Syntheses and Properties of π-Conjugated Polymers Containing Chromophore. 2. Introduction of Porphyrin Units into Main Chain of Water-Soluble Small Band Gap Polymer

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*

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A novel water-soluble small band gap (below 0.5 eV) polymer containing porphyrin units in its main chain was prepared from pyrrole, sodium *o*-benzaldehyde sulfonate and dipyrryletioporphyrin by addition-condensation polymerization.

A number of studies have been done about photoinduced electron transfer (ET) and energy transfer (EN) systems having porphyrin units as a chromophore.[1] In these studies, long-range ET and EN have been investigated to achieve efficiently charge separation in several molecular systems where redox centers are connected by "molecular wires" such as polyenes and polyynes.[1c-e] Here Osuka et al. [1d] reported that both the ET and EN rate constants obeyed exponentially donor-acceptor distance up to 27 Å. However, the band gap of the molecular wire used must be larger than 1.5 eV for undoped polyacetylene.[2a]

If a molecular wire has longer-range π-conjugation and high conductivity, longer-range ET and EN would occur. Experimental[2] and theoretical[3] investigations have been done to prepare small band gap polymers, which have long-range π-conjugation and are expected to have high conductivities in their undoped state, since π-conjugated polymers such as polyacetylene have high conductivities only in their doped states. Therefore, we expect longer-range ET and EN using a small band gap polymer as a molecular wire.

We reported the synthesis of π-conjugated polymer containing porphyrins as a chromophore.[4] However, the energy band gap of the polymer obtained was not small as 2.4 eV, contrary to our expectation because of local π-conjugation. Recently, we synthesized water-soluble small band gap polymers whose energy band gaps were below 0.5 eV.[5]

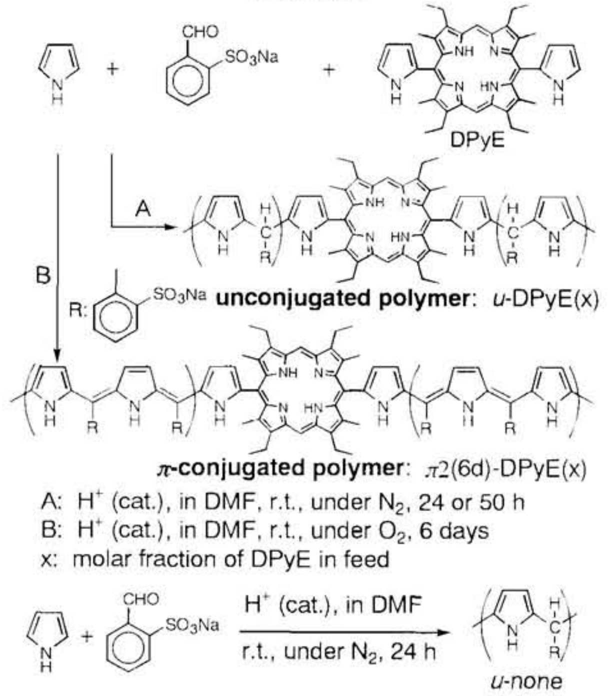
In this paper, we report the introduction of porphyrin units into the main chain of the water-soluble small band gap polymer in order to study the possibility of the long-range ET and EN.

Preparation routes are shown in Scheme 1. Addition-condensation polymerizations were conducted as follows: for example, 0.136 g (2.03 mmol) of pyrrole, 0.122 g (0.200 mmol) of 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,10-dipyrrylporphine (dipyrryletioporphyrin: DPyE[4]), and 0.116 g (0.610 mmol) of *p*-toluenesulfonic acid monohydrate were dissolved in 2.0 cm^3 of *N,N*-dimethylformamide (DMF), where DPyE was soluble in DMF due to protonation. Then, sodium *o*-benzaldehyde sulfonate (0.460 g, 2.21 mmol) dissolved in 2.0 cm^3 of DMF was added and oxygen was bubbled for 40 min. The mixture was allowed to stand in the dark under oxygen atmosphere at room temperature for 6 days and then, poured into around 40 cm^3 of ethanol containing 0.1 g of *p*-toluenesulfonic acid monohydrate to dissolve the unreacted DPyE. The resulting precipitate was washed successively with ethanol containing *p*-toluenesulfonic acid monohydrate, twice with ethanol, and dried (yield: 0.472 g 70%). The polymer thus obtained is abbreviated as π2(6d)-DPyE(1/10).

Other polymers were prepared similarly and abbreviated as shown in Scheme 1.

Figure 1 shows the absorption spectra of polymers and DPyE.

Scheme 1.



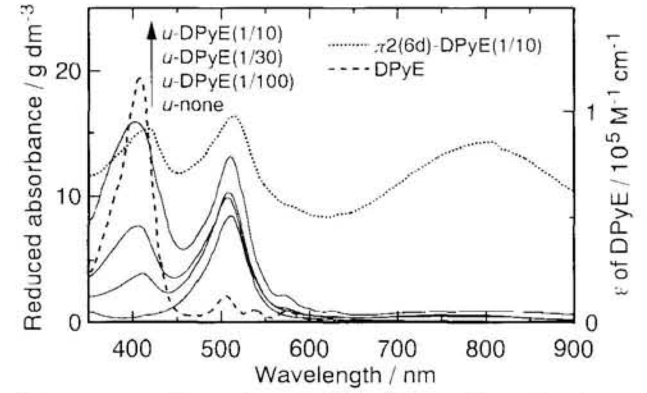


Figure 1. Absorption spectra of unconjugated polymers containing different amounts of porphyrin unit (solid lines), π-conjugated polymer, and DPyE: all polymers and DPyE were dissolved in phosphate buffer solution (pH 6.9) and in DMF, respectively.

