CHEMISTRY LETTERS, pp. 2043-2046, 1994.

Synthesis of Novel π-Conjugated Polymer Containing Porphyrins

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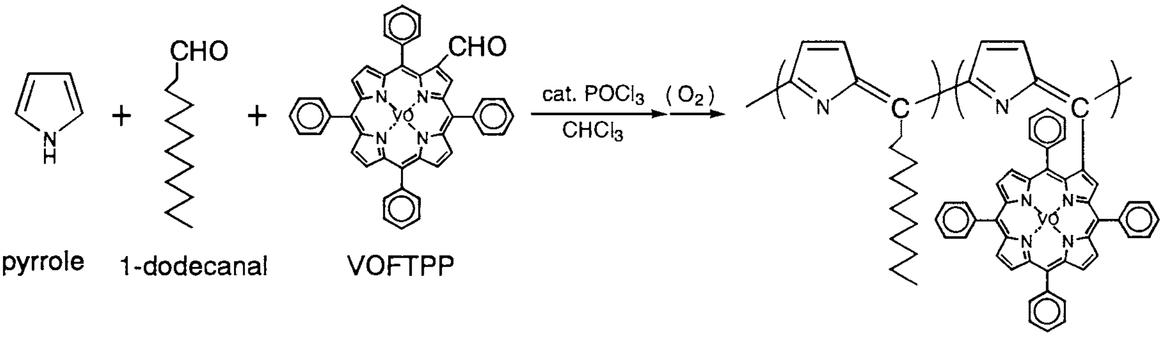
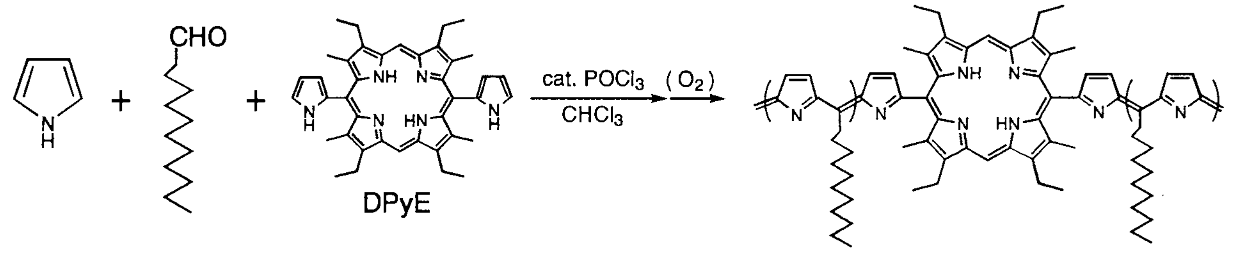
Polymers containing porphyrins were synthesized from pyrrole, 1-dodecanal, and (2-formyl-5,10,15,20-tetraphenylporphyrinato)oxovanadium(IV) or 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,10-dipyrrylporphine. The number-average molecular weights of the resulting polymers were about 3000. NMR and absorption spectral data show the formation of the π-conjugated polymer.

Porphyrin and metalloporphyrin have high functionality and play an important role in living such as photosynthesis, oxygen carrying, and enzyme. On the other hand, many π-conjugated polymers, e.g., polyacetylene and polypyrrole, have been developed as the advanced materials possessing excellent electronic properties. Thus the π-conjugated polymers containing porphyrins as a result of conjugation of both functionalities may exhibit characteristic features such as a photon-harvesting system, a long range charge separation, a multi-electron transfer, and a solar battery.

We planned to prepare the π-conjugated polymers containing some porphyrins as follows: formylporphyrin or dipyrrylporphyrin is added to the condensation reaction of pyrrole with aldehyde. This may be an extension of familiar porphyrin syntheses such as Rothemund reaction(1) and its modified methods,(2,3) since some uncyclized by-products are always concurrently obtained.





