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Radiation-induced Polymerization of 3-octylthiophene

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Abstract

In order to develop a new synthetic method and to study mechanism of oxidative polymerization of conducting polymers, polymerization of 3-octylthiophene in several organic solvents by γ -irradiation was examined. Polymers bimodal distribution with molecular weights at 500-1,000 and 2,000-3,000 were generated by the irradiation of chloroform solutions. The values of monomer conversion ($G(-M)$) decreased from 445 to 10 with doses from 0.99 kGy to 594 kGy. The large $G(-M)$ values and dose dependence of $G(-M)$ cannot be explained with widely accepted mechanism for electrochemical polymerization or chemical oxidative polymerization. Another mechanism, which proceeds through chain reactions, is proposed. This mechanism explains the large $G(-M)$ and the dependence on the dose.

Keywords: radiation-induced polymerization; γ -radiation; poly(3-alkylthiophene); conducting polymers

1. Introduction

Conducting polymers have great potential for many applications, such as capacitors, organic transistors, light-emitting diode, solar cells, sensors, anti-static coating (Skotheim and Reynolds, 2007). By using these polymers, production of low cost, light, flexible and large area electronic device is expected (Arias et al., 2010). Many studies have been performed on these materials.

Conducting polymers are polymerized by electrochemical and chemical methods. The chemicals method can be divided into simple oxidative polymerizations using oxidizing agents (Sugimoto et al., 1986) and various organic chemical methods using various coupling reactions, such as Grignard metathesis reactions (Loewe et al., 2001), the Rieke method (Chen and Rieke, 1993; Chen et al., 1993; Chen and Rieke, 1992), and the McCullough method (McCullough et al., 1993a; McCullough et al., 1993b) etc. By using the latter methods, regioregular polymers can be prepared. However, these methods require expensive reagents and careful treatments. Polymers produced by the oxidative polymerizations will be used for applications to commercial products.

A mechanism in Figure 1 has been accepted as electrochemical and chemical oxidative polymerizations of pyrrole and thiophene derivatives (Andrieux et al., 1991; Genies et al., 1983). However, some mechanisms contrary to this scheme have been proposed (Niemi et al., 1992; Wei et al., 1991).

The oxidative polymerizations are induced by formation of cations of the monomers. The cations can be generated by ionizing radiation under various conditions. The produced cations may

polymerize. The oxidative polymerization without oxidizing agents also may give some insight on the mechanism of the polymerizations.

In this paper, we then report polymerization of 3-octylthiophene by γ -irradiation. 3-Octylthiophene was selected as a monomer since poly(3-octylthiophene) is soluble in some solvents (Elsenbaumer et al., 1986; Kaeriyama and Masuda, 1991; Sugimoto et al., 1986), and hence easy to analyze by various methods.

2. Experimental and computational details

3-Octylthiophene was purchased from Tokyo Chemical Industry Co., Ltd., chloroform and the other solvents from Junsei Chemical Co., Ltd. The solutions of 3-octylthiophene were degassed by freeze-pump-thaw cycles and sealed in quartz optical cells or glass ampules.

The samples were irradiated with γ -ray from the ^{60}Co source at Hokkaido University at ambient temperature. Absorbed doses were evaluated with an ionization chamber.

Photoabsorption measurements of the solutions in the quartz cells were performed with a Shimadzu UV-3600 spectrophotometer in an ambient temperature. Molecular weight distributions were measured with a Shimadzu Prominence gel permeation chromatography (GPC) System (CBM-20A, LC-20AD, CTO-20A, SPD-20A) with a Shimadzu GPC803 column. Polystyrene standards purchased from Showa Denko K. K. were used.

The energies of initial and intermediate species were obtained by computation by density functional (DFT) theory with B3LYP5 exchange and correlation functionals and with 6-31G (d) basis set. The calculations were performed with the PC GAMESS/Firefly QC package (Granovsky) under Windows, which is partially based on the GAMESS (US) (Schmidt et al., 1993) source code. The computer used was a PC with 2.93 GHz Intel Core i7 CPU and 8.0 GB RAM. Facio was used as a pre-processor (Suenaga, 2005).

3. Results

3.1 Absorption spectra of irradiated solutions

Photoabsorption spectra of γ -irradiated neat 3-octylthiophene (3OT) and their 1 mol dm^{-3} solutions in chloroform and in hexane are shown in Figure 2. Their spectra were red-shifted compared to the unirradiated 1 mol dm^{-3} solutions in hexane before irradiation. The shifts of the chloroform solution are larger than the shifts of the neat 3OT and the hexane solution.

