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### Electrical Conductivity and Physical Properties of Poly(Dipropargylsilane Derivatives) Doped with Electron Acceptors

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# **ELECTRICAL CONDUCTIVITY AND PHYSICAL PROPERTIES OF POLY(DIPROPARGYLSILANE DERIVATIVES) DOPED WITH ELECTRON ACCEPTORS**

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### ABSTRACT

Films of poly(dipropargylsilane derivatives) were easily prepared by solvent casting. The resulting red-black films were relatively flexible and ductile. By doping with electron acceptors, the electrical conductivity increased up to the order of  $10^{-1}$ – $10^0$  S/cm. The activation energy for the conduction of doped film was 4 kcal/mol. The change in Raman, IR, and UV-visible spectra by doping suggests electron transfer from the poly(dipropargylsilane derivatives) to the dopant, leading to the formation of polaron. It also was observed that doping with  $I_2$  drastically destroys the crystallinity of the polymer.

### INTRODUCTION

Polyacetylene has been intensively studied over the past decades because of its unique properties [1]. Polyacetylene is, however, unstable in air and insoluble in the usual organic solvents. Thus, substituted polyacetylenes [2] have been investigated to improve their stability because they have somewhat low conductivity due

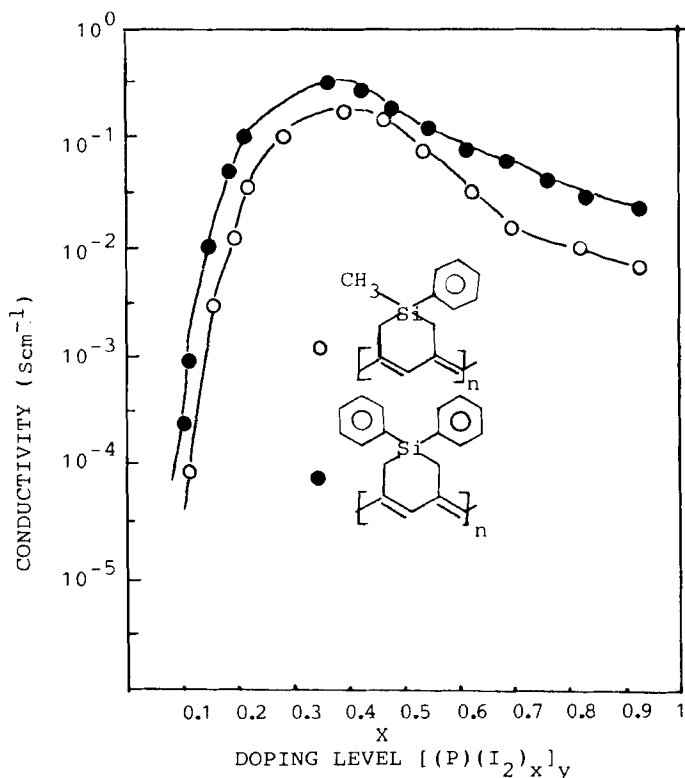


FIG. 1. Electrical conductivity of poly(methylphenyldipropargylsilane) and poly(diphenyldipropargylsilane) film as a function of  $I_2$  doping level after exposure to iodine.

TABLE 1. Conductivity and Doping Level of Bromine-Doped Poly(Dipropargylsilane Derivatives) Film<sup>a</sup> as a Function of Time

Polymer	Doping time, min	Composition of doped polymer <sup>b</sup>	Electrical conductivity, S/cm <sup>c</sup>
Poly(MPPS)	3	(C <sub>13</sub> H <sub>14</sub> Si)(Br) <sub>0.16</sub>	1.8 × 10 <sup>-2</sup>
Poly(MPPS)	5	(C <sub>13</sub> H <sub>14</sub> Si)(Br) <sub>0.37</sub>	1.0 × 10 <sup>-1</sup>
Poly(MPPS)	10	(C <sub>13</sub> H <sub>14</sub> Si)(Br) <sub>0.46</sub>	4.5 × 10 <sup>-3</sup>
Poly(DPPS)	3	(C <sub>18</sub> H <sub>16</sub> Si)(Br) <sub>0.18</sub>	1.9 × 10 <sup>-2</sup>
Poly(DPPS)	5	(C <sub>18</sub> H <sub>16</sub> Si)(Br) <sub>0.38</sub>	8.4 × 10 <sup>-2</sup>
Poly(DPPS)	10	(C <sub>18</sub> H <sub>16</sub> Si)(Br) <sub>0.59</sub>	2.9 × 10 <sup>-3</sup>

<sup>a</sup>Films of these polymers were cast by toluene solution.

