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Photochemical oligomerization pathways in 2,5-diiodothiophene film

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Abstract

The photochemical oligomerization mechanisms of 2,5-diiodothiopene in a multilayer film was studied with matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS). The photo-dissociation of 2,5-diiodothiophene and subsequent reactions of the dissociated radical with surrounding molecules and other radicals can lead to the growth of oligothiophene species. The molecular weight distribution of the oligothiophene products indicated that the average number of iodine atoms in the oligothiophene molecule increases with the number of thiophenyl units in the molecule. All possible oligomerization mechanisms could be categorized in two pathways—the oligomer growth by insertion of a thiophenyl unit versus the growth by insertion of an iodothiophenyl unit. Using a modified Flory's model for a linear step polymerization process, we found that the probability of thiophenyl and iodothiophenyl insertion in each C—C bond formation is ∼0.63 and ∼0.37, respectively. The model also predicted the most probable oligomer length to be about 3–4, which was consistent with the photoluminescence and FTIR analysis.

Keywords: Photo-polymerization; Oligomerization; Oligothiophene; Polythiophene

1. Introduction

Polythiophenes and oligothiophenes are of great interest due to their potential applications to flexible solar cells, electronics, and displays [1–3]. Typically, alkyl-substituted polythiophenes are widely studied since they are soluble in organic solvents, which make the materials processing easy [2,4–7]. Unsubstituted polythiophenes and large oligothiophenes are not soluble or fusible; so fabrication of devices using these compounds is difficult. This difficulty can be avoided if oligothiophene and polythiophene species are produced directly at the target substrates. Some of the widely used *in situ* synthesis techniques are electrochemical and plasma synthesis techniques [3,8–10]. Recently, an *in situ* photochemical method to synthesize thin films and micro-patterns of oligothiophene is developed [11–16]. In the photochemical process, precursor molecules (2,5-diiodothiophene) are deposited on a desired substrate and then irradiated with UV photons in an argon environment. The photo-dissociation of the C—I bond in the precursor molecule produces 2-iodothiophenyl radical (I-*Th*$^\bullet$), which can undergo further reactions in the precursor film to form oligothiophenes. The direct coupling of these two radicals will form a dimeric species (I-*Th*-*Th*-I). Since there are two terminal C—I bonds, this dimer can undergo further photo-dissociation and coupling reactions, making longer chain oligomers. Since the photo-dissociation process is selective to the C—I bond, this process does not cause the fragmentation of thiophene ring structure (c-C_4H_2S). The fragmentation is often observed in the plasma polymerization process. The photochemical process can be applied to non-conducting substrates that cannot be used in the electrochemical process. Since the photon is involved in the synthesis, various micro-patterns can easily be produced by using photomasks [11].

This paper discusses the oligomerization pathways during the photochemical reaction of 2,5-diiodothiophene in the condensed multilayer film. Since the product distribution is governed by the reaction pathways and their probabilities, the molecular weight distribution of the oligothiophene species provides information on the photochemical reaction mechanisms. In this study, the molecular weight distribution of the oligothiophene film produced photochemically on a glass substrate was obtained with matrix-assisted laser desorption-ionization (MALDI) mass spectrometry (MS). The molecular weight distribution data were analyzed with a modified Flory's model for linear step growth polymerization. This analysis revealed that there are

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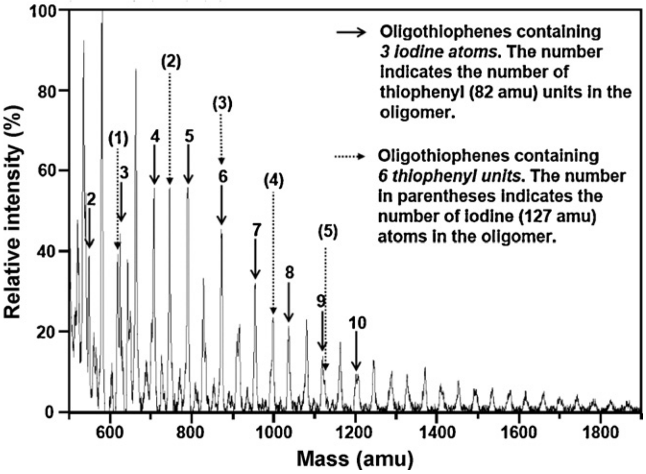

Fig. 1. MALDI-MS of photochemically synthesized oligothiophene film. The peaks of oligothiophene series containing three iodine atoms with different numbers of thiophenyl units (solid arrows) and those containing six thiophenyl units with different numbers of iodine atoms (dotted arrows) are marked.

two monomer units (thiophenyl unit and iodothiophenyl units) involved in the oligothiophene growth. The data fitting with the model found the insertion probability of these two units in each C–C bond formation step as well as the most probable oligomer chain length.

