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Preparation of Vinyl Copolymers Bearing Porphyrin or Magnesium Porphyrin Dimers as Pendants

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ABSTRACT: Porphyrin dimers (Por-D*n*; $n = 1$–6) were prepared by binding two *meso*-tetrakis(*p*-carboxyphenyl)porphyrins with $H_2N(CH_2)_nNH_2$ via an amide linkage followed by esterification of the remaining six carboxyl groups per the resulting dimer molecule with five molar equivalents of *p*-methylbenzyl bromide and excess *p*-vinylbenzyl chloride in the presence of triethylamine to afford dimers containing one vinyl group. From the absorptivity and fluorescence intensity in $CHCl_3$ solutions, two porphyrin rings within Por-D1 and Mg Por-D1, prepared in a conventional manner, showed the largest interactions. The dimers thus prepared were subjected to copolymerizations with *N*-vinyl-2-pyrrolidone in DMF at 80 °C for 4 h. Copolymers soluble in aqueous solvents and maintaining the spectral properties of *meso*-porphyrins and Mg *meso*-porphyrins were thus obtained. Such copolymers could also be prepared by using a polymer reaction.

Introduction

There are a lot of publications[1] concerning the preparation of porphyrin and metalloporphyrin dimers, as simulated to the stacking structure of natural chlorophyll.

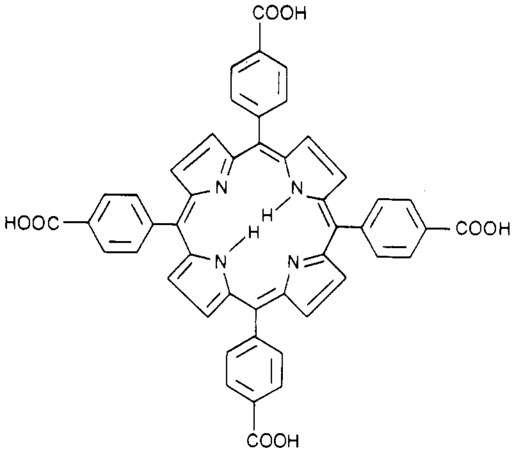
As for the incorporation of these dimers into polymer chains, however, only one report by us was found in the literature,[2] to our knowledge.

In this paper, we wish to report the preparation of vinyl polymers bearing synthetic porphyrin and Mg porphyrin dimers as pendant groups, since the previous publication[2] dealt with the modification of natural porphyrins such as chlorophyll *a* and protoporphyrin IX.

Vinyl polymers soluble in aqueous solvents were prepared by the copolymerization of the porphyrin and Mg porphyrin dimers involving a polymerizable vinyl double bond with *N*-vinyl-2-pyrrolidone (VP). These copolymers were also prepared by means of a polymer reaction.

Both the preparation of these polymers and the synthesis of the corresponding polymerizable dimers by the present procedures represent new research.

The starting compound was *meso*-tetrakis(4-carboxyphenyl)porphyrin, synthesized from pyrrole and 4-formylbenzoic acid[3] as shown below.



porphyrin [Por-(COOH)$_4$]

Thus, a solution of Por-$(COOH)_4$ in anhydrous DMF was treated with an equimolar amount of isobutyl chloroformate (R = isobutyl) in the presence of excess triethylamine to afford a mixed anhydride (**2**), which was then stirred with a $^1/_2$ molar equiv of $H_2N(CH_2)_nNH_2$. The resulting dimer (**3**) was esterified first with 5 molar equiv of *p*-methylbenzyl bromide and then with excess *p*-vinylbenzyl chloride to provide the desired dimer, Por-D*n*.

Experimental Section

Materials. All reagents employed were of the highest purity and used as received, unless otherwise noted. *N,N*-Dimethylformamide (Tokyo Kasei; DMF) was dried over Linde type 4A molecular sieves and distilled under reduced pressure before use. α,α'-Azobis(isobutyronitrile (Tokyo Kasei; AIBN) was purified by reprecipitation of an ethanolic solution into water. Methylenediamine ($n = 1$) was isolated by the addition of the equimolar amount of 1,5-diazabicyclo[5.4.0]undecene-5 (DBU) to a solution of the HCl salt in DMF. Por-$(COOH)_4$ was prepared from pyrrole and 4-formylbenzoic acid in refluxing propionic acid according to the method of Adler and co-workers.[3]

Instrumentation. Visible, IR, and ^1H NMR spectra were recorded on a Hitachi 200-10 and a Hitachi 215 spectrophotometers and a JNM-PMX-60 spectrometer, respectively. Fluorescence spectra were taken on a Hitachi F-1200 fluorescence spectrometer. Elemental analyses were conducted with a Perkin-Elmer 250 instrument. MWs ($\bar{M}_n$) were determined with a Corona 117 vapor pressure osmometer under standard conditions ($CHCl_3$, 5 g/L, 60 °C).