3.3 Molecular weight distribution of polymers from irradiated solutions

The redshifts of the irradiated neat 3OT and the solutions can be ascribed to the polymerizations of 3OT. Gel permeation chromatograms of γ -irradiated 0.1, 0.5, 1.0, 1.5 and 2.0 mol dm^{-3} solutions of 3OT in chloroform were measured. Oligomers with molecular weights of several thousands were observed. The G-values of the monomers conversion ($G(-M)$) are shown in table 1.

The apparent G-values for the number of 3OT transferred to the polymers per 100 eV ($G(-M)$) were calculated were calculated by the following equation:

$$G(-M) = \frac{S_0 - S}{S_0} \cdot \frac{1.602 \times 10^{-19} c N_A}{D(\text{Gy})} \times 100 \quad (1)$$

, where S_0 and S are the areas of the monomer in gel permeation chromatograms before and after irradiation, respectively. c is the monomer concentration, N_A the Avogadro number, and D the absorbed

dose in Gy. $G(-M)$ increased in this concentration region.

The GPC of 1.0 mol dm⁻³ solutions of 3OT irradiated to doses of 99 kGy–594 kGy are shown in Figure 3. The molecular weight distributions calculated from the GPC were shown in Figure 4.

The molecular weight and $G(-M)$ increased with increasing the absorbed dose.

The apparent $G(-M)$ for the solutions of 1.0 mol dm⁻³ 3OT in chloroform and the residual monomer concentration after the irradiation are shown in Table 2. It is about 445 at 0.99 kGy and decreases with increasing the absorbed dose.

4. Discussion

In this study, we have demonstrated that the polymerization of 3OT occurs even by γ -irradiation. The efficiency of the polymerization in chloroform is higher than the efficiencies in neat and in hexane. This difference will arise from that of stability of the cation of 3OT in the solutions.

However, our results conflict with the widely accepted mechanism in Figure 1. G-values of ionization (G_i) are from 4 to 5 (Tabata et al., 1991). Two ionizations are required to consume a monomer by the mechanism in Figure 1. Hence the $G(-M)$ should be less than 2.5 by this mechanism. These results conflict with our results about $G(-M)$, which are from 10 to 445 in 1.0 mol dm⁻³ solutions of 3OT in chloroform.

We then propose a mechanism as shown in Figure 5. A cation of 3OT produced by ionizing radiation reacts with a neutral 3OT, and induces chain reactions. This may explain our results: a cation of 3OT may consume many 3OT and produces a polymer. The increase in $G(-M)$ with increasing the concentration of 3OT will arise from the increase in the chain length in the polymerization of 3OT. Combination between the cation and anion will be a termination reaction. The number of the monomers for the propagating cations reacting with the monomers before encountering with the anion increases with increasing the concentration of 3OT. The decrease with increasing dose is also due to decrease in the concentration of 3OT. In addition, reactions between the propagating cations with neutral oligomers will occur, and it decreases the consumption of the monomers. $G(-M)$ thereby decreases with increasing the dose.

By the DFT calculations, the initial reaction in Figure 1 is 1.16 eV endothermic, whereas that in Figure 5 is 0.21 eV exothermic. At least, the initial reaction of the new mechanism is more probable.

In electrochemical polymerization, cations of monomer are produced with much higher concentration at the anode compared with the concentration in solutions irradiated with ionizing radiation. Electrons flow through the electrode against the cathode. The couplings between monomer cations will then be more probable. This may cause the difference in the mechanisms.

5. Conclusions

3-Octylthiophen polymerized even by γ -irradiation of its solutions in chloroform. $G(-M)$ are 445 with the irradiation to a dose of 0.99 kGy, and it decreased with increasing the absorbed dose to be 10 at a dose of 594 kGy. The $G(-M)$ is large to explain by the widely accepted mechanism of the polymerizations of thiophene derivatives for electrochemical and chemical oxidative polymerizations. 3OT will polymerize through a chain reaction of cations of 3OT by γ -irradiation. The difference would be caused by the difference in the local concentration of the cations in the solutions of the electrochemical and chemical oxidative polymerizations and in the in the solutions by γ -irradiation.