2. Experimental method

Experimental details of the photochemical process to make thin films of oligothiophene are described in our previous work [11]. 2,5-Diiodothiophene was deposited on a glass substrate by physical vapor deposition from a heated source in ambient conditions. The glass substrate was cleaned with a 5:1:1 mixture of H_2O, NH_4OH, and H_2O_2 at 70 °C for 10 min prior to use. The substrate was directly placed on the evaporation source until 200–300 nm thick 2,5-diiodothiophene film was deposited on the glass substrate. The deposited 2,5-diiodothiophene film was then irradiated with a 200 W mercury UV lamp for 3 min in an argon environment. The oligothiophene film produced on the glass substrates was scraped off and mixed with α-cyano-4-hydroxycinnamic acid (a matrix for MALDI) and transferred onto a MALDI-MS sample plate. The mass spectra of the oligothiophene products were obtained with a Micromass MALDI-L/R system.

3. Results and discussion

The MALDI mass spectrum of the photochemically synthesized oligothiophene is shown in Fig. 1. The data below 500 amu are not analyzed since this region is not well resolved due to fragmentations of the molecules during the MALDI process [17]. Organic contaminations during the sample preparation can also make the data analysis of the low mass region difficult. Scrutinizing the region higher than 500 amu of the MALDI-MS data, one can find two repeating units. One is 82 amu which is the thiophenyl group (c-C_4H_2S, noted as *Th* hereafter). The other is 126 amu which corresponds to the mass difference between the iodine and hydrogen atoms. This indicates the iodine substitution at the hydrogen position.

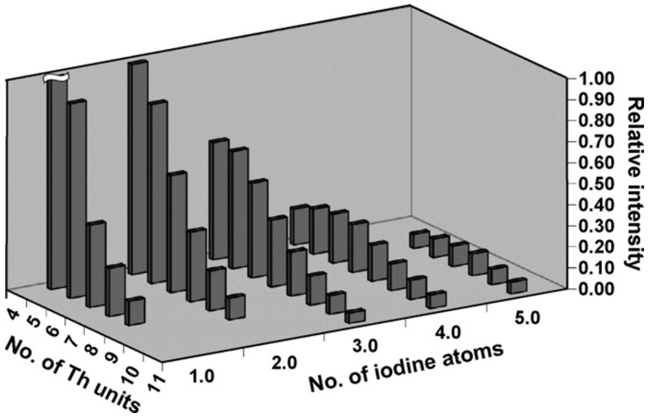

Fig. 2. MALDI-MS data plotted as a function of thiophene units and iodine atoms in the oligothiophene species. The intensity is normalized with the I–(c-C_4H_2S)$_4$–I peak (4 *Th* and 2 I).

From these trends, the MALDI-MS data can be deconvoluted to a series of oligothiophene molecules with a different number of iodine substitutions. Fig. 2 plots the normalized intensity of the oligothiophene species as a function of the number of thiophenyl units (from 4 to ∼11) as well as the number of iodine atoms (from 1 to 5). The peaks are normalized with the peak intensity of the species containing four thiophenyl units and two iodine atoms which corresponds to I–(c-C_4H_2S)$_4$–I. In this plot, the peak corresponding to I–(c-C_4H_2S)$_4$–H is out of scale. Fig. 2 clearly shows the presence of oligothiophene species with a different number of iodine atoms. The average number of iodine atoms incorporated into the oligothiophene increases with the increase of the number of thiophenyl units.

The presence of the 82 amu unit indicates the production of oligothiophene species and the structural intactness of the thiophenyl ring (c-C_4H_2S). If the oligothiophene is produced through direct coupling of photogenerated radicals (I-$Th^\bullet + {}^\bullet Th$-I, I-$Th^\bullet + {}^\bullet Th$-*Th*-I, *etc.*), the number of iodine atoms for any chain length oligomers should always be two. The presence of oligothiophene species with the same number of thiophenyl units but different numbers of iodine atoms clearly suggests that there is more than one oligomerization pathway.

Fig. 3 shows various possible reactions for the formation of dimers from the monomer. The formation of 2-iodothiophenyl radical and iodine atom from the photo-dissociation of the C–I bond is well established [18]. These photogenerated radicals and atoms will initially have a high kinetic energy which will be rapidly quenched by collisions with neighboring molecules [19]. During this quenching process, they can react with the neighboring molecules [20]. The photogenerated 2-iodothiophenyl radical can react with the neighboring 2,5-diiodothiophene molecule in two different ways [21–28]. One is to replace the iodine in the neighboring molecule to form a dimeric species (I-*Th*-*Th*-I). This reaction will release an iodine atom (reaction 2-1 in Fig. 3). The other is to abstract the hydrogen from 2,5-diiodothiophene and produce 2-iodothiophene and a 2,5-diiodothiophenyl radical (reaction 2-2). In fact, the photo-

