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Cation Radicals of Hexyl-substituted Oligothiophenes in Solution. Comparison with Poly[3-(long alkyl)thiophenes]

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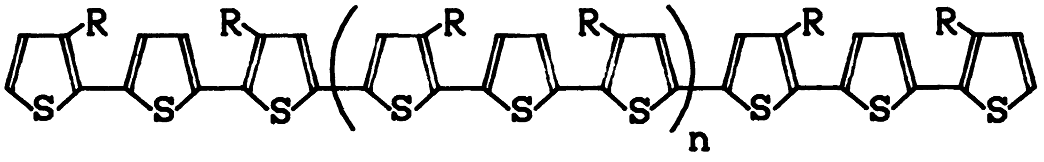
Hexyl-substituted oligothiophenes (sexi-, novi-, duodeci-, and quindecithiophenes) were oxidized with two equivalents of $FeCl_3$ in dichloromethane. The visible-near IR and ESR spectra of the solutions showed that oxidized species in the oligothiophenes were cation radicals and were spread over thiophene rings between 6 and 8. The absorption spectra of the solutions were similar to those of poly[3-(long alkyl)thiophenes] in oxidized states in solution.

Because of their high electric conductivities in oxidized states and electrochromism, π-conjugated polymers have attracted enormous attention for many years. The conduction mechanism containing carrier generation upon oxidizing has been studied intensively still now. Most of the polymer were infusible and insoluble in organic solvents owing to the stiffness of the main chains consisting of conjugated bonds. These properties prevent the satisfactory elucidation of the mechanism. Although poly[3-(long alkyl)thiophenes] having good solubility and considerable conductivity in oxidized states were prepared,1) NMR measurements of the poly(alkylthiophenes) showed that the polymers contained about 25 mole-% head-to-head configuration, indicating that the effective conjugation length is limited by twists of the polymer chain.2) Recently, several researchers prepared oligothiophenes that have well-defined structures, and studied the oxidized or neutral oligomers as model compounds of conducting polythiophenes.3-6) The oligothiophenes underwent two-steps oxidation to produce cation radicals (polarons) or π-dimers of those in the first one and dications (bipolarons) in the second one. However, we found that the first and second oxidation of more soluble hexyl-substituted sexithiophene (**1**) yielded cation radicals and trication radicals, respectively.7) We will report here on the features of the cation radicals of **1**, hexyl-substituted novithiophene (**2**), duodecithiophene (**3**), and quindecithiophene (**4**) and a comparison of the cation radicals with those of poly[3-(long alkyl)thiophenes].



$R=C_6H_{13}$

1 : n = 0
2 : n = 1
3 : n = 2
4 : n = 3

1, **2**, **3**, and **4** were prepared by a reductive coupling reaction of 5,5''-dibromo-3,3''-dihexyl-2,2':5',2''-terthiophene according to the previously reported method.[8] Solutions of the oligothiophenes ($9.1-3.6X10^{-6}$ M) were prepared in freshly distilled dry dichloromethane, so as to become a constant concentration for a thiophene unit in the solutions. For the visible-near IR and ESR measurements, ferric chloride was added stepwise to a quartz cell and a capillary tube each containing the solutions of the oligothiophenes. The ESR spin concentration of the solutions was calibrated by a standard dichloromethane solution of 1,1-diphenyl-2-picrylhydrazyl.

