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Oxidation of Long Alkyl-substituted Sexithiophene with $FeCl_3$

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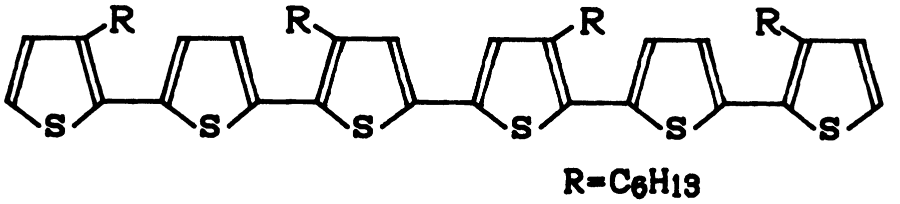
The visible-near IR and ESR spectral changes of long alkyl-substituted oligothiophene during the chemical oxidation indicated that the first oxidation yielded cation radicals (polarons) and the successive second oxidation did not dications (bipolarons) but trication radicals.

During the recent years, π-conjugated polymers have attracted a great deal of attention owing to their electrical and optical properties. Poly[3-(long alkyl)thiophenes] among the conjugated polymers was investigated intensively due to good solubility and considerable conductivity in doped (oxidized) states.1) N.m.r. measurements of the poly(alkyl-thiophenes) showed that the polymers contained about 25 mole-% head-to-head configuration, indicating that the effective conjugation length are limited by twists of the polymer chain.2) Several researchers prepared oligothiophenes that have well-defined structures, and studied the oxidized or neutral oligomers for comparison with conducting polythiophenes.3-5) The oligothiophenes underwent two stepwise oxidations to produce radical cations (polarons) or π-dimers of those in the first one and dications (bipolarons) in the second one. However, the oxidized species would not be sufficiently soluble in solvents since those were crystallized3) and dimerized.5) We prepared long alkyl-substituted oligothiophene (LAOT) that would be more soluble, and found the second oxidation of LAOT preferentially produced trication radicals instead of dications (bipolarons) proposed by the studies of oxidized polythiophenes and oligothiophenes.

LAOT was prepared from 3,3''-dihexyl-2,2':5',2''-terthiophene6) in two step pro-



LAOT

cedures involving the monobromination of the terthiophene derivative in the 5-position followed by reductive coupling according to similar procedures described for the preparation of α-sexithiophene.7) After the product was purified by liquid chromatography, identified as LAOT by NMR spectroscopy. Solutions of LAOT (9.1×10^{-6} M) and ferric chloride (2.2×10^{-3} M) were prepared in freshly distilled dry dichloromethane, respectively. For the visible-near IR and ESR measurements, the ferric chloride solution was added stepwise to a quartz cell and a capillary tube each containing a solution of LAOT. These procedures for the measurements were carried out under nitrogen at ambient temperature. The ESR spin concentration of the solutions was calibrated by a standard dichloromethane solution of 1,1-diphenyl-2-picrylhydrazyl.

The absorption and ESR spectra of the LAOT solution had an absorption band at 3.02 eV (log ε 4.58) corresponding to π-π^* transition (Fig. 1, solid line) and a neg-