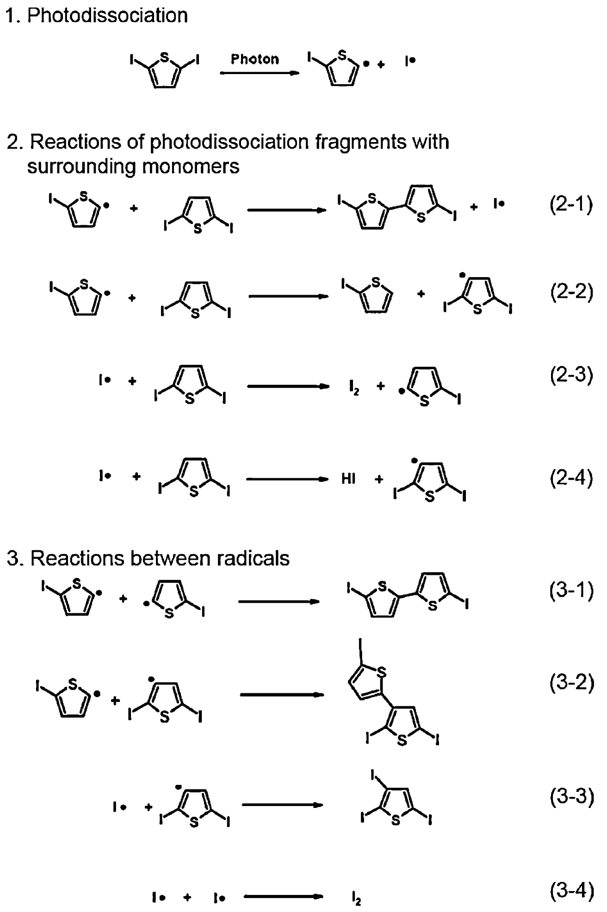

Fig. 3. Schemes for photo-dissociation of 2,5-diiodothiophene and subsequent reactions of the photogenerated radicals and monomers in the film.

generated 2-iodothiophenyl radical can also abstract the iodine atom from the neighboring 2,5-diiodothiophene molecule; but, this reaction will produce the species identical to the reactants. The photogenerated iodine atom can abstract an iodine atom from the neighboring molecule and produce I_2 and a 2-iodothiophenyl radical (reaction 2-3). It can also abstract the hydrogen and make HI and a 2,5-diiodothiophenyl radical (reaction 2-4).

The thiophenyl radicals and iodine atoms in the film can also undergo coupling reactions. The coupling between two 2-iodothiophenyl radicals will produce a α-α' coupled dimmer (reaction 3-1) [29]. The coupling between the 2-iodothiophenyl and 2,5-diiodothiophenyl radicals will produce a α-β coupled dimer (reaction 3-2). The coupling between 2-iodothiophenyl and iodine forms the parent molecule. The coupling between 2,5-diiodothiophenyl and iodine forms 2,3,5-triiodothiophene (reaction 3-3). The reaction between iodine atoms forms molecular iodine (reaction 3-4).

Analyzing the structures of the dimer species formed through these reactions, it can be seen that there are two types of monomeric units inserted between the C–I bond of the precursor molecule. They are the thiophenyl unit (reactions 2-1 and 3-1) and the iodothiophenyl unit (reaction 3-1). Further activation of these dimers and subsequent reactions will produce trimers, tetramers, pentamers, *etc*. During these reactions, the basic growing units will be the same as the dimer formation. The 2,3,5-triiodothiophene product of reaction 3-3 can also be excited by photon and involved in oligomerization reaction. In this case, the resulting species will have an increase of one iodothiophenyl unit at the chain end. Therefore, the overall photochemical processes for the oligomer growth can be considered as the oligomerization reaction of the thiophenyl and iodothiophenyl units.

The molecular weight distribution of the oligomers produced from these two monomeric units can be modeled with a Flory's model originally developed for the molecular weight distribution of the linear step polymerization [30]. The overall photochemical process can be assumed as a linear step oligomerization process in which either a thiophenyl or iodothiophenyl unit is added to the chain at every step. Following the equal reactivity principle of the Flory's model, we assume that the reaction probability of an oligomer with another monomer or oligomer is independent of the number of thiophenyl and iodothiophenyl units it carries. According to the Flory's model for step oligomerization, if the extent of oligomerization reaction (monomer consumption) is p ($0 \leq p \leq 1$), the probability of finding an oligomer with x number of monomer unit (x-mers), p_x, is given by the following equation:

