Photochemical Polymerization of Dithienothiophenes

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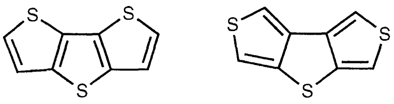
Photochemical polymerizations of dithienothiophenes were investigated. Photo-irradiation to the solution containing dithienothiophene and appropriate electron acceptor gave polydithienothiophene having *ca.* 10^4 (vs. PSt.) of molecular weight. The cation radical of the monomer was efficiently generated through photoinduced electron transfer from the excited state of the monomer to the electron acceptor. Then the successive coupling reaction resulted in a formation of the polymers.

Conjugated polymers have provided a wide variety of research subjects with respect to their electrical and optical properties. For molecular engineering of conjugated polymers toward the molecular electronic devices, fine fabrication in micro- and nano-meter scale is indispensable. From this point, we have realized the conjugated polymer thin film of alternating hetero layers by electrochemical polymerization.[1] Photochemical polymerization[2] is considered to be one of the useful candidates for the fine fabrication method in the two-dimensional direction of the polymer thin film. In this study, photochemical polymerizations of dithienothiophenes, which have been reported to be monomers for low band gap polymers,[3] were investigated.

Monomers, dithieno[3,2-*b*:2',3'-*d*]thiophene (**1**) and dithieno[3,4-*b*:3',4'-*d*]thiophene (**2**) (Figure 1), were synthesized following the procedure reported by De Jong and Janssen.[4] Their oxidation potentials of ground and excited states, which were estimated from polymerization potentials, fluorescence and phosphorescence spectra, were summarized in Table. *p*-Dinitrobenzene (DNB) and CCl_4 were adopted as electron acceptors in this study. Since their reduction potentials are -0.69 and -1.4 V vs. SCE,[5] they are considered to be sufficient for the electron transfer reaction from the excited monomers (**1** and **2**). The absorption spectra of the acetonitrile solutions containing both of the monomer and the acceptor (5-500 μM each) were identical to the superposition of those of the monomer and the acceptor, proving that the ground state complexes were not formed or negligible under the present experimental conditions.

All the photochemical reactions were carried out in quartz test tube after deaeration with argon gas. According to steady state irradiation of the Xe lamp (500 W) to the acetonitrile solution containing 10 mM of the monomer (**1** or **2**) and the electron acceptor (DNB or CCl_4), the solution changed to yellow immediately, and consequently to dark brown. Black film and precipitates were also obtained inside wall and bottom of the irradiated test tube, respectively. The precipitates were purified by filtration and rinsing with acetonitrile. A large portion of the products were soluble in adequate organic solvents, such as tetrahydrofuran. GPC analyses of the products, which were obtained by 1 h of photo-irradiation, showed formation of the polymers of **1** and **2** having molecular weight up to 1×10^3 (vs. PSt.). Weight-averaged molecular weights of polymers were 5×10^2 and 4×10^2, respectively, which corresponded to *ca.* 7mer of starting monomers. Taking the insoluble part of the polymers into account, the averaged molecular weight of all the polymers will be larger than the above values. FT-IR spectra of the polymers were practically identical to those of the polymers synthesized by electrochemical polymerization. ^{1}H nmr of the polymers showed subtle peaks at about 4.4 ppm which indicated α-position of thiophene rings in the polymer chains were partly protonated. The result accords with the facts that the polymers show broad absorption in UV-Vis. region with maxima at 300-400 nm (Figure 2) which are shorter than those of the corresponding polymers synthesized electrochemically[3] and are indicating short conjugation length resulted from separation of π-conjugation by saturated bonds.



1 **2**

Figure 1. Dithieno[3,2-*b*:2',3'-*d*]thiophene (**1**) and dithieno-[3,4-*b*:3',4'-*d*]thiophene (**2**).