<sup>b</sup>Extent of doping was obtained by the weight uptake method.

<sup>c</sup>Conductivity was measured with the 4-point probe dc method.

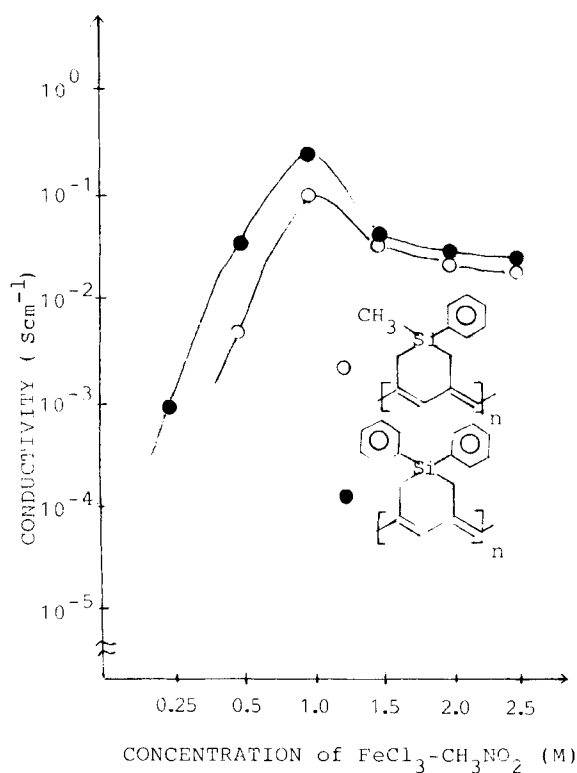


FIG. 2. Electrical conductivity of poly(dipropargylsilane derivatives) film as a function of concentration [*M*] of FeCl<sub>3</sub> in CH<sub>3</sub>NO<sub>2</sub>.