$$p_x = p^{x-1}(1-p) \tag{1}$$

The original Flory's model deals with one type of monomer unit; hence there is only one molecular weight value for a given chain length oligomer. But in the case of the photochemical reactions of 2,5-diiodothiophene, the monomeric unit added at every oligomerization step can be either thiophenyl (*Th*) or iodothiophenyl (*ThI*). Consequently, the molecular weight of the same chain length oligomer can vary depending on the number of iodine atoms in the molecule. If the probability of adding the *Th* and *ThI* unit is a and b, respectively, the number of x-mers with different molecular weight will be equal to total number of terms in the binomial expansion of $(a+b)x$. Then, the probability of finding an x-mers composed of n *Th* units and m *ThI* units ($n+m=x$) can be expressed as [31]:

$$G_{n,m} = \frac{(x-1)!}{n!m!} a^n b^m \tag{2}$$

In this modified Flory model, Eq. (1) gives the probability of finding a series of x-mers in the entire mixture and Eq. (2) gives the probability of finding a specific oligomer molecule containing n number of *Th* units and m number of *ThI* units in the give x-mer series. Therefore, the overall probability of finding a specific x-mer with n *Th* units and m *ThI* units in the overall distribution is given by the product of Eqs. (1) and (2):

$$p_{n,m} = p^{(x-1)}(1-p)\frac{(x-1)!}{n!m!} a^n b^m \tag{3}$$

The experimental MALDI-MS data can be fitted with Eq. (3) to find the extent of monomer consumption (p) and the probability of *Th* and *ThI* insertion (a, b). Fig. 4 compares the experimental data and the simulated result with the best-fit parameters: $p=0.67$, $a=0.63$, and $b=0.37$. It can be seen that the model reproduces the experimental results very well. The

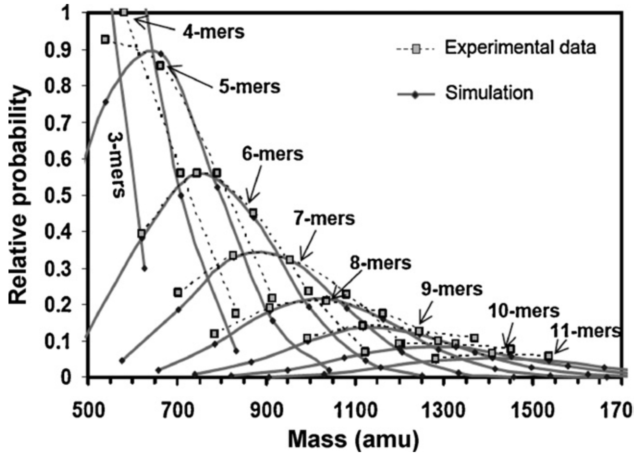

Fig. 4. Simulation result of the molecular weight distribution of the photochemically synthesized oligothiophene species. The lines are drawn as a guide for the oligomers containing the same number of thiophenyl units but different numbers of iodine atoms. The simulation data comes from the modified Flory's model with the assumption that the extent of monomer consumption is 67% and the probability of adding thiophenyl and iodothiophenyl units in each oligomerization step is 0.63 and 0.37, respectively.

number average chain length, $\bar{x}$, of the oligomer species can be estimated using the Carother's equation [32]:

$$\bar{x} = \frac{1}{1-p} \tag{4}$$

For $p = 0.67$, the number average chain length of the photochemically produced oligothiophene species is calculated to be ∼3.

Although the trimer series peaks are not clearly resolved in MALDI-MS due to interferences from the fragmentation and contamination peaks in the low molecular weight region, this prediction is in good agreement with the photoluminescence (PL) and IR spectroscopy analyses [11]. In the previous study reported in the literature for the same reactions, we have analyzed the PL emission spectra of the produced oligothiophene films and found that the peak emission wavelength is about 540 nm. This corresponds to π-electron conjugation over 3–4 thiophenyl units. The IR peak positions of the C–C symmetric and antisymmetric stretching vibration peaks of the thiophenyl ring are 1430 and 1492 cm^{-1}, respectively. These peak positions are consistent with the vibrational spectra of short oligomers with 3–4 thiophenyl units. The close agreement between the average conjugation length determined from the PL and IR experiments and the theoretically calculated number average chain length from MALDI-MS supports the validity of the model.

4. Conclusions

The photochemical reaction pathways of 2,5-diiodothiophene in the multilayer film are elucidated from the molecular weight distribution of the produced oligothiophene species. The photogenerated 2-iodothiophenyl radical and iodine atom react with neighboring parent molecules as well as other radicals and atoms. The reactions with the parent molecules can produce 2,5-diiodothiophene radicals or 2,3,5-triiodothiophene species that can lead to extra iodine atoms attached to the produced oligothiophene species. The overall oligomerization process can be described with the modified Flory's model for the linear step polymerization. The model analysis finds that the probability of the chain growth via thiophenyl and 2-iodothiophenyl insertion is 0.63 and 0.37, respectively.

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