Syntheses and Properties of π-Conjugated Polymers Containing Chromophore. 1. Water-Soluble Small-Bandgap Polymer Backbone

Hiroyuki Aota,* Takeshi Reikan, Akira Matsumoto, and Mikiharu Kamachi†
Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center, Kansai University, Suita, Osaka 564-80
†Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560

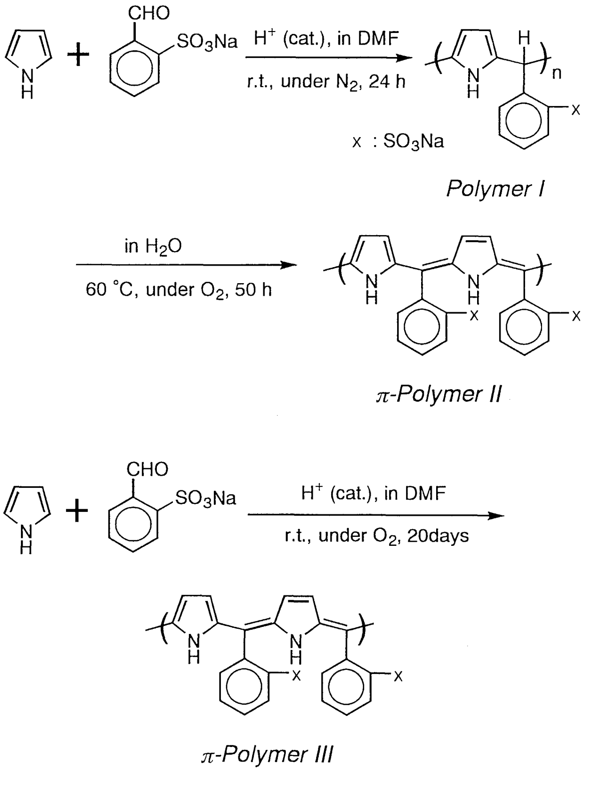
(Received February 14, 1997; CL-970106)

Water-soluble polymers were prepared from pyrrole and sodium *o*-benzaldehydesulfonate by addition-condensation polymerization. The bandgap of the polymer obtained was estimated to be less than 0.5 eV.

It is well known that π-conjugated polymers such as polyacetylene, polypyrrole, and polythiophene have high conductivities only in their doped state. Recently, theoretical[1,2] and experimental[3-6] approaches have been attempted to prepare small-bandgap polymers having high conductivities in their undoped state.

On the other hand, long-range photoinduced electron transfer (ET) and energy transfer (EN) have been studied to achieve efficiently charge separation in several molecular systems where redox centers are connected by "molecular wires" such as polyenes and polyynes.[7-9] Here Osuka et al. [9] reported that both the ET and EN rate constants obeyed exponentially donor-acceptor distance up to 27 Å. Considering the structures of these molecular wires used,[7-9] the energy bandgaps of the wires must be larger than 1.5 eV for undoped polyacetylene.[3] If a molecular wire could have high conductivity like copper, longer-range photoinduced ET and EN would be expected to occur.

Scheme 1.



Recently, we reported the synthesis of π-conjugated polymer containing porphyrins as a chromophore.[10] However, the energy bandgap of the polymer obtained was not small as 2.4 eV, contrary to our expectation because of local π-conjugation. In this letter, we report the syntheses of water-soluble small-bandgap polymers, probably acting as a new type of molecular wire. Preparation routes are shown in Scheme 1.

Addition-condensation polymerizations were conducted as follows: For example, 1.335 g (19.90 mmol) of pyrrole and 0.381 g (2.00 mmol) of *p*-toluenesulfonic acid monohydrate as a catalyst were dissolved in 10 cm^3 of *N,N*-dimethylformamide (DMF) under nitrogen and then, sodium *o*-benzaldehydesulfonate (4.165 g, 20.01 mmol) dissolved in 10 cm^3 of DMF was added. The reaction mixture was stood in the dark with stirring under nitrogen at room temperature for 24 h and then, poured into around 100 cm^3 of ethanol. The resulting precipitate was purified by reprecipitation from water/ethanol three times and dried. Yield; 3.93 g (76.5%). Found: C, 44.19%; H, 3.75%; N, 4.65%. Calcd. for $C_{11}H_8NNaO_3S \cdot 2.2H_2O$: C, 44.50%; H, 4.21%; N, 4.72%. The polymer obtained is denoted as *Polymer I*.