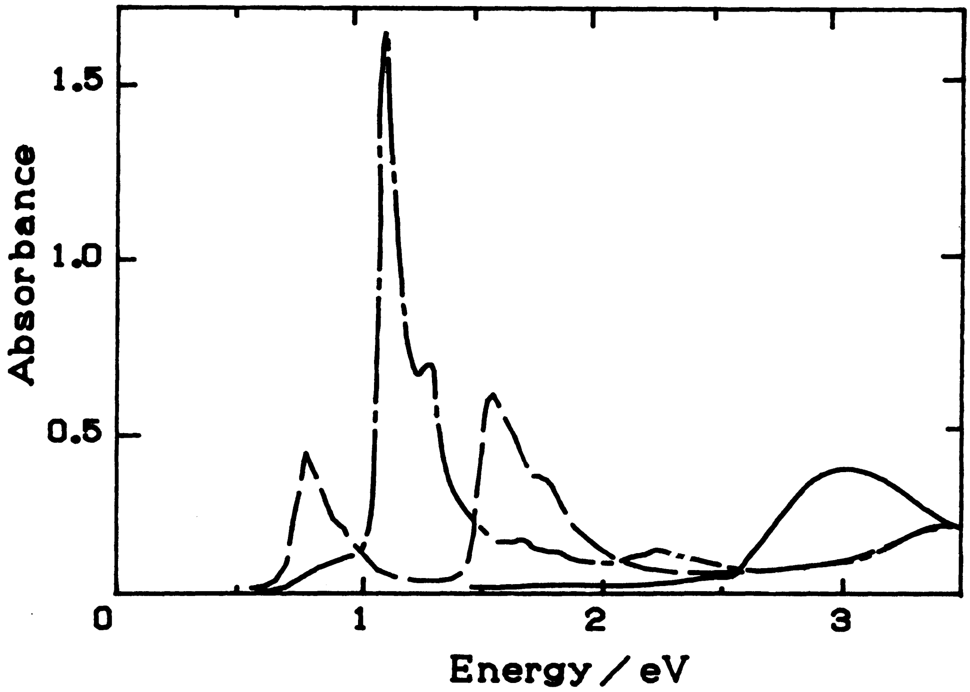


Fig. 1. The absorption spectra of the neutral and oxidized LAOT, —— : LAOT solution, — — : LAOT solution oxidized using 2 equivalents of ferric chloride, —·— : LAOT solution oxidized using 6 equivalents of ferric chloride.

ligible signal, respectively. It is generally admitted that two equivalents of ferric chloride are necessary for one electron oxidation of oligothiophenes.[3,5] With the addition of two equivalents of ferric chloride to the LAOT solution, the π-π^* transition band completely disappeared and two strong absorption bands at 0.82 and 1.59 eV with a shoulder on the high-energy side appeared. (Fig. 1, dashed line) Moreover, the addition resulted in the appearance of the intense e.s.r. signal (ΔH_{pp}=5.3-5.9) centered at g=2.003 as is typically for organic radical. The number of spins per an LAOT molecule derived from the spin concentration was approximately 0.8, close to 1. (Fig. 2) The intensity of these absorption bands and ESR signal grew until two equivalents of ferric chloride were added to the LAOT solution. These observations demonstrate that the first oxidation of LAOT was one electron oxidation and generated radical cations (polarons). This result is consistent with the conclusions reported previously.[3-5] When four equivalents of ferric chloride were introduced into the radical cationic LAOT solution, a new strong absorption band at 1.17 eV and two weak ones at 1.33 and 2.25 eV appeared and the bands attributed to the cation radical of LAOT vanished. (Fig. 1, dotted line) The intensity of the bands ascribed to the radical cations decreased, and the three new bands grew as ferric chloride was introduced incrementally. However, the additional introduction of ferric chloride led the feature and the intensity of the ESR signal to no alteration. (Fig. 2) Further, free ferric chloride that absorbs at 3.54 eV (log ε 3.98) was hardly detected in the absorption spectra, suggesting that all ferric chloride was con-

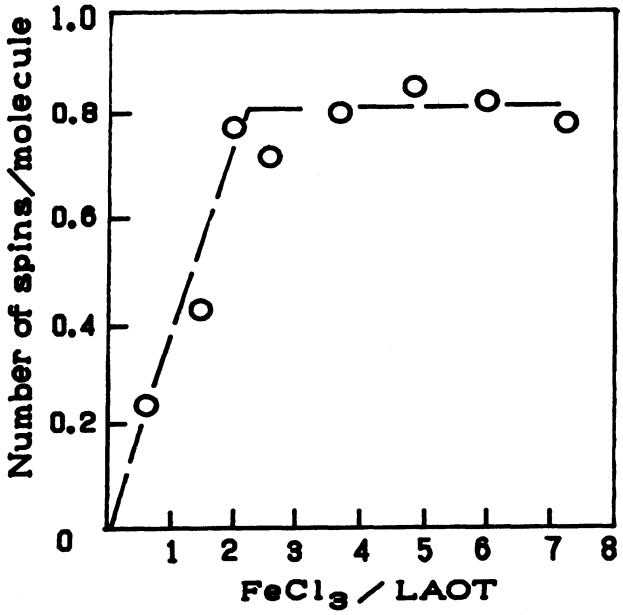


Fig. 2. The number of spins per a LAOT molecule against the amount of ferric chloride added. The parameter "$FeCl_3$/LAOT" represents the mol ratio of ferric chloride to LAOT.

sumed for oxidizing LAOT. When more than four equivalents of ferric chloride were added, the absorption and ESR spectra remained unchanged. Finally, bubbling ammonia gas through the oxidized LAOT solution lead to the absorption spectra of the original LAOT. From these observations, we can conclude that the cation radical of LAOT converts into the trication radicals in the second oxidation step, since only the mono and trication radicals are expected to exhibit ESR signal. Therefore, this conclusion indicates that trication radical is more stable on free energy than dication (bipolaron), at least in LAOT. In addition, this indication is not in agreement with theoretical studies of Bredas et. al.,[8] who predicted that the unit of bipolaron was present stably and become the spinless charge carrier in doped polythiophenes or polypyrroles.

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