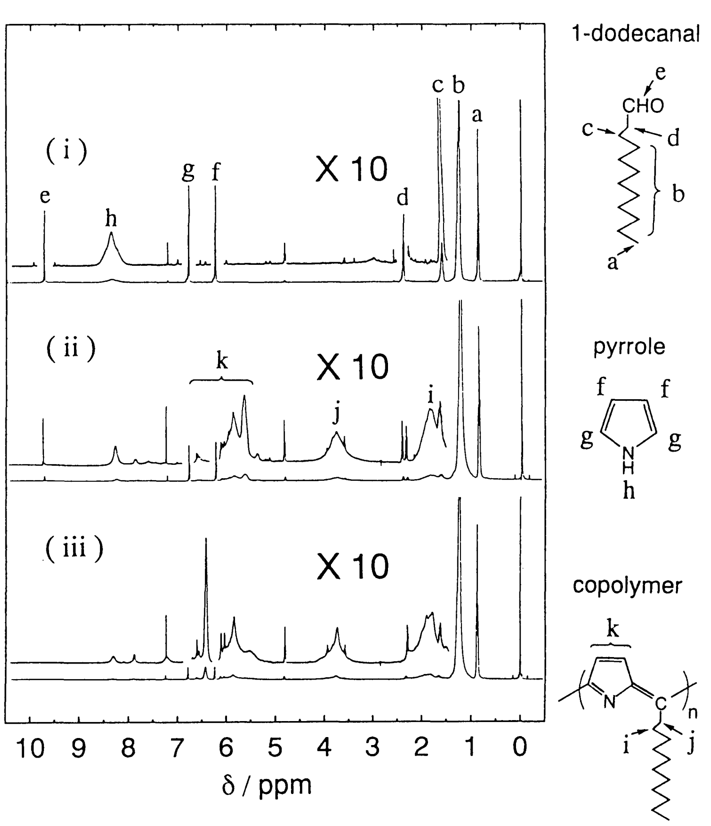


Fig. 1. ^{1}H-NMR spectra of pyrrole-1-dodecanal system at different reaction times: (i) 0 min; (ii) 50 min; (iii) 210 min.

First, we tried to establish the appropriate pyrrole-aldehyde reaction system and conditions by changing reactants, solvents, and catalysts, and thus, we chose 1-dodecanal as an aldehyde portion because the resulting polymer was soluble in tetrahydrofuran (THF).

Figure 1 shows the ^{1}H-NMR spectra of a reaction system at different reaction times, in which the system was composed of 0.2 mmol of pyrrole, 0.2 mmol of 1-dodecanal, 0.02 mmol of phosphoryl chloride, and 0.6 ml of $CDCl_3$. As the reaction proceeded, some characteristic changes were observed as follows: 1) the peaks of the formyl proton at 9.74 ppm and of the pyrrole ones at 6.25, 6.79, and 8.37 ppm decreased, although at 210 min the formyl proton completely disappeared but the pyrrole ones still remained a bit, 2) a new broad absorption band at around 6 ppm corresponding to methylene protons, k, of reacted pyrrole units appeared, 3) the peaks of the methylene protons adjacent and second adjacent to the formyl group were shifted with broadening from 2.40 to 3.78 ppm and 1.61 to 1.82 ppm, respectively, demonstrating the change from carbonyl to CC double bond. These results show that the reaction proceeded through the condensation of 1-dodecanal with pyrrole to form the π-conjugated polymer. Also, the existence of only unreacted pyrrole at 210 min suggests the occurrence of an unequimolar reaction of pyrrole with 1-dodecanal. This may be caused by the reaction at β-position of the pyrrole units in the polymer. We examined the ^{1}H-NMR spectral change of the reaction system with 2-fold molar ratio of 1-dodecanal to pyrrole; as the reaction proceeded the pyrrole protons perfectly disappeared, and concurrently the broad peaks around 6 ppm shifted to 6.5 ppm and gradually decreased, clearly suggesting the reaction even at the β-position of the pyrrole units in the polymer.

Table 1. Molecular weights of resulting copolymers in pyrrole-1-dodecanal systems at various feed molar ratios

$\frac{[\text{1-dodecanal}]}{[\text{pyrrole}]}$	$\overline{\mathrm{Mn}}\mathrm{x}10^{-3}$	$\frac{\overline{\mathrm{Mw}}}{\overline{\mathrm{Mn}}}$
0.7	2.0	1.6
1.0	2.9	16
1.2	5.3	19
2.2	7.5	78

The reaction at the β-position of pyrrole unit leads to a formation of a branched polymer. Polymerizations at different molar ratios of 1-dodecanal to pyrrole were carried out. The molecular weights of the resulting polymers, measured by size exclusion chromatography (SEC) calibrated with standard polystyrenes, are shown in Table 1. Number-average molecular weights gradually increased with increasing the molar ratios, while an increase in polydispersity coefficients, $\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$, was quite steep. Thus, branched polymers were formed in this polymerization as a result of the reaction at the β-position of pyrrole units. Figure 2 shows the absorption spectra of the resulting polymers in THF; these polymers had a broad absorption band with a peak at around 510 nm. This means the presence of π-conjugation in the polymers. Here it should be noted that no formation of porphyrin as a cyclic π-conjugated system occurred because no peak of Soret band at around 420 nm appeared except the 0.7 system.