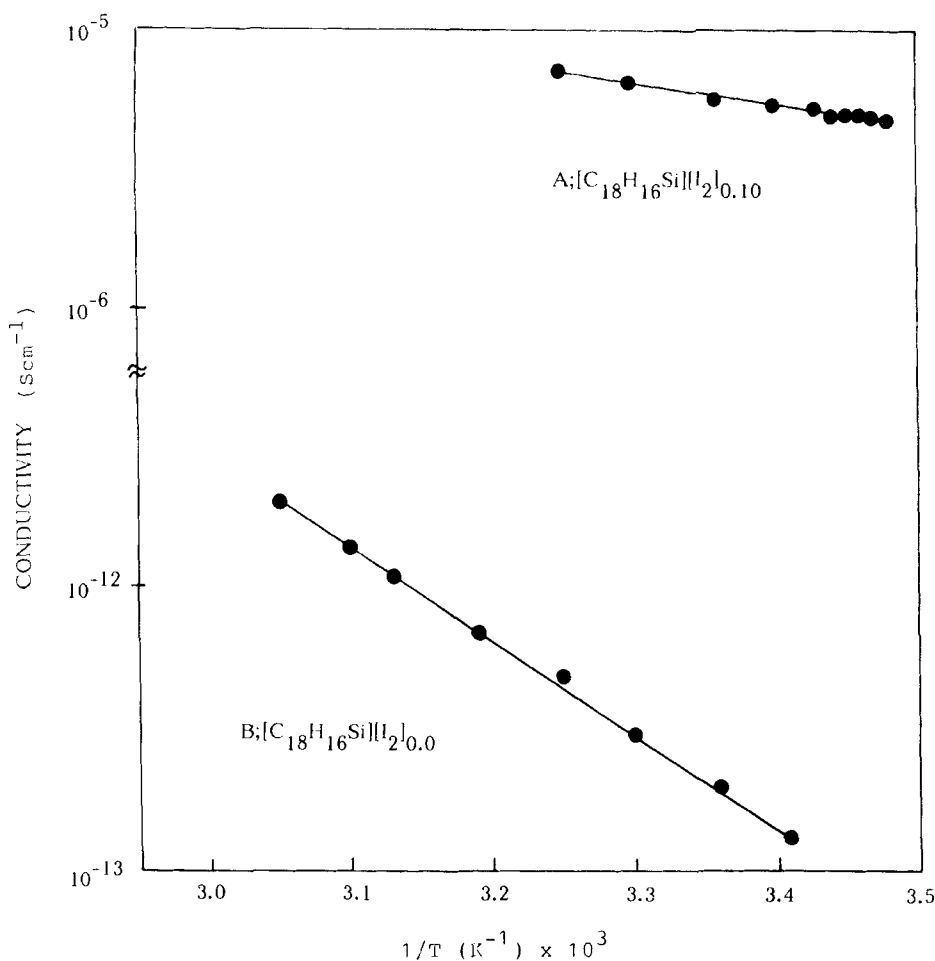


FIG. 3. Arrhenius plots for conductivity of poly(diphenyldipropargylsilane): (A) doped, (B) undoped.

to their hindered coplanarity. In the case of the polymerization of nonconjugated diynes, cyclopolymer appears to ameliorate their deleterious steric effects, leading to a more coplanar polyene backbone [3]. Recently, Gibson et al. reported that the polymerization of 1,6-heptadiyne by the free-standing method using a Ziegler-Natta catalyst led to films *in situ*, and the resulting films were unstable to air and insoluble in all organic solvents [4]. In our previous work we found that cyclopolymer of dipropargylsilane derivatives obtained with Mo- and W-based catalysts are soluble in most organic solvents and stable to air oxidation [5].

This article describes the preparation of flexible films of poly(dipropargylsilane derivatives) by solution casting and the conductivity of films doped by electron acceptors. Further, the changes in physical properties and structure of poly(dipropargylsilane derivatives) by doping are also discussed.

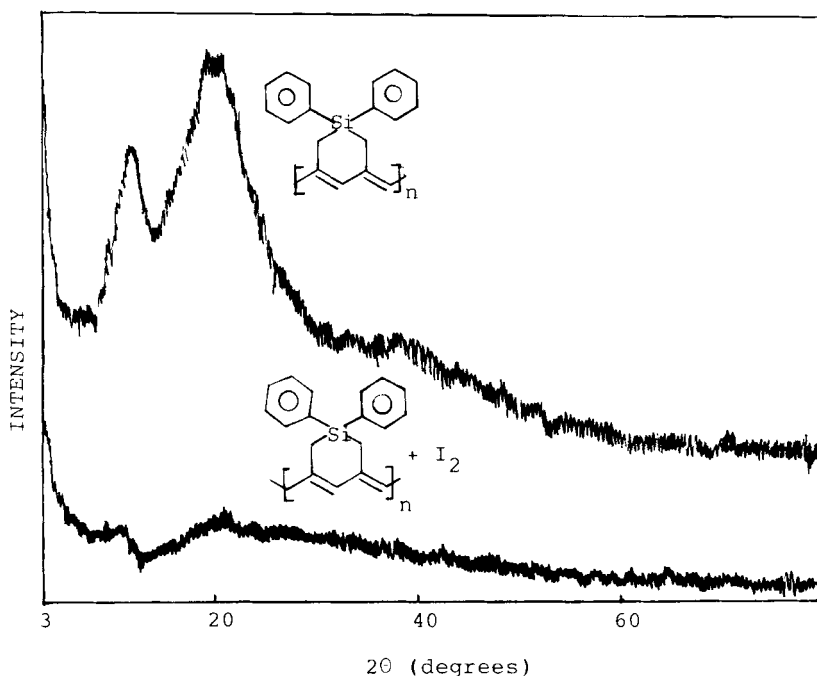


FIG. 4. X-ray diffractograms of poly(diphenyldipropargylsilane) and  $I_2$ -doped poly(diphenyldipropargylsilane).

## EXPERIMENTAL

Methylphenyldipropargylsilane (MPPS) and diphenyldipropargylsilane (DPPS) were synthesized by a reported method [5]. Polymerization was carried out by  $MoCl_5-(n-Bu)_4Sn$  (1:4) in chlorobenzene at  $60^\circ C$  for 24 h. All solvents were purified in the usual manner. Iodine, bromine, and ferric chloride of guaranteed grade were used without purification. Films were prepared by casting solutions of polymers in toluene on Teflon plates and drying them in a nitrogen atmosphere for 24 h. The films were removed from the Teflon plates and further dried under vacuum at room temperature for 12 h.