Oxidation was carried out to convert *Polymer I* to π-conjugated polymer as follows: 2.00 g of *Polymer I* was dissolved in 100 cm^3 of water and then, oxidized by bubbling oxygen at 60 °C for 1, 2, 5, 12, 24, and 50 h. The oxidized polymers were recovered by freeze-drying. The π-conjugated polymer obtained after 50 h oxidation is denoted as *π-Polymer II*.

For comparison, the addition-condensation polymerization was run under oxygen instead of nitrogen for 20 days although the other conditions were same to the preparation of *Polymer I*. Found: C, 41.72%; H, 3.55%; N, 4.42%. Calcd. for $C_{11}H_7NNaO_3S \cdot 3.2H_2O$: C, 42.09%; H, 4.30%; N, 4.46%. The polymer obtained is denoted as *π-Polymer III*.

All the polymers obtained are soluble in water, slightly soluble in methanol and DMF, and insoluble in ethanol, acetone, and tetrahydrofuran.

Judging from both reduced viscosity of the polymers obtained and our previous work[10] using 1-dodecanal instead of *o*-benzaldehydesulfonate, the number average molecular weights of the polymers obtained may be between 3000 and 5000: η_{sp}/c (dl/g) at the concentration of 0.40 g/dl in phosphate buffer (pH=6.9) at 30 °C; 0.24 for *Polymer I*; 0.30 for *π-Polymer II*; 0.29 for *π-Polymer III*; and 0.51 for standard sodium polystyrene sulfonate ($\overline{Mn}$=8000: Scientific Polymer Products, INC.).

^{1}H-NMR spectra of the polymers in D_2O were examined in detail; the absorption band of the methine bridge proton of *Polymer I* was clearly observed at 6.2 ppm and its intensity

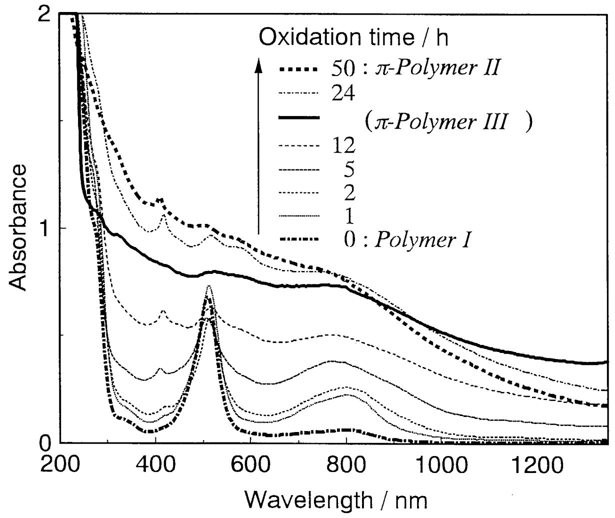


Figure 1. Absorption spectra of phosphate buffer solution of polymers obtained at different oxidation times; [polymer] = 0.10 g / L.

decreased with an increase in the oxidation time, indicating the formation of π-conjugated system.

In order to avoid self-acid-doping, the absorption spectra of the polymers were measured in phosphate buffer (pH 6.9). All spectra are shown in Figure 1. Absorption bands around 500 and 800 nm in *Polymer I* must be due to the locally generated π-conjugated system consisting of two and three pyrrole units, respectively. In fact, about 7% loss of the methine bridge proton of *Polymer I* is estimated from its NMR data. Here it should be noted that dipyrromethene[11] absorbs the visible light around 500 nm. The absorption intensity around 500 nm firstly increased at 1 h, and subsequently decreased at 2 h and then, maintained up to 5 h, while the intensity around 800 nm increased gradually with reaction time. This indicates the formation of the locally generated π-conjugated system; about 70% of the methine proton is present at 5 h.

Over 5 h oxidation, the light absorption occurs in all the region up to 1350 nm, indicating further oxidation leading to the formation of a extended π-conjugated system. However, the absorbance over 800 nm decreases slightly by continuing the oxidation from 24 h to 50 h; this suggests the destruction of the extended π-conjugated system by further oxidation.