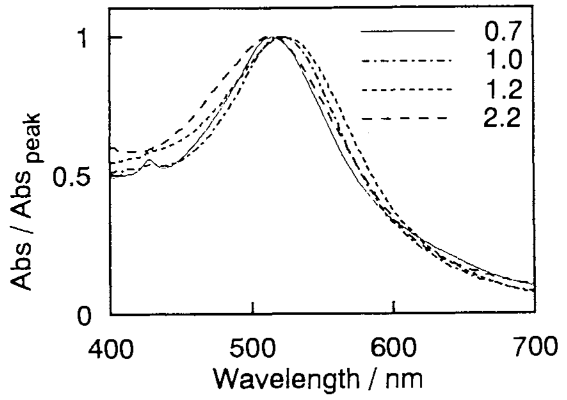


Fig.2. Absorption spectra of THF solutions of resulting polymers; see Table 1.

Second, we tried to incorporate porphyrin units into the π-conjugated polymer chain. (2-Formyl-5,10,15,20-tetraphenylporphyrinato)oxovanadium(IV) (VOFTPP) was synthesized as reported previously.[4] 2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,10-dipyrrylporphine (dipyrryletioporphyrin DPyE) was prepared from 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrymethane with 2-formylpyrrole according to the literature.[5] The polymerization in the presence of VOFTPP was carried out as follows: 0.134 g of pyrrole (2.00 mmol), 0.332 g of 1-dodecanal (1.80 mmol), and 0.141 g of VOFTPP (0.20 mmol) were dissolved in 4 ml of chloroform, and then 0.031 g of phosphoryl chloride (0.20 mmol) was added. The reaction mixture stood in the dark at room temperature for 24 h and then, it was poured to precipitate the polymer into around 100 ml of methanol/water (80/20) mixture. The resulting precipitate was washed three times with methanol and dried (yield: 75 wt%). The polymerizations in the presence of DPyE were performed as follows: for example, 0.122 g of DPyE (0.20 mmol), 0.121 g of pyrrole (1.80 mmol), and 0.076 g of p-toluenesulfonic acid (0.40 mmol) were mixed in 2 ml of chloroform. Successively, 0.369 g of 1-dodecanal (2.00 mmol) in 2 ml of chloroform and 0.028 g of phosphoryl chloride (0.18 mmol) were added. The reaction mixture stood in the dark at room temperature for 24 h and then, it was poured into 100 ml of methanol containing a small amount of p-toluenesulfonic acid which is needed to dissolve the unreacted DPyE. The resulting precipitate was washed three times with methanol and dried (yield: 64 wt%). Polymerization in the absence of porphyrin was conducted similarly in the presence of VOFTPP. These polymers were denoted as VOFTPP-1/10, DPyE-1/10, DPyE-1/50, DPyE-1/100, and copolymer-D, respectively. Here the hyphenated 1/10, 1/50, 1/100, and D correspond to the feed mole fractions of porphyrin units and 1-dodecanal, respectively. The molecular weights of the resulting polymers are summarized in Table 2. The number-average molecular weights were about 3000; thus about 10 monomer units are in a polymer chain. ^{1}H-NMR spectrum of VOFTPP-1/10 in $CDCl_3$ showed a broad band at around 8 ppm due to porphyrin unit. In addition, the absorption due to formyl proton of VOFTPP disappeared in the polymer. The incorporation of VOFTPP unit into the polymer chain was further confirmed by SEC: Figure 3 shows the SEC curves of VOFTPP-1/10 monitored with RI detector and UV detectors at 437 nm (Soret band peak of the monomer VOFTPP), 505 nm (polymer backbone), and 550 nm (Q band peak). All SEC curves showed almost same profiles, thus this polymer containing the porphyrin units in the polymer chain, although a small amount of non-bonded porphyrin was detected at around 56 ml of elution volume.