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It is noteworthy that all the polymers were dissolved in phosphate buffer (pH 6.9) to avoid self-acid-doping. Here the values on ordinate indicate the reduced absorbances defined as absorbance / [polymer concentration (g/dm^3)].

The absorbances for unconjugated polymers around 400 nm due to Soret band increased with increasing the molar fraction of DPyE in feed, indicating the introduction of porphyrin units into the polymer chain. The contents of DPyE unit in the polymers are estimated by comparing with the molar extinction coefficient of DPyE in DMF: 1/17 for *u*-DPyE(1/10), 1/41 for *u*-DPyE(1/30), and 1/92 for *u*-DPyE(1/100). The content in π2(6d)-DPyE(1/10) may be equal in *u*-DPyE(1/10) because the preparation method was almost the same. Judging from reduced viscosity, the molecular weight of π2(6d)-DPyE(1/10) is about 3000 (degree of polymerization is about 12): η_{sp}/c (dL/g) at the concentration of 0.40 g/dL in phosphate buffer (pH=6.9) at 30 °C were 0.023 for π2(6d)-DPyE(1/10) and 0.035 for standard sodium polystyrene sulfonate (Mn=4950: Scientific Polymer Products, INC.). Thus, 70% of polymer chains are supposed to contain one DPyE unit in π2(6d)-DPyE(1/10).

For π2(6d)-DPyE(1/10), the strong absorption over 600 nm means the formation of π-conjugation and an absorption edge measured for the film sample of this polymer was over 2500 nm. This is the same as our previous work[5] for a small band gap polymer without porphyrin unit. Thus, no breakage of π-conjugation is caused by the introduction of porphyrin units and the energy band gap of this π-conjugated polymer is below 0.5 eV.

Figure 2 shows decay profiles and the first-order plots of the radical generated by visible light irradiation to the polymer solutions. The radical generated in π2(6d)-DPyE(1/10) decayed slower than that in *u*-DPyE(1/10) and the decay obeyed first-order kinetics only for π2(6d)-DPyE(1/10). Accumulations and the first-order decay rate constants (k) of the radical generated by visible or near IR light irradiation are summarized in Table 1. The visible light irradiation excited the polymer backbone and/or DPyE units. On the other hand, near IR light irradiation excited only π-conjugated polymer backbone because of no absorption band of DPyE.

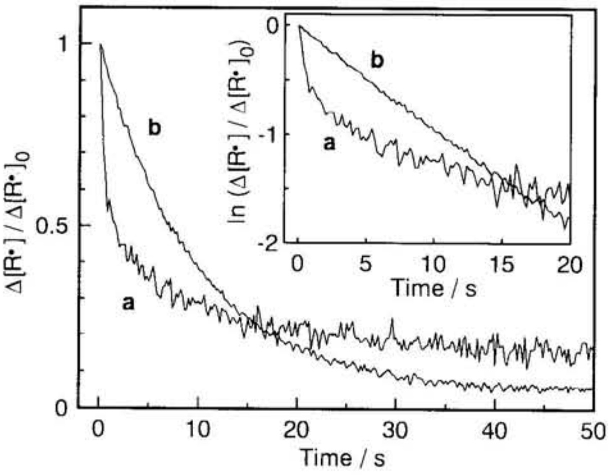

Figure 2. Decay profiles and the first-order plots (insertion) of the radical generated by visible light irradiation: monitored by ESR; **a**, *u*-DPyE(1/10); **b**, π2(6d)-DPyE(1/10).

Table 1. Accumulation and First-order Decay Rate Constant of Radical Generated by Visible or Near IR Light Irradiation[a]

polymer code	Vis.(UV35+IRA25s)[b]		Near IR(R69)[b]	
	Δ[R•]$_0$/M[c,d]	k/s	Δ[R•]$_0$/M[c,d]	k/s
π2(6d)-DPyE(1/10)	1.5×10^{-5}	9.1×10^{-2}	3.4×10^{-5}	9.1×10^{-2}
π2(6d)-none	7.1×10^{-6}	8.1×10^{-2}	1.5×10^{-5}	8.4×10^{-2}
u-DPyE(1/10)	1.7×10^{-5}	4.3×10^{-1} [e]	6.0×10^{-6}	— [f]
u-none	4.7×10^{-6}	— [f]	8×10^{-7}	— [f]

[a] [sample] = 10 g/dm^3 in phosphate buffer; light source : Xenon lamp (Ushio UXL-500D-O). [b] Irradiation was carried out through Toshiba glass filters. [c] Calibrated by TEMPOL(1.0×10^{-5} M) in phosphate buffer. [d] Δ [R•]$_0$ is concentration of radical generated by light irradiation for one minute. [e] Rate constant for fast decay component was estimated up to 2 s after finished irradiation. [f] No significant value is obtained.

The values of k for four π-conjugated polymer systems are almost the same and very small. This suggests that all radicals generated on π-conjugated polymer by excitation of porphyrin unit and/or polymer backbone decay in the same slow process. This long-lived radical may be available to other chemical reactions such as hydrogen generation.

The radical concentration accumulated by visible light irradiation for both the polymers containing DPyE units is almost the same and higher than that for "none" polymers. This shows that porphyrin excitation leads to generate the radical effectively. Fluorescence intensities of polymers containing DPyE units were very small compared with monomeric DPyE. This suggests that the EN and/or ET occur from an excited DPyE unit to the same polymer backbone leading to radical generation.

Now we are planning to introduce both porphyrin and anthraquinone units into one small band gap polymer backbone in order to study the long-range ET and EN.

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