Preparation of Por-D*n*. In a typical example, Por-D2 was synthesized as follows. To a solution of Por-$(COOH)_4$ (1 g, 1.3 mmol) in DMF (150 mL) were added under ice–salt cooling (-5 °C) first triethylamine (TEA; 0.71 mL, 5.1 mmol) and then isobutyl chloroformate (0.17 mL, 1.3 mmol) with exclusion of moisture. The mixture was stirred at -5 °C for 10 min, ethylenediamine (0.042 mL, 0.64 mmol) was added, and the reaction mixture was first stirred at 0 °C for 1 h and then at 25 °C overnight. To the resulting mixture, *p*-methylbenzyl bromide (0.46 mL, 3.2 mmol) was added and the mixture was stirred at 60 °C for 24 h. Excess *p*-vinylbenzyl chloride (CMC; Seibi Chemicals; 0.9 mL, 2.3 mmol) was then added, followed by 72 h stirring at 25 °C. The reaction mixture was poured into ice–water and chloroform extraction was made. The extract was dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator. Crude product was obtained finally by treating the residue with hexane. It was then subjected to silica gel (Wakogel C-300) column chromatography using first $CHCl_3$–acetone and then $CHCl_3$–MeOH, both in 5:1 v/v, as the elution solvent system. From the results of TLC examinations, the second band eluted by $CHCl_3$-MeOH was the desired product. Yield was 5% on the basis of the crude product.

Anal. Calcd for $C_{147}H_{112}N_{10}O_{14}$ (Por-D2): C, 78.75; H, 5.00; N, 6.25. Found: C, 78.92; H, 4.88; N, 6.31. IR (KBr) 1720 (ester); 1650, 1540 (amide); 980, 900 (vinyl) cm^{-1}. NMR ($CDCl_3$ + DMSO-d_6) δ 2.4 (m, 15 H, 5 CH_3), 3.6 (m, 4 H, CH_2CH_2), 5.5 (t, 13 H, $CH_2{=}$ + 6 CH_2), 5.9 (d, 1 H, $CH_2{=}$), 6.8 (q, 1 H, $={CH}$), 7.5 (q, 24 H, Ar H), 8.4 (q, 32 H, Ar H), 8.8 (s, 16 H, pyrrole). λ_{max}^{vis} ($CHCl_3$) 420(2.99 × 10^5 L mol^{-1} cm^{-1}), 515 (0.14), 550 (0.07), 590 (0.05), 645 (0.02) nm. MW ($\bar{M}_n$): Calcd 2242. Found 2730.

Fractions eluted with $CHCl_3$–acetone and the first band by $CHCl_3$–MeOH were all monomeric porphyrins, as judged from their molecular weights. Por-D*n* other than D2 were prepared in the same manner. Their analytical data were also satisfactory. The results are summarized in Table I. The absorption spectrum