Table 2. Molecular weights of polymers containing porphyrin units

polymer code	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w / \overline{M}_n$
copolymer-D	2.4	10
VOFTPP-1/10	2.0	1.4
DPyE-1/10	3.5	1.8
DPyE-1/50	3.4	1.7
DPyE-1/100	3.0	1.7

Figure 4 shows the absorption spectra of copolymer-D, VOFTPP-1/10, VOFTPP, and oxo(5,10,15,20-tetraphenylporphyrinato)vanadium (IV) (VOTPP) in THF: spectra for the polymers are represented as reduced absorbance, corresponding to the measured absorbance divided by polymer concentration, and for VOFTPP and VOTPP are as molar extinction coefficient (ε). The content of the VOFTPP unit in the polymer estimated from the absorption intensity was about 8 mol%, thus the polymerizability of VOFTPP being good despite of its bulkiness. Some spectral characteristics are summarized as follows: 1) the peak of Soret band was shifted from 437 nm for the monomer VOFTPP to 417 nm for VOFTPP-1/10, being slightly longer than the peak of VOTPP, 2) the peak intensity ratio of Soret band to Q band for VOFTPP-1/10 is smaller than that for VOTPP, 3) the reduced absorbance for VOFTPP-1/10 is much stronger than that for copolymer-D, and especially, the absorption tailed over 700 nm region in contrast with no absorption for VOTPP. These results show that the π-electron density of the porphyrin ring of VOFTPP-1/10 was higher than that of VOFTPP and slightly lower than that of VOTPP; this is due to the conversion of the formyl group to the polymer backbone accompanied by the formation of π-conjugated system. In addition, some electronic interactions must be present between the porphyrin unit and the π-conjugated backbone.

Detailed studies on structure and physicochemical properties of the polymer are now in progress.

This work was partly supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 05855144) from the Ministry of Education, Science and Culture, Japan.

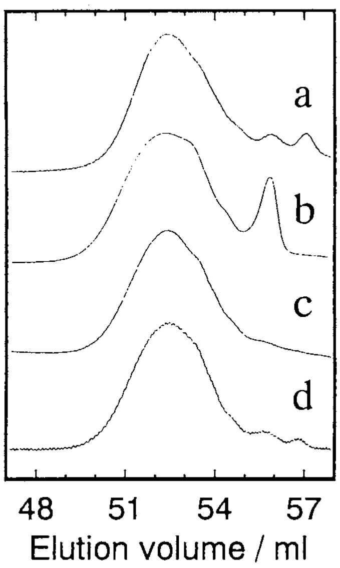


Fig. 3. SEC curves of VOFTPP-1/10 monitored with RI detector (a) and UV detectors at (b) 437, (c) 505, and (d) 550 nm, respectively.

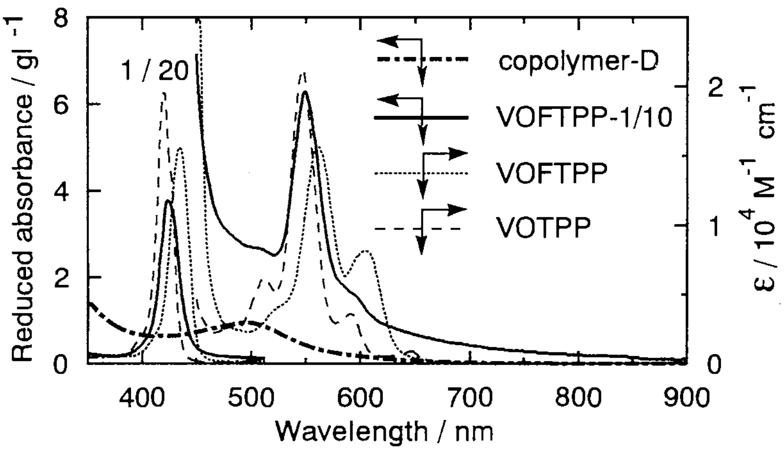


Fig.4. Absorption spectra of copolymer-D, VOFTPP-1/10, VOFTPP, and VOTPP in THF.

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(Received July 13, 1994)