Systems

compd	$n_{C=C}$	ν_2/cm^{-1}	ref
1-hexene	1	1638	7
isoprene	2	1637	
alloocimene	3	1629	
vitamin A acetate	5	1580	
β-carotene	11	1521	
Ph(CH=CH)$_n$Ph	5	1567	4
	6	1552	
EtOOC(CH=CH)$_n$COOEt	1	1664	8
	2	1622	
	3	1621	
	4	1596	
	5	1570	
	6	1562	
	7	1550	
	8	1540	
β-carotene	11	1527	6
lycopene	11	1516	
β-carotene	11	1520	9

The equation of Maddams et al. was of the form $\nu_2 = \nu + ae^{-bn}$, where n stands for $n_{C=C}$, a and b are constants (151.24 cm^{-1} and 0.07808, respectively), and ν corresponds to the limiting value of ν_2 for an infinite length chain of conjugated C=C units; the position of the ν_2 band is very accurately determined in the Raman spectra of polyenes as a consequence of a resonance Raman effect,[2] also observed by us when studying the polymerization of C_2H_2 on TiO_2 (rutile) surface.[3]

The above values for a and b in the exponential equation were derived by Maddams et al. from ν_2 values in the literature[4-6] for low molecular weight polyenes, while the limiting value, ν, was obtained from the Raman spectra of *trans*-polyacetylenes, recorded with the excitation wavelengths at 676.4 and 752.2 nm (when a long-wavelength excitation beam is used, resonance due to long-chain polyenes with low ν_2 values occurs).

The literature data used by Maddams et al. to obtain the above values for a and b have been collected in Table I, together with some other data from the literature.[7-9] However, when the exponential equation, with the constants of Maddams et al.,[1] is applied to these data to obtain the number of conjugated C=C units as a function of the experimental ν_2 values for low molecular weight polyenes (n = 1–11), $n = -\ln((\nu_2 - \nu)/a)/b$, the results shown in Figure 1 (full circles) are obtained. In Figure 1, the number of C=C units, as calculated by applying the equation above to the experimental ν_2 values collected in Table I, n_c, have been plotted vs. the actual $n_{C=C}$ values for these polyenes, n_t. The points fit a straight line defined by the equation $n_c = 1.542n_t - 4.555$, with regression coefficient $r = 0.9839$; i.e., for long chains of polyenes (where the independent term of this equation will be negligible) the $n_{C=C}$ values calculated by using the exponential equation would be ca. 50% larger than the real ones.

The value of $\nu = 1461 \pm 1$ cm^{-1} has been reported by several authors from studies with differently obtained polyenes,[1,10,11] and even lower values have been reported by Kuzmany[12] (1459 cm^{-1}) and Kletter et al.[13] (1457 cm^{-1}). Other authors had previously proposed nonexponential, but reciprocal, equations of the type $\nu_2 = \nu + b/n_{C=C}$ to determine $n_{C=C}$ from ν_2; so, Lichtmann and Fitchen[14] proposed $\nu = 1450$ cm^{-1}, as determined from the wavelength-independent, low-frequency origin of the band, as the limiting value to be used with this reciprocal equation; Kuzmany[12] claims the equation $\nu_2 = 1459 + 720/(n_{C=C} +$