On the other hand, the spectrum profile of *π-Polymer III* is broader than that of *π-Polymer II*. In particular over 800 nm, the absorbance is much higher. This means that *π-Polymer III* has more extended π-conjugated system than *π-Polymer II*.

Figure 2 shows the absorption spectra of films of *Polymer I*, *π-Polymer II* , and *π-Polymer III*. Here the values on ordinate indicate reduced absorbances defined as

$$\text{Reduced absorbance} = A_{\text{film}} \times A_{\text{sol, 500}} / A_{\text{film, 500}}$$

where, A_{film}, $A_{\text{sol, 500}}$ and $A_{\text{film, 500}}$ are the absorbances of a polymer film, the phosphate buffer solution of the polymer at 500 nm, and the film at 500 nm, respectively. Under 1.0 eV region, the absorbance of *π-Polymer III* is clearly higher than that of *π-Polymer II*; thus the absorption edge reached 0.5 eV. This indicates that *π-Polymer III* has a fairly extended π-conjugated system and the energy bandgap estimated from the absorption edge is less than 0.5 eV, being lower than theoretical one 1.10 eV.[1] The value below 0.5 eV is the same as the lowest one reported[6] for the different type of π-conjugated polymer.

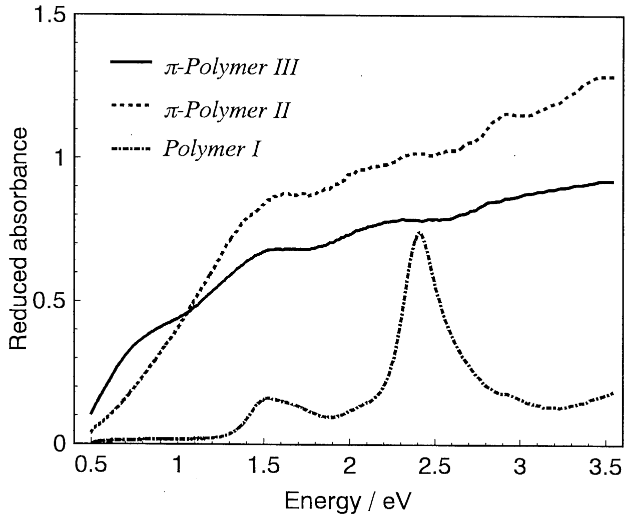


Figure 2. Absoption spectra of film of polymers.

Now we are planning to introduce chromophores such as porphyrin and pyrene into this small-bandgap polymer backbone in order to check the usefulness of our polymers as molecular wires.

This work was partially supported by a Grant-in-Aid for Encouragement of Young Scientists (No.08751034) from the Ministry of Education, Science, Sports, and Culture, Japan, Kansai Research Foundation for technology promotion, and the Asahi Glass Foundation.

References

1 J. M. Toussaint, B. Thémans, J. M. André, and J. L. Brédas, *Synth. Met.*, **28**, C205 (1989).
2 J. M. Toussaint and J. L. Brédas, *Macromolecules*, **26**, 5240 (1993).
3 S. A. Jenekhe, *Nature*, **322**, 345 (1986).
4 T. Kanbara, Y. Aihara, and T. Yamamoto, *Polymer Applications (Kobunshi Kako)*, **40**, 418 (1991).
5 W. -C. Chen and S. A. Jenekhe, *Macromolecules*, **28**, 465 (1995).
6 M. Karikomi, C. Kitamura, S. Tanaka, and Y. Yamashita, *J. Am. Chem. Soc.*, **117**, 6791 (1995).
7 F. Effenberger, H. Schlosser, P. Bäuerle, S. Maier, H. Port, and H. C. Wolf, *Angew. Chem.,Int. Ed. Engl.*, **27**, 281 (1988).
8 H. Imahori, Y. Tanaka, T. Okada, and Y. Sakata, *Chem. Lett.*, **1993**, 1215.
9 A. Osuka, N. Tanabe, S. Kawabata, I. Yamazaki, and Y. Nishimura, *J. Org. Chem.*, **60**, 7177 (1995).
10 H. Aota, Y. Itai, A. Matsumoto, and M. Kamachi, *Chem. Lett.*, **1994**, 2043.
11 A. Gossauer and J. Engel, in "The Porphyrins," ed by D. Dolphin, Academic Press, New York (1978), Vol. II, Chap. 7, p. 222.