Photochemical Polymerization of Oligothiophenes

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Photochemical polymerization of oligothiophenes was investigated from steady-state and laser-flash photolysis. Photoirradiation to bithiophene or terthiophene solutions containing p-dinitrobenzene or CCl_4 gave their α-linked polymers. It was concluded that the coupling reaction of oligothienyl radicals formed through the photoinduced electron transfer from the excited oligothiophenes to the electron acceptor resulted in a formation of polymeric products.

Conjugated polymers have been regarded as promising materials for the electronics and optics in the future. Since their properties are much affected by not only the molecular structure but also the higher-order structures in micro- and nanometer scale, the fine fabrication is indispensable for their materialization. From this point, photochemical polymerization[1] is considered to be one of the useful candidates for the fine fabrication method in the two-dimensional direction because of the recent advancement in optical techniques. In this study, photochemical polymerization of α-linked oligothiophenes was investigated, because the oligothiophenes can be easily excited with UV light from the excimer laser.

2,2'-Bithiophene (**1**) or 2,2':5',2"-terthiophene (**2**) was used as starting monomer for the photochemical polymerization. Their oxidation potentials in the ground state and the excited states were summarized in Table. As an electron acceptor, p-dinitrobenzene (DNB) or CCl_4 was used, since their reduction potentials (-0.64 and -1.40 V vs. SCE, respectively[2]) are sufficient for the electron transfer reactions from the excited monomers.

All the photochemical reactions were carried out in quartz test tubes 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 10 mM of DNB, the solution changed to yellow immediately, and consequently to dark brown. Black films and precipitates were also obtained inside wall irradiated and at the bottom of the test tube, respectively. A portion of the products were soluble in adequate organic solvents, such as tetrahydrofuran. GPC analyses of the tetrahydrofuran solution of the products obtained by 1 hr of photo-irradiation indicated formation of the polymers of **1** and **2** having molecular weight up to 4×10^3 and 2×10^3 (vs. PSt.), which were corresponding to *ca.* 50mer and 20mer of the starting monomers, respectively. Weight-averaged molecular weights of the polymers were 5×10^2 and 4×10^2, respectively.

Table. Oxidation potentials of ground and excited state of monomers.

monomer	oxidation potential / V vs. SCE		
	ground state [a]	S_1 [b]	T_1 [b]
1	1.09	-2.23	-0.64
2	0.86	-2.01	-0.92

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

When the photochemical reactions were carried out in CCl_4 solution containing 10 mM of monomers, the formation of polymers with molecular weight up to 9×10^3 and 8×10^3 were confirmed, respectively. Their weight-averaged molecular weight were 7×10^2 and 6×10^2. It could be reasonably concluded that higher concentration of the electron acceptor resulted into the generation of the polymers with higher molecular weight.

The polymeric products of **1** and **2** having *ca.* 5×10^2 of molecular weights showed broad absorptions in UV-VIS. region peaked at 326 and 368 nm, respectively (Figure 1), which are shorter than those of the corresponding polymers synthesized chemically or electrochemically.[3] This suggests that their conjugation lengths were shorter than those of the fully conjugated polythiophenes. FT-IR measurements of the products obtained from **1** and **2** showed absorption bands specific to α-linked polythiophene, such as C-H out-of-plane bend (793 cm^{-1}).[4] On the other hand, ^1H NMR of the products showed subtle peaks at 4.3 ppm which indicate α-position of thiophene rings in the polymer chains are partly protonated. The result accords with the data of the UV-VIS. absorption, where short conjugation length could be attributed to the partial saturation of conjugated polymer chains. The partly protonated structure seems to give higher solubility to photochemically polymerized polythiophenes. When the polymerization was carried out using CCl_4 as an electron acceptor, polythiophene partly substituted with CCl_3 was obtained.[5] Using CCl_4 as an electron acceptor, CCl_4 anion radical was considered to be

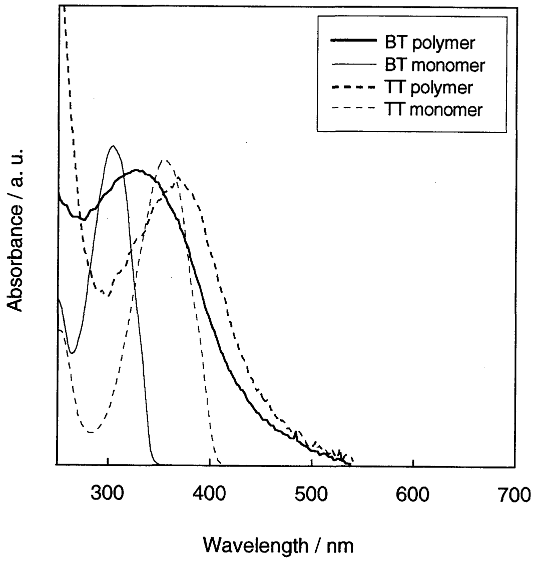

Figure 1. Absorption spectra of the monomers and the photochemical polymerization products having *ca.* 5×10^2 (vs. PSt.) of molecular weight. Reactions were carried out by 1 hr of Xe lamp (500 W) irradiation to the acetonitrile solution containing 10 mM of the monomers and DNB.