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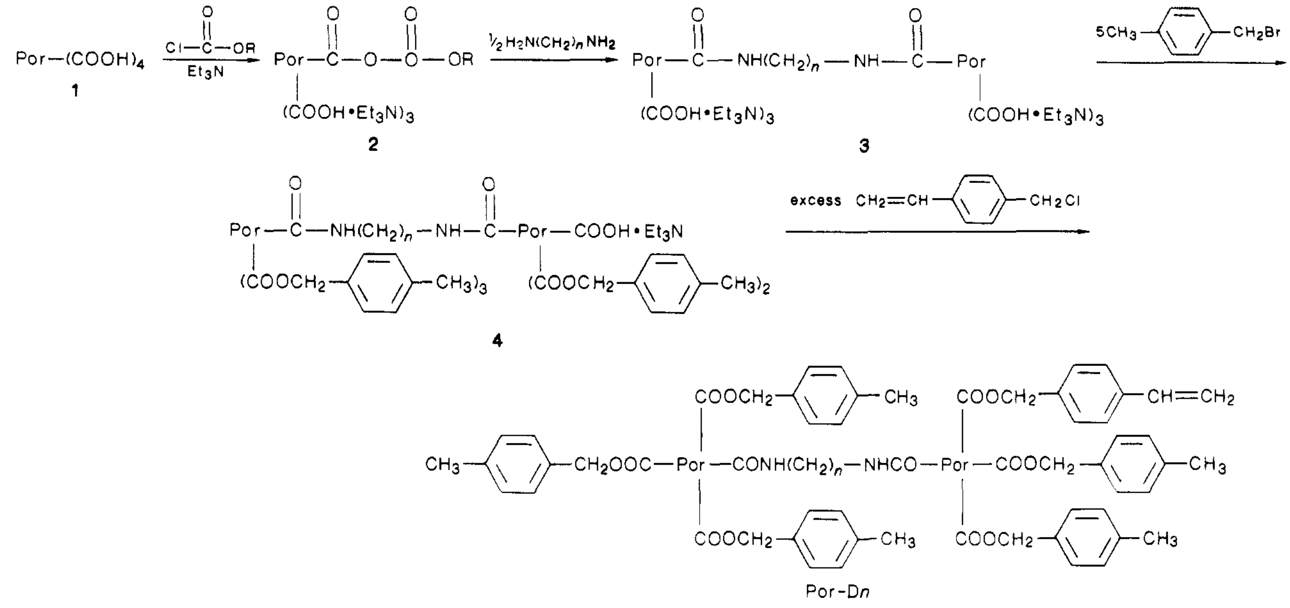


(1)

Table I
Porphyrin Dimers (Por-D*n*) Prepared According to Equation 1

Pro-D*n*	yield, %	$\bar{M}_n$[a]	Soret band (420 nm)[b] absorptivity, ×10^5 L mol^{-1} cm^{-1}	fluoresc peak[c] (656 nm) intensity, ×10^9 L mol^{-1} cm^{-1}
M[d]	19	1235 (1206)	4.06	0.619
D1	9	1970 (2228)	2.72	1.55
D2	5	2730 (2242)	2.99	1.42
D3	13	2577 (2256)	3.38	1.14
D4	12	2514 (2270)	3.52	1.16
D5	11	2278 (2284)	3.60	1.00
D6	12	1808 (2298)	3.65	1.02

[a] Measured by vapor pressure osmometry at 3–4 mg/L concentrations in $CHCl_3$. Figures in parentheses indicate calculated values. [b] Based on porphyrin ring. Measurements were done below 4 mg/L concentrations in $CHCl_3$. [c] Values also on the basis of porphyrin ring were obtained by excitation at 416 nm. Concentrations, below 7 mg/L in $CHCl_3$. [d] Por-tetrakis(*p*-methylbenzyl) ester.

of a typical Por-D*n* in $CHCl_3$ is shown in Figure 1.

Introduction of Mg Atom into Por-D*n*. Essentially, Eschenmoser and co-workers' method[4] was followed.

Thus, in a typical example, Por-D3 (220 mg, 0.1 mmol) was stirred with the reaction product of EtMgI and 3,5-di-*tert*-butyl-4-hydroxytoluene (2.4 g, 11 mmol) in CH_2Cl_2 (50 mL) at 20 °C for 30 min, followed by washing with aqueous NaH_2PO_4 and precipitation into hexane. The crude product was subjected to recrystallization from $CHCl_3$–hexane and subsequent SiO_2 column chromatography using $CHCl_3$–MeOH (5:1 v/v). The second band provided Mg Por-D3 in 28% yield. Mg by elemental analysis was 2.01% (calcd 2.11). IR (KBr) 1720 (ester); 1650, 1540 (amide); 980, 900 (vinyl) cm^{-1}. NMR ($CDCl_3$) δ 2.4 (m, 15 H, 5 CH_3), 3.8 [m, 6 H, $(CH_2)_3$], 5.2–5.9 (m, 14 H, 6 CH_2 + CH_2=), 6.8 (q, 1 H, =CH), 7.5 (q, 24 H, Ar H), 8.4 (m, 32 H, Ar H), 8.8 (s, 16 H, pyrrole). λ_{max}^{vis} ($CHCl_3$) 428 (3.09×10^5), 517 (0.14×10^5), 565 (0.12×10^5), 605 (0.07×10^5), 645 (0.03×10^5) nm.