The $G(-M)$ values were larger than half of G-values of ionization. However, the products contain the large

amount of small oligomers, and yields of polymers with high molecular weight are low. Very large dose and removal of the oligomers is necessary to obtain the polymers usable for the practical applications. Irradiations with high dose rate or addition of chemicals to stabilize intermediate cations may solve these problems.

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Figure Captions

Figure 1. Mechanism of the polymerization of aromatic heterocyclic monomers by the electrochemical or chemical oxidative polymerization.

Figure 2. Optical Absorption spectra of neat 3-octylthiophene(3OT), 1 mol dm⁻³ solutions of 3OT in chloroform and in hexane irradiated with γ -ray to a dose of 50-60 kGy (55.1 kGy, 49.5 kGy, and 57.8 kGy, respectively) and spectrum of 1 mol dm⁻³ solutions of 3OT in hexane before irradiation.

Figure 3. Gel permeation chromatograms of 1 mol dm⁻³ solutions of 3-octylthiophene in chloroform irradiated with γ -ray to doses of 99, 198, 396, and 594 kGy.

Figure 4. Molecular weight distributions of products in 1 mol dm⁻³ solutions of 3-octylthiophene in chloroform irradiated with γ -ray to doses of 99, 198, 396, and 594 kGy.

Figure 5. Mechanism of the polymerization of 3-octylthiophene by radiation-induced polymerization.

Tables

Table 1. Dependence on the concentration of 3-octylthiophene(3OT) of the residual monomer concentrations in the irradiated solutions and the apparent G-values of the number of 3OT polymerized ($G(-M)$) for 3-OT solutions in chloroform irradiated with γ -ray to a dose of about 200 kGy.

Initial Monomer Concentration / mol dm ⁻³	Residual Monomer Concentration / mol dm ⁻³	Absorbed Dose / kGy	$G(-M)$
0.1	0.02	195	2.6
0.5	0.03	196	15
1.0	0.10	198	29
1.5	0.21	200	42
2.0	0.49	202	49

Table 2. The residual monomer concentrations in the irradiated solutions and the apparent G-values of the number of 3-octylthiophene polymerized for the solutions of 1.0 mol dm⁻³ 3OT in chloroform (*G(-M)*).

Dose / kGy	Monomer Concentration / mol dm ⁻³	<i>G (-M)</i>
0	1.00	-
0.99	0.93	445
9.9	0.64	232
25	0.68	81
50	0.47	67
74	0.29	61
99	0.24	48
198	0.10	29
396	0.04	14
594	0.02	10