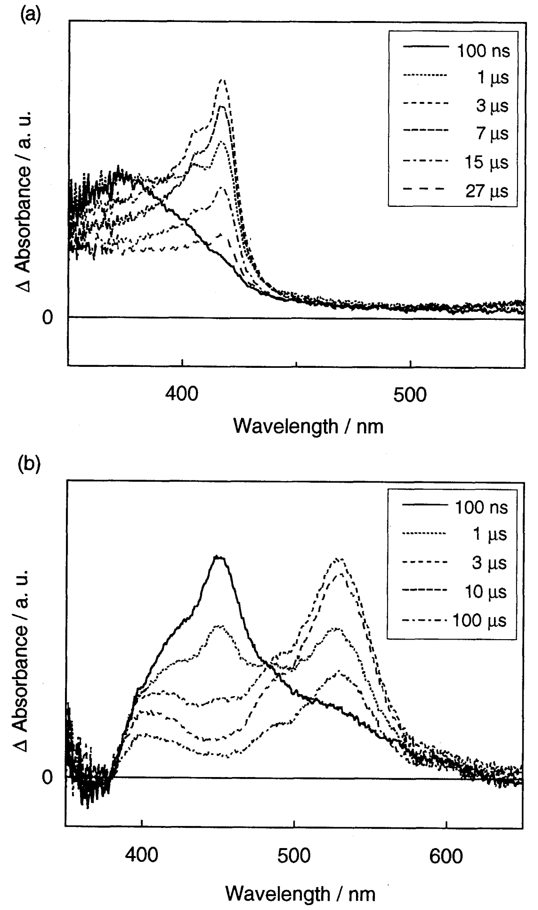

Figure 2. Difference absorption spectra of the acetonitrile solution containing 50 μM of monomer (**1** (a), **2** (b)) and the same amount of DNB after excitation with XeCl excimer laser (308 nm, fwhm 20 ns).

formed in the photoinduced electron transfer reaction. The anion radical resulted in a formation of CCl_3 radical, which will cause substitution reaction on the polymers.

In the laser flash photolysis using XeCl excimer laser (308 nm, fwhm 20 ns) of the deaerated acetonitrile solution containing 50 μM of **1** and **2**, absorptions peaked at 374 and 448 nm were observed, respectively, at 100 ns after the laser pulse excitation (Figure 2). These transient absorptions are assigned to those of triplet excited state of the monomers ($T_n \leftarrow T_1$).[6] In the absence of the electron acceptor, their decay life times were estimated to be 26 and 54 μs, respectively. In the presence of DNB, the transient absorptions decayed within a few μs, and new absorptions appeared at 417 and 531 nm, respectively. They are assigned to the absorptions of their cation radicals.[6] The observations are indicating that the cation radicals were generated effectively through the photoinduced electron transfer from triplet excited state of the monomers to the electron acceptor. In the case of laser flash photolysis of the acetonitrile solution containing CCl_4 as an electron acceptor, transient absorptions assigned to those of the cation radicals of the monomers appeared immediately after the laser pulse excitation. Taking the relationship between oxidation potentials of the monomers and that of CCl_4 into account, the cation radicals were considered to be generated through electron transfer from singlet excited state of the monomers to CCl_4. Actually, fluorescence of monomers were quenched in the presence of the CCl_4, according to Stern-Volmer equation. The quenching rate constants were estimated to be $\sim 8.6 \times 10^{10}$ and 9.5×10^{10} $M^{-1}s^{-1}$ for **1** and **2**, respectively.[7] The corresponding polymers seem to be generated by the polymerization mechanism involving successive coupling and deprotonation reaction of the generated cation radicals, as in electrochemical polymerization mechanism.[4] Considering the fact that the α-position of thiophene rings in polymer chain were partly protonated, the deprotonation process occurred incompletely under the present polymerization conditions. To obtain fully conjugate polymer, the polymerization conditions on the photochemical polymerization should be improved.

In this study, we showed that the photo-irradiation to the solution containing the oligothiophene and the electron acceptor gave α-linked polymers. The present photochemical polymerization method will provide basis for the construction of conjugated polymer material not only in two-dimensional direction but also in layered structures. We have constructed the alternating layered structure of the conjugated polymer thin films aiming at novel functional materials based on the artificial superlattice structure.[8] The fine fabrication using the present photopolymerization method is in progress.

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References and Notes

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5 When the polymerization was carried out in CCl_4 solution, the ratio of CCl_3 to the thiophene unit in the polymer chain was estimated to be 0.25 from elemental analysis.

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7 Stern-Volmer constants were estimated to be 1.71 and 2.84 M^{-1} for **1** and **2**, respectively. The fluorescence life time were reported to be ~200 and 300 ps (S. Rentsch, H. Chosrovian, D. Grebner, and H. Naarmaan, *Synthetic Metals*, **55-57**, 4740 (1993)).

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