Each absorption spectrum of the hexyl-substituted oligothiophene in dichloromethane showed a $\pi-\pi^*$ transition band at higher than 2.7 eV (Fig. 1, solid line). It is generally admitted that two equivalents of ferric chloride are necessary for one electron oxidation of oligothiophenes.[3,5] After two equivalents of ferric chloride were added to the solutions of the hexyl-substituted oligothiophenes, the $\pi-\pi^*$ transition band disappeared or reduced and two strong absorption bands at about 1.5 eV and less than 1.0 eV with a shoulder or a tailing on the high-energy side appeared (Fig. 1, dashed line). The subsequent addition of ferric chloride to the mixture led to new absorption bands in the spectra of the hexyl-substituted oligothiophenes. These additional change in the spectra will be discussed in detail elsewhere. These observations indicate that the oxidized species in the hexyl-substituted oligothiophenes are cation radicals. Further, the addition of two equivalents of ferric chloride resulted in the appearance of the intense ESR signal (ΔH_{pp}=4-6) centered at g=2.003 as is typically for organic radicals. The numbers of spins per a molecule of **1**, **2**, **3**, and **4** derived from the spin concentrations were approximately 0.80, 0.75, 0.73, and 0.60, respectively. These low values of spins for the hexyl-substituted oligothiophenes are interpreted by the formation of the diamagnetic π-dimers of the cation radicals, which the shoulders and the tailing in the spectra of the oligothiophenes imply.[6] These ESR data support the conclusion indicated in absorption data.

With the addition of two equivalents of ferric chloride, the $\pi-\pi^*$ transition band of **1** vanished, whereas the transition bands of **2**, **3**, and **4** remained. These show that the cation radicals formed in the hexyl-substituted oligothiophene chains spread over thiophene rings between 6 and 8. The two absorption bands ascribed to the cation radicals of the oligomers were shifted to the low-energy side and broadened with increasing the oligomer length. These phenomena may be accounted for by a interaction between the cation radical and the neutral parts in the oxidized oligomers.