Iodine-doped films were obtained by placing the film in a vacuum desiccator containing about 10 g of solid iodine in a Petri dish for a given time. Doping with bromine was performed by exposure to bromine in a desiccator at atmospheric pressure. In the case of doping with  $FeCl_3$ , films were immersed in a nitromethane solution of  $FeCl_3$  at room temperature for a given time. The range of  $FeCl_3$  concentration used was 0.25–2.5 M. The films were dried under vacuum. The doping levels were determined by the weight uptake method. Pressed pellets about 2 mm thick were employed for x-ray studies.

### Measurement

Electrical conductivities were measured by the 4-point probe dc method with an HP 3435A Digital Multimeter. The activation energies were determined by using

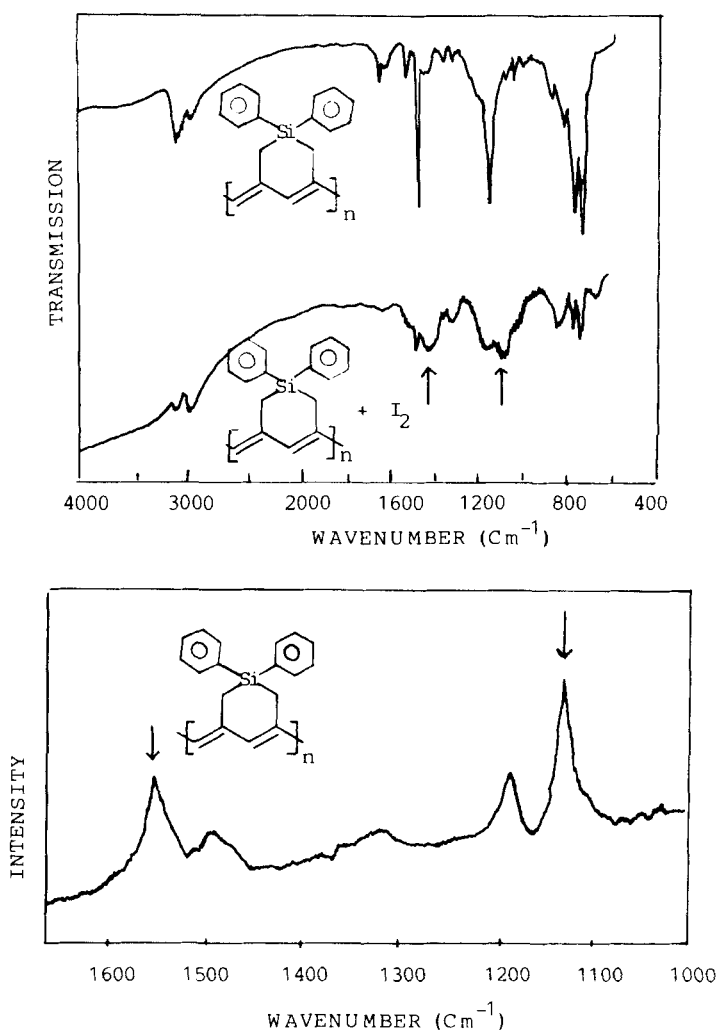


FIG. 5. IR spectra of undoped and iodine-doped poly(diphenyldipropargylsilane) and Raman spectrum of undoped poly(diphenyldipropargylsilane).

a Harrison 6206B dc power, an HP 3490A Multimeter, and a Keithly 616 Digital Electrometer. Constant voltage was applied, and the current was monitored as a function of temperature. Temperature control was achieved with a Delta Design Environmental Oven and monitored with a thermocouple mounted within 1 cm of the sample. Infrared (IR) spectra were recorded using a Perkin-Elmer 283B spectrometer of a potassium bromide pellet. UV-Visible spectra were obtained with a Beckman DU-6 spectrometer. Thermogravimetric analyses (TGA) were performed in a nitrogen atmosphere at a heating rate of 20°C/min with a DuPont 1090 analyzer. Wide-angle x-ray diffractograms were obtained on a Rigaku-Rotaflex. The Raman spectrum was obtained with a 0.85 m Double Spectrometer SPEX with an Ar<sup>+</sup> laser source for 6471 Å excitation and 200 mW laser power. Light scattered from the sample was selected at a 45° angle to the incident light.