Table. Oxidation potentials of ground and excited states of the monomers

monomers	oxidation potentials / V vs. SCE		
	ground state [a]	S_1 [b]	T_1 [b]
1	1.07	-2.26	-1.5
2	1.04	-2.63	-1.6

[a] Data were onset potentials on electrochemical polymerization. [b] Data were estimated from oxidation potentials and emission (fluorescence and phosphorescence) spectra.

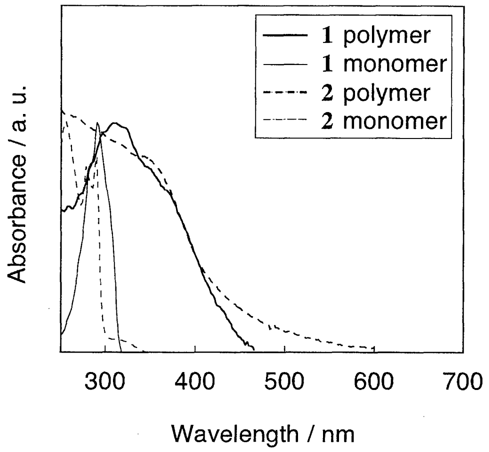


Figure 2. Absorption spectra of the monomers and the photochemical polymerization products having *ca.* 5×10^2 (vs. PSt.) of molecular weight. Reactions were carried out by 1 h of Xe lamp (500 W) irradiation to the acetonitrile solution containing 10 mM of the monomers and DNB.

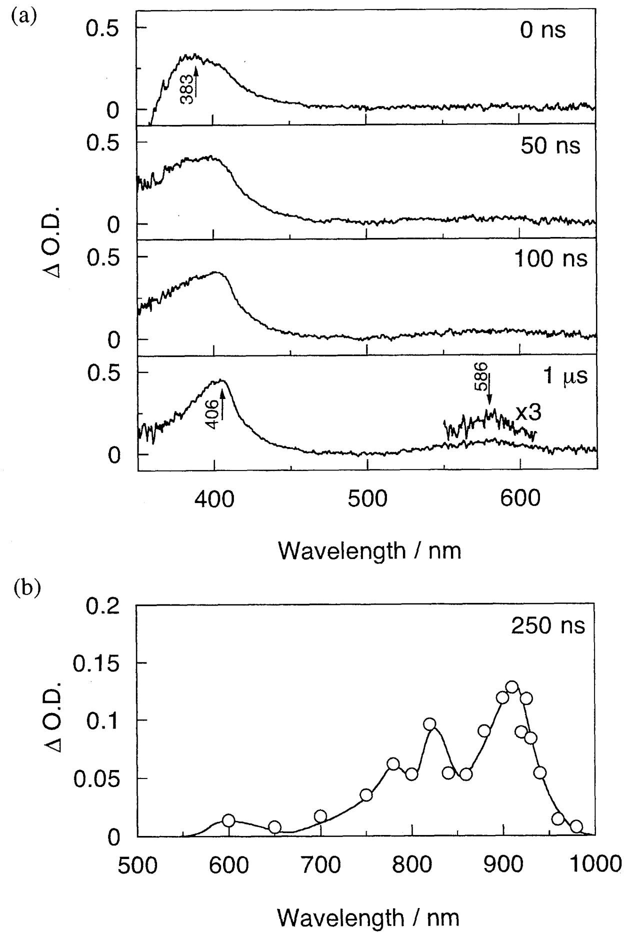


Figure 3. Difference absorption spectra of the acetonitrile solution containing 1 mM of **1** and 500 µM of DNB after excitation. (a) excitation :XeCl excimer laser (308 nm, fwhm 20 ns). (b) Nd:YAG laser (FHG 266 nm, fwhm 6 ns).

