

## Spectroscopic Analysis of the Reaction Processes of Ethylenedioxythiophene and the Dimer Cation Radicals in Acetonitrile

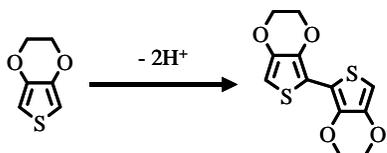
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Thiophene derivatives are well-known molecules to form the conducting polymers during the electrochemical oxidation. The reactivity of the thiophene derivative cation radicals formed in solution is usually so high that the detection of the short-lived cation radicals is quite difficult. In addition, the oxidation potentials of the dimers and the trimers are usually positive to that of the monomer, so that the electron transfer reactions should be considered as well as the chemical reactions to form the dimers etc. Thus, even in homogeneous solution, the reaction processes of the monomer cation radicals are expected to become complicated, though the electrode reaction processes are further complex.

In the present work, to make clear the dimerization and polymerization mechanisms involving the thiophene derivatives cation radicals in solution, at first, we observed the changes in the absorption spectra after oxidizing ethylenedioxythiophene (EDOT) in acetonitrile solution using an electron transfer stopped-flow method. The oxidation potential of EDOT is comparatively negative to that of thiophene due to the effect of ethylenedioxy group. To form the cation radical of EDOT, we mixed the acetonitrile solutions tris-(2,4-dibromophenyl) amine cation radical (TDBPA $\cdot^+$ ) and EDOT in the stopped-flow apparatus, and observed the time changes in the absorption spectra in an optical cell using a rapid-scan spectrophotometer with the minimum time interval of 1 ms.

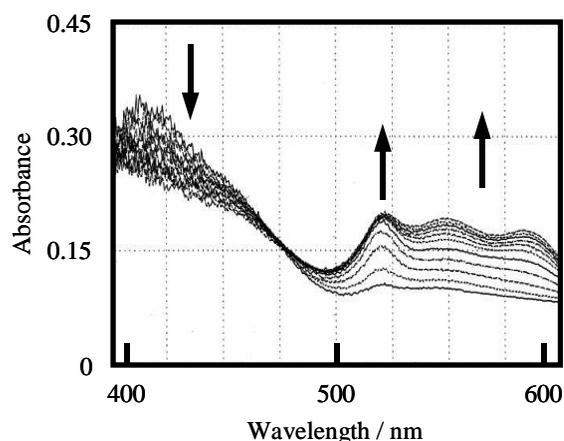
A typical result obtained in the case of EDOT is shown in Fig. 1. With the time interval of 2 ms, we could observe that a peak around 418 nm decreased immediately just after the mixing. Concurrently, in the longer wavelength region, three absorption peaks, whose maxima were 520, 552 and 590 nm, were observed to increase. The later behavior and the intensity of peaks were sensitive to the concentrations of the neutral molecules.

To assign the origins of these peaks manifested in the case of EDOT $\cdot^+$ , we synthesized the dimer of EDOT ((EDOT) $_2$ ) with the radical coupling reaction of EDOT $\cdot^+$  with *n*-BuLi and *N,N,N,N*-tetramethylethylenediamine.

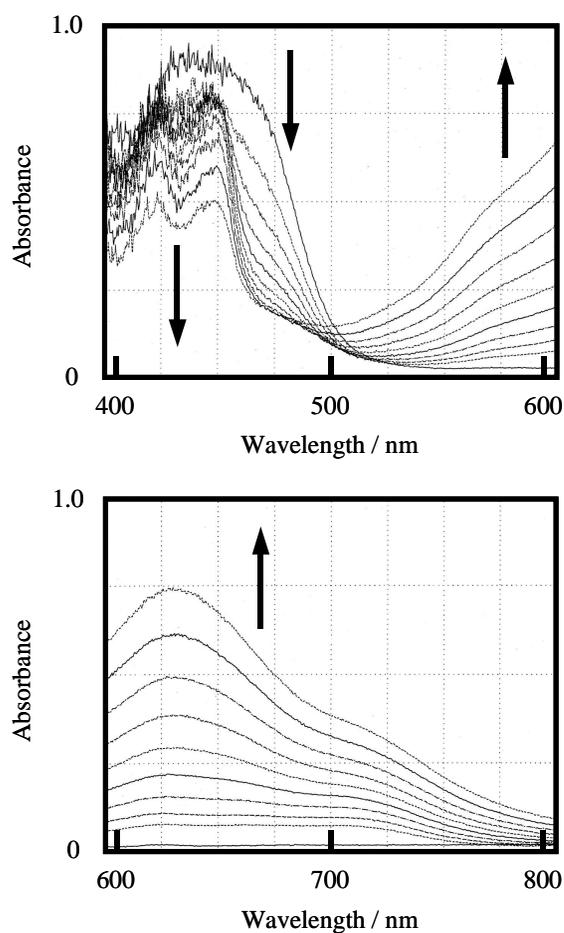


The changes in the absorption spectra in the oxidation of (EDOT) $_2$  were also observed similarly using tris(4-bromophenyl)amine cation radical (TBPA $\cdot^+$ ). In this case, a broad peak around 650 nm was observed to increase gradually, together with the initial decrease in a shoulder around 470 nm of the main peak and follow-up decrease of the peaks composed of two absorption maxima at 418 and 440 nm (Fig. 2). However, in comparison with the results of EDOT, the increases around 550 nm were not observed in the absorption spectra.

These results indicate that the cation radicals of (EDOT) $_2$  nor the tetramer (i.e. the dimer of (EDOT) $_2$ ) hardly detected spectrophotometrically in the polymerization processes of EDOT $\cdot^+$  in solution. As the possibility, even though the dimer cation radical ((EDOT) $_2$  $\cdot^+$ ) is formed in the reaction of EDOT $\cdot^+$ , (EDOT) $_2$  $\cdot^+$  is expected to interact with the monomer EDOT or EDOT $\cdot^+$  to form the trimer ((EDOT) $_3$ ) cation radical in the follow-up reactions.



**Fig. 1.** Time resolved absorption spectra observed after mixing EDOT and TDBPA $\cdot^+$ . Time interval of each spectra is 2 ms, composed of 10 spectra.



**Fig. 2.** Time resolved absorption spectra observed after mixing (EDOT) $_2$  and TBPA $\cdot^+$ . Time interval of each spectra is 50 ms, composed of 10 spectra.