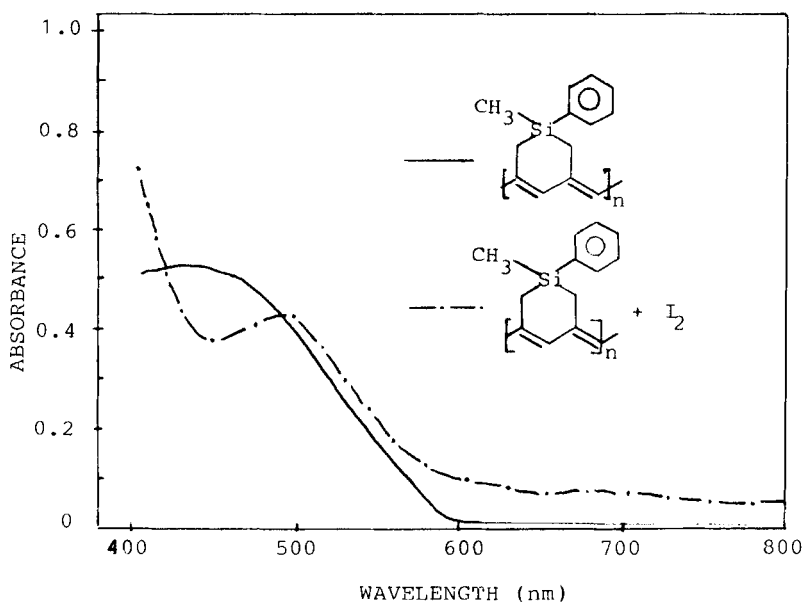


FIG. 6. UV-Visible spectra of undoped and iodine-doped poly(methylphenyldipropargylsilane).

## RESULTS AND DISCUSSION

Figure 1 shows the electrical conductivity of poly(DPPS) and poly(MPPS) films as a function of  $I_2$  doping level. The maximum conductivities of film-type polymers were  $10^{-1}$ – $10^0$  S/cm. It is suggested that the interfibrillar and/or interchange hopping of film-type polymer is more favorable than that of the pellet type ( $10^{-3}$ – $10^{-5}$  S/cm) [5]. As the concentration of dopant is increased, a decrease in conductivity is observed after a maximum conductivity was observed at 35 mol% of  $I_2$  to the repeating unit. This is probably due to the saturation of conjugated double bond and allylic rearrangement by excess dopant, resulting in a loss of conjugation [4].

Table 1 shows the dependence of the conductivity of bromine-doped film on the doping level. Conductivity is noted to depend upon the doping time and the amount of bromine incorporated into the polymer film. The maximum conductivity of bromine-doped film is lower than that of iodine-doped film. It is suggested that bromine is more reactive for the addition of a double bond than is iodine [6].

When the films were immersed into a solution of ferric chloride in nitromethane, an increase in conductivity was also observed. At constant doping time, the conductivity was increased as the concentration of ferric chloride increased up to 1.0 M (Fig. 2). The decrease of conductivity at higher ferric chloride dopant levels is probably due to the addition reaction of chlorine to carbon-carbon double bonds [7].

The activation energy for conduction was determined from the dependence of conductivity on temperature (Fig. 3). It was found that the activation energy for the undoped poly(DPPS) is 14–15 kcal/mol whereas the iodine-doped film of poly(DPPS) has the low value of 4 kcal/mol.