Table II summarizes the results obtained. An absorption spectrum of Mg Por-D*n* in $CHCl_3$ is also shown in Figure 1.

Mg Por-D*n* other than Mg Por-D3 were prepared in the same manner. Analytical data were all satisfactory.

Preparations of Copolymers of Por-D*n* and Mg Por-D*n* with *N*-Vinyl-2-pyrrolidone and Related Copolymers. A solution of Por-D*n* or Mg Por-D*n* (15 mg), VP (1.0 g), and AIBN (10 mg) in DMF (1 mL) was put into a glass ampule, which was sealed under nitrogen in a conventional manner and let stand at 80 °C for 4 h. The polymer solution thus obtained was dialyzed through a cellulose tubing (Visking) against distilled water for a week. The resulting solution was filtered and the filtrate was freeze dried to provide a purified polymer.

All polymers thus prepared were soluble in water and aqueous MeOH. IR (KBr) of all the polymers indicated a vinyl polymer backbone at 2860 and 2930 cm^{-1}. Figure 2 shows visible absorption spectra of typical polymers of Por-D*n* and Mg Por-D*n* in water. Table III summarizes the copolymerization behaviors with VP for Por-D*n* and Mg Por-D*n*. The amounts of Por-D*n* and Mg Por-D*n* units in copolymers were determined spectroscopically and, for Mg Por-D*n*, these data were in agreement with those calculated from the results of Mg analysis.

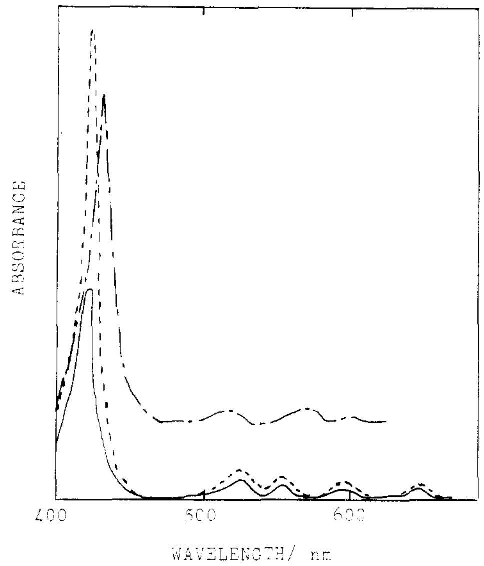


Figure 1. Visible absorption spectra in $CHCl_3$ for typical Por-D*n* and Mg Por-D*n*. (—) Por-D1; (– – –) Mg Por-D1; (- - -) Por-tetrakis(*p*-methylbenzyl) ester. Concentration, 3 mg/L. An arbitary scale was adopted for the ordinate to make comparison easy.

Table II
Introduction of Mg Atom into Por-D*n*

Mg Por-D*n*	Soret band (428 nm)[a] absorptivity, ×10^5 L mol^{-1} cm^{-1}	fluoresc peak[b] (617 nm) intensity, ×10^9 L mol^{-1} cm^{-1}
Mg M[c]	3.48	1.27
Mg D1	2.31	1.62
Mg D2	2.66	
Mg D3	3.09	1.28
Mg D4	3.13	
Mg D6	3.30	1.21

[a] Based on porphyrin ring. [b] Also based on porphyrin ring. Excitation wavelength, 424 nm. Both absorptivity and fluorescence were measured at the same concentration ranges as those in Table I. [c] Mg por-tetrakis(*p*-methylbenzyl) ester.