In the laser flash photolysis of the deaerated acetonitrile solutions containing 200 µM of **1** and **2**, absorption bands appeared at 384 and 422 nm, respectively, immediately after the laser pulse excitation. These transient absorptions are assigned to those of triplet excited state of dithienothiophenes ($T_n \leftarrow T_1$). In the absence of the electron acceptor, their decay life times were estimated to be 6.2 and 5.1 µs, respectively. In the laser flash photolysis of the solution containing **1** and DNB, the absorption band at 384 nm decayed within a few hundred ns, and new absorption bands appeared at 406 and 586 nm (Figure 3 (a)). They are assigned to the absorption of cation radical of **1**; their peak positions correspond well to those of cation radicals of **1** generated by γ-ray irradiation.[6] Furthermore, in near-infrared region, absorption bands appeared at 780, 820, and 910 nm (Figure 3 (b)). They are assigned to the absorption of the anion radical of DNB.[7] In the case of the solution containing **2** and DNB, absorption band assigned to $T_n \leftarrow T_1$ transition of **2** disappeared within a few hundred ns, and absorption bands assigned to those of the cation radical of **2** (820 and 880 nm)[6] and the anion radical of DNB appeared. These results indicate that the cation radicals of monomers and the anion radical of the DNB are generated effectively through the photoinduced electron transfer from triplet excited state of the monomers to DNB. On the other hand, fluorescence of the monomers were strongly quenched in the presence of CCl_4 according to Stern-Volmer equation. The quenching rate constants were estimated to be 3.9×10^8 and 2.4×10^{10} $M^{-1}s^{-1}$ for **1** and **2**, respectively.[8] The bimolecular quenching of the fluorescence indicates that electron transfer from singlet excited state of the monomer to CCl_4 contributes to the generation of the cation radical of the monomers. Thus, it can be concluded that the initial stage of the photochemical polymerization of dithienothiophene is generation of the cation radical through photoinduced electron transfer from excited state of the monomer to the electron acceptor. The corresponding polymers seems to be generated by the polymerization mechanism involving successive coupling and deprotonation reaction of the cation radical, as in electrochemical polymerization mechanism. Considering the fact that the α-position of thiophene rings in polymer chain are partly protonated, the deprotonation process occurs incompletely under the present polymerization conditions.

In this study, we showed photo-irradiation to the solution containing dithienothiophene and the electron acceptor gave the polymer. The present photochemical polymerization method will provide the basis for the construction of conjugated polymer material with artificial structures not only in two-dimensional direction but also in depth direction of polymer films. The fine fabrication using the present photochemical polymerization method is in progress.

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References and Notes

1 T. Iyoda, H. Toyoda, M. Fujitsuka, R. Nakahara, H. Tsuchiya, K. Honda, and T. Shimidzu, *J. Phys. Chem.*, **95**, 5215 (1991); M. Fujitsuka, R. Nakahara, T. Iyoda, T. Shimidzu, and H. Tsuchiya, *J. Appl. Phys.*, **74**, 1283 (1993).

2 H. Segawa, T. Shimidzu, and K. Honda, *J. Chem. Soc., Chem. Comm..*, **1989**, 132; T. Iyoda, M. Kitano, and T. Shimidzu, *J. Chem. Soc., Chem. Comm.*, **1991**, 1618; M. Fujitsuka, T. Sato, H. Segawa, and T. Shimidzu, *Chem. Lett.*, **1995**, 99.

3 A. Bolognesi, M. Catellani, S. Destri, W. Porzio, C. Talliani, and R. Zamboni, *Mol. Cryst. Liq. Cryst.*, **187**, 259 (1990).

4 F. De Jong and M. J. Janssen, *J. Org. Chem.*, **36**, 1645 (1971).

5 A. J. Bard and H. Lund, Encyclopedia of Electrochemistry of the Elements, Marcel Dekker, New York (1980), Vol. 14.

6 The cation radical of **1** generated by γ-ray irradiation in freon solution at 77 K showed absorptions with maxima at 351, 411, and 595 nm. In the case the cation radical of **2**, peak positions were 410, 880, and 918 nm.

7 T. Shida, Electronic Absorption Spectra of Radical Ions, Elsevier, Amsterdam (1988).

8 Stern-Volmer constants were estimated to be 1.55 and 1.77×10 M^{-1} for **1** and **2**, respectively, and fluorescence life times were 4.0 and 7.5×10^{-1} ns.