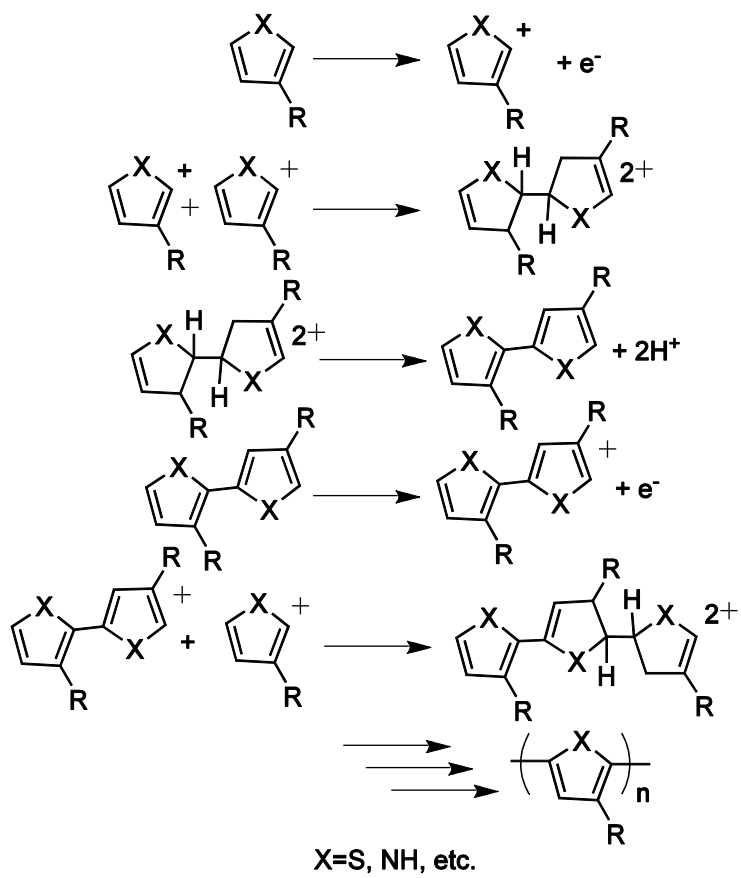


Figure 1. A. Ishigaki and H. Koizumi

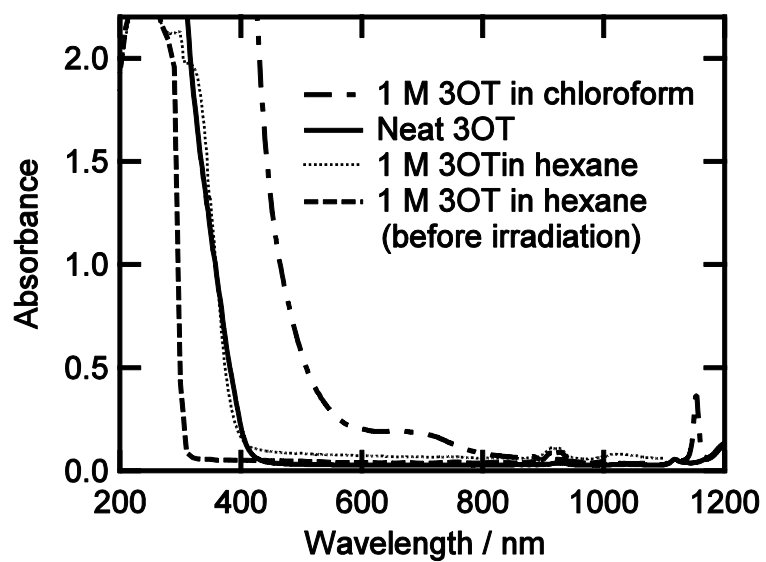


Figure 2. A. Ishigaki and H. Koizumi

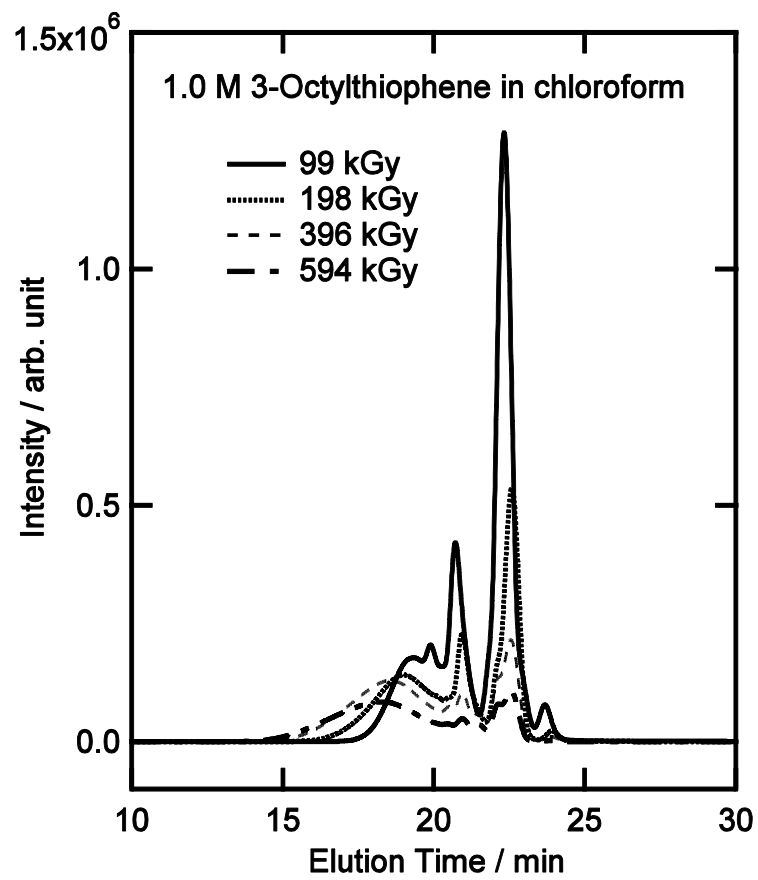