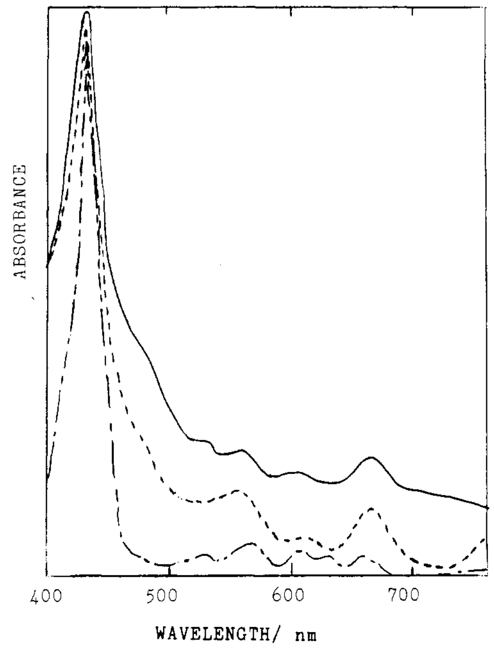


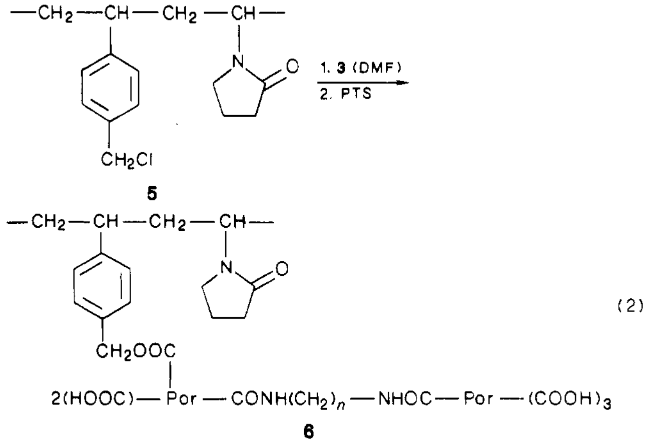
Figure 2. Visible absorption spectra in water for typical copolymers of Por-D*n* and Mg Por-D*n* with VP. (—) Copolymer of Por-D1 in Table III (- - -) copolymer of Mg Por-D1 in Table III; (-··-) copolymer of Por-tetrakis(*p*-methylbenzyl) ester in Table III. Concentration, 0.5 g/L. An arbitary scale was adopted also for the ordinate.

Table III
Copolymerization of Por-D*n* or Mg Por-D*n* with *N*-Vinyl-2-pyrrolidone (VP)[a]

		polymer	
Por or Mg Por	conversn, %	Por or Mg Por/polymer, %[b]	[η], dL/g[c]
M[d]	48	0.452	0.22
D1	46	0.472	0.20
D2	47	0.688	0.23
D3	41	0.427	0.22
D4	53	0.562	0.22
D5	52	0.511	0.21
D6	40	0.522	0.23
Mg M[e]	61	0.885	0.25
Mg D1	55	0.576	0.36
Mg D2	62	0.865	0.38
Mg D3	66	0.623	0.44
Mg D4	63	0.588	0.38
Mg D6	55	0.598	0.19

[a] Por or Mg Por, 15 mg; VP, 1 g; AIBN, 10 mg; DMF, 1 mL. 80 °C for 4 h. [b] Determined comparing the absorbance (Soret band) of polymer with that of the corresponding Por or Mg Por in $CHCl_3$. [c] For aqueous solution at 25 °C. [d] Por-tetrakis(*p*-methylbenzyl) ester. [e] Mg Por-tetrakis(*p*-methylbenzyl) ester.

Alternatively, related copolymers were prepared by using a polymer reaction. In a typical example, a solution of *p*-vinylbenzyl chloride (CMS; 0.1 g, 0.65 mmol), VP (2.0 g, 18 mmol), and AIBN (0.1 g) in DMF (6 mL) was heated in a sealed tube under nitrogen, prepared in a conventional manner, at 50 °C for 72 h. The resulting copolymer (**5**) was isolated by precipitation into ether in 96% conversion. Elemental analyses showed that the CMS/VP ratio in the copolymer and that in the monomer mixture were almost identical. Intrinsic viscosity [η] in DMF at 25 °C was 0.57 dL/g. A solution of **5** (1.0 g, 0.3 mmol as CMS) and porphyrin dimer **3** (n = 2; 0.5 g, 0.25 mmol) in DMF (10 mL) was then stirred at 50 °C for 48 h under a nitrogen stream. The reaction mixture was acidified with addition of *p*-toluenesulfonic acid (PTS) to isolate the COOH group, dialyzed against water as above, and freeze-dried to afford copolymer **6** (n = 2) in 94% yield. The content of porphyrin dimer in copolymer as determined spectroscopically was 1.4 mol % (47% on the basis of the porphyrin dimer **3** employed).