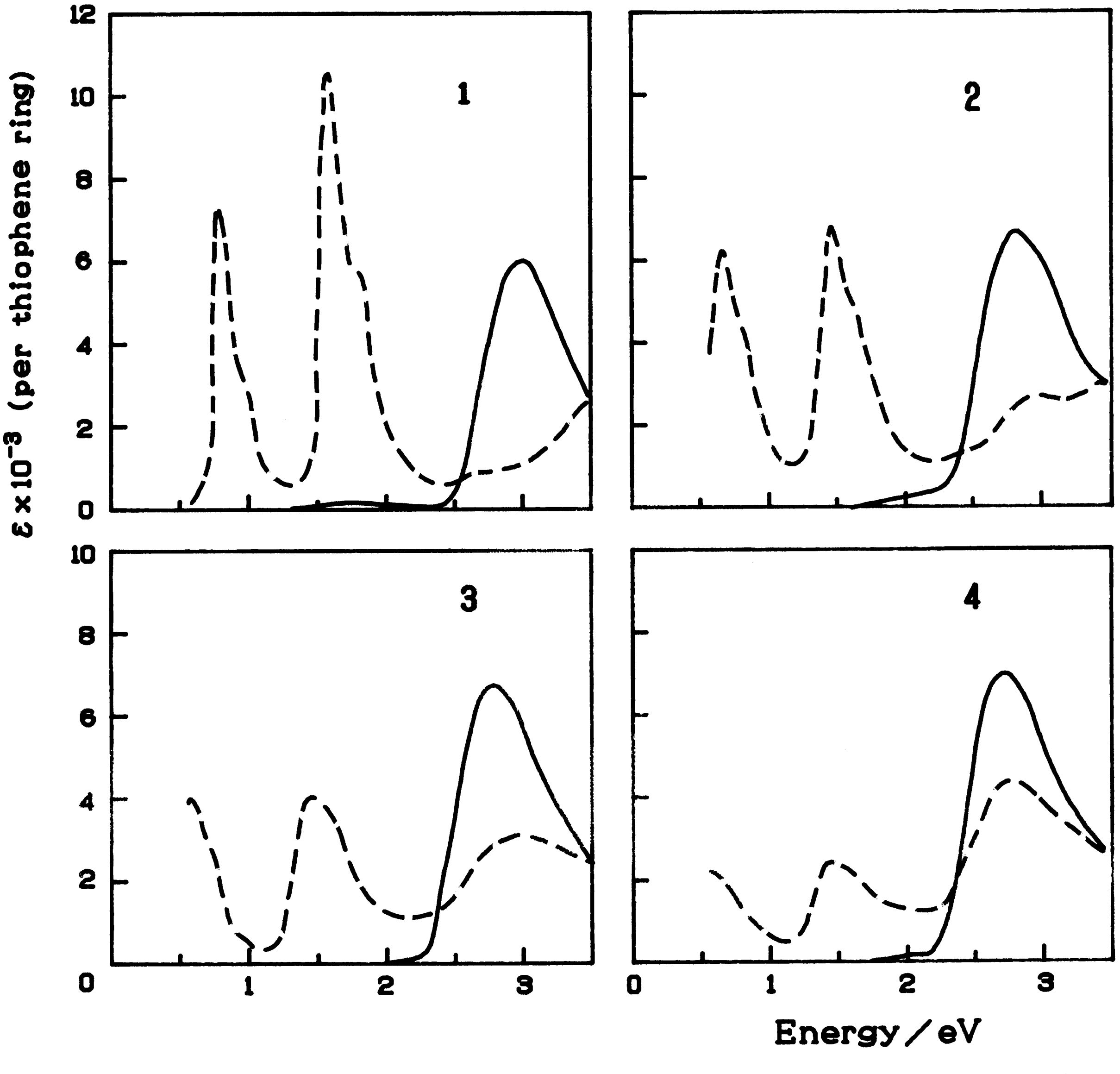


Fig. 1. The absorption spectra of neutral and oxidized oligothiophenes with hexyl substituents, ——— : neutral solutions, — — — : solutions oxidized using two equivalents of ferric chloride.

Moreover, these absorption spectra of the cation radicals are similar to those of oxidized (doped) poly(3-dodecylthiophene) in solution[9] (Fig. 2, dashed line) and polyhexylthiophene) oxidized with $NOPF_6$ in solution[10]. In particular, those of 4 are almost the same as those of the poly(alkylthiophenes). The energy of the bands related to the oxidized species in the poly(alkylthiophenes) were, as well as the shapes of the spectra, similar to those of the hexyl-substituted oligothiophenes (1.5 and less than 1.0 eV). The two absorption bands at lower than 2 eV of the poly(alkylthiophenes) had been attributed to dication (bipolaron) states from analogy with polythiophene films.[9,10] The observations in this paper lead us to conclude that oxidized species of poly(alkylthiophene)s are also cation radicals.

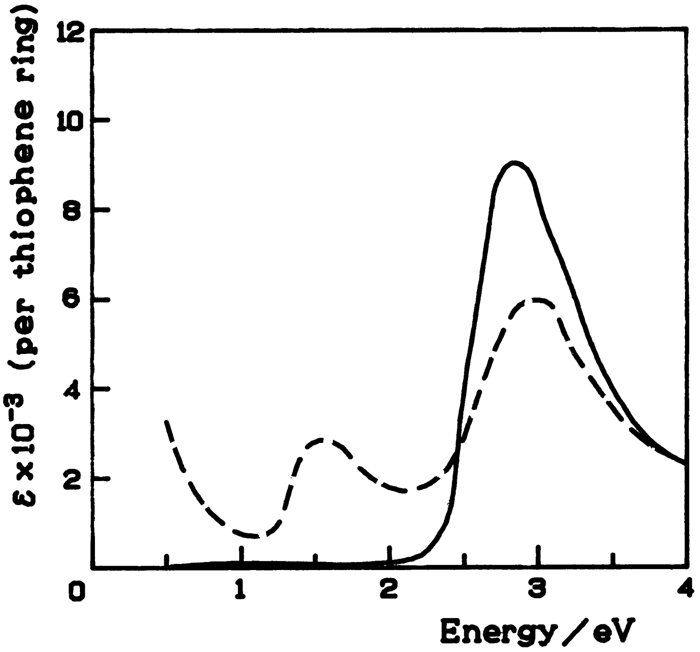


Fig. 2. The absorption spectra of poly(3-dodecylthiophene) in solution. ———— : neutral one, — — — : oxidized one.

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