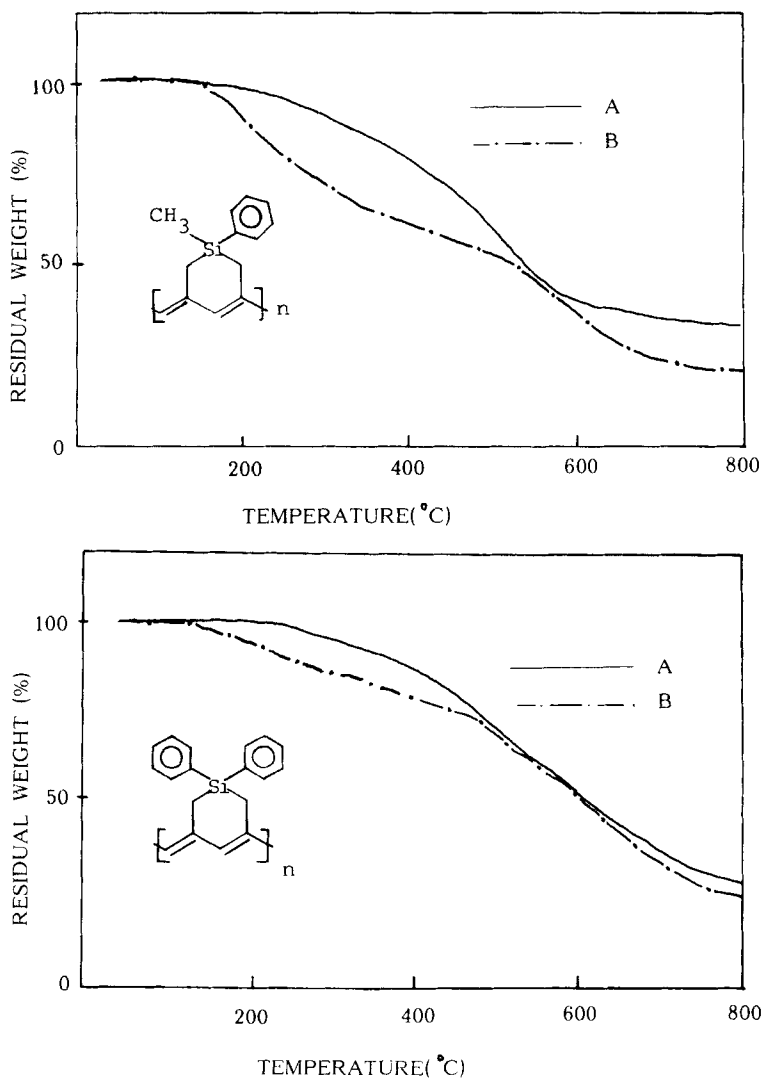


FIG. 7. TGA thermograms of poly(dipropargylsilane derivatives): (A) undoped, (B) doped.

Wide-angle x-ray diffractograms of undoped and iodine-doped poly(DPPS) are compared in Fig. 4. According to the diffractogram, poly(DPPS) has a semicrystalline structure [2]. However, when poly(DPPS) was doped with iodine, it became amorphous. It is believed that the intercalation of a large dopant species between the chains destroys the original molecular order. It is rather well established [8] that  $I_3^-$ , and in a lesser amount  $I_5^-$ , are the primary chemical species formed when polyconjugated polymer is doped with iodine. These ionic species are fairly large and must be able to hinder the polymer from maintaining the original molecular order.

Figure 5 shows the IR spectra of undoped and iodine-doped poly(DPPS) and the Raman spectrum of undoped poly(DPPS). The Raman spectrum of undoped poly(DPPS) shows several broad bands. Among them, the band around  $1150\text{ cm}^{-1}$  is assigned to the C—C stretching mixed with C—H in-plane bending vibration, and the band at  $1550\text{ cm}^{-1}$  is due to the C=C stretching vibration. These bands may be compared to *trans*-PA ( $1050\text{--}1150$ ,  $1450\text{--}1550\text{ cm}^{-1}$ ) [9, 10] and  $\beta$ -carotene ( $1160$ ,  $1520\text{ cm}^{-1}$ ) [11].

Doping also produces two broad bands at  $1400$  and  $1100\text{ cm}^{-1}$  in the IR spectrum. These two IR bands can be related to the two Raman bands at  $1150$  and  $1550\text{ cm}^{-1}$  of undoped poly(DPPS). This bathochromic shift most probably results from the weakened bond resulting when electrons transfer from the polymer chain to the dopant. These two stretching modes, which are inactive in the IR spectrum of the undoped polymer, become active by doping because of their coupling with the charge oscillation in the backbone.

Figure 6 shows the UV-Visible spectra of undoped and iodine-doped poly(MPPS) in 1,2-dichloroethane. In the spectrum of iodine-doped poly(MPPS), while the absorption intensity in the range of  $450\text{--}490\text{ nm}$  decreases, the broad absorption band due to charge transfer appears in the range of  $600\text{--}800\text{ nm}$  [3]. The thermal stability of iodine-doped polymer is lower than that of undoped one, as shown in Fig. 7. It is suggested that the interaction of polymer with dopant is reduced in the high temperature region and the dopant falls out.

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