Figure 3. A. Ishigaki and H. Koizumi

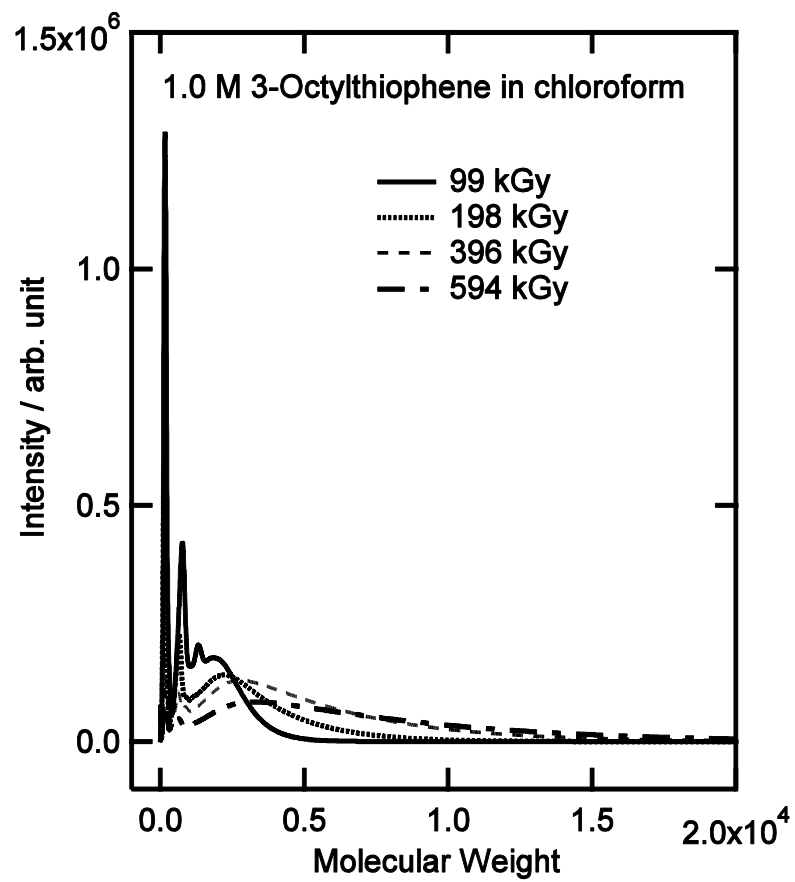


Figure 4. A. Ishigaki and H. Koizumi

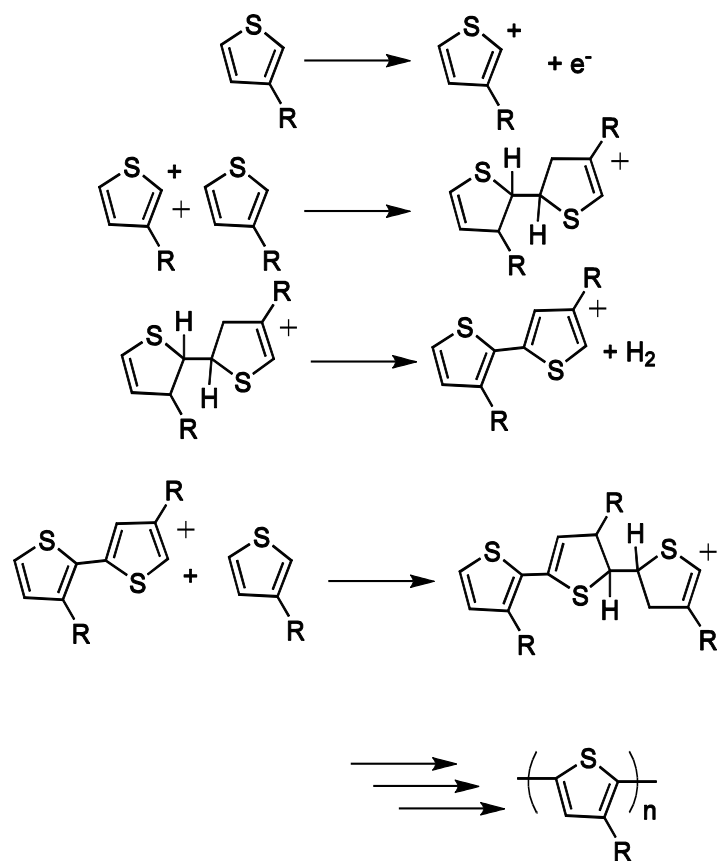


Figure 5. A. Ishigaki and H. Koizumi