(2)

Results and Discussion

Por-D*n* Synthesis. Por-D*n* was synthesized starting with Por-$(COOH)_4$ without isolated intermediate products. Thus, Por-$(COOH)_4$ in DMF solution was first converted to mixed anhydride **2** and dimerized with the addition of $^1/_2$ molar equiv of $H_2N(CH_2)_nNH_2$ via an amide linkage in the presence of triethylamine (TEA). Then, five out of six COO^- groups of the resulting dimer **3** were esterified with equivalent *p*-methylbenzyl bromide, and then the remaining COO^- group was further esterified with excess CMS to provide a dimer bearing a vinyl group (Por-D*n*). The crude product thus isolated was subjected to silica gel column chromatography. Separation was good and satisfactory analytical data were obtained. Por-D*n* thus prepared provided single spot by TLC.

Introduction of Mg Atom into Por-D*n*. A conventional procedure[4] was followed and the introduction of Mg atom into Por-D*n* was confirmed by both Mg analysis and the bathochromic shifts of the visible absorption maxima of the purified products in $CHCl_3$ solutions.

Visible Absorption Spectra and Fluorescence. The visible absorption spectra in Figure 1 coincide with those for typical *meso*-porphyrins and Mg porphyrins[5] and demonstrate that porphyrin and Mg porphyrin moieties in dimer molecules were kept intact throughout this synthetic procedure series. Moreover, it is clear from Tables I and II that the absorptivity (Soret band, 420 and 428 nm) and maximum fluorescence intensity (656 and 617 nm) for Por-D*n* and Mg Por-D*n* are dependent upon the chain length linking two porphyrin or Mg porphyrin rings. Thus, as regards the absorptivity per porphyrin moiety, hypochromism[6] having the minimum values for D1, i.e., n = 1, was observed, indicating that porphyrin ring–ring interactions within a dimer molecule exist and are the largest in the cases of both Por-D1 and Mg Por-D1. No appreciable shifts of visible absorption maxima were observed. The relationships described above were observed also for absorption maxima other than Soret band.

The same tendency was recognized for fluorescence intensity also per porphyrin moiety, with the maximum values in the case of D1. Therefore, it is concluded that porphyrin ring–ring interactions within a dimer molecule in a $CHCl_3$ solution are the largest in the case of D1 for both Por-D*n* and Mg Por-D*n*.

Preparations of Copolymers of Por-D*n* and Mg Por-D*n* with VP and Related Copolymers. Since the ring–ring interactions were recognized within the dimers prepared above, the goal of our research has been to prepare polymers bearing the intact Por-D*n* and Mg Por-D*n* units as pendant groups and soluble in aqueous solvents.

Although values of both conversion and intrinsic viscosity for copolymers in Table III are not large, higher temperatures and longer polymerization times than 80 °C and 4 h, respectively, cause the deterioration of the porphyrin and Mg porphyrin moiety in the polymer, as judged from visible absorption spectrum. Values of percent porphyrin or Mg porphyrin moiety in polymer, as determined from absorptivity in $CHCl_3$, were much lower than that (1.5) in the initial vinyl monomer combination, indicating rather poor copolymerizability of Por-D*n* or Mg Por-D*n*. However, since the polymer solutions in DMF were dialyzed against water and the resulting water-insoluble portions (remaining Por-D*n* or Mg Por-D*n* and others) were removed by filtration, the purified polymers contained only copolymerized Por-D*n* or Mg Por-D*n*, which were solubilized in water as a result of copolymerization.

An alternative method consisting of a polymer reaction between copolymer **5** and porphyrin dimer **3** also provided copolymers similar to those by copolymerization (eq 2). The introduction of Mg atom into copolymer **6** could be carried out as in the corresponding Por-D*n*.

The Property of Copolymers. Copolymers of VP with about 1 mol % or less of Por-D*n*, Mg Por-D*n*, and related polymerizable porphyrin dimers were soluble in either water or aqueous organic solvents and are ready for the investigation of their redox functions in aqueous solutions, although the number of porphyrin dimer units per polymer chain could not be determined. VP as comonomer component was selected first for obtaining copolymers soluble in aqueous media and second for activating anionic reactants such as Fast Red A[1] in a function similar to polar aprotic solvents such as *N*-methyl-2-pyrrolidone.[7]

Considering the use of porphyrin and metalloporphyrin dimers, especially as photocatalysts, it may be advisable to bind these functional compound systems to a polymer molecular chain, from the standpoints of easy regulation of structure, solubility, readiness of separation of the catalyst from products, etc.

The results of the functions of these copolymers as photocatalysts, as simulated to photosynthesis in nature, are promising and shall constitute the object of another article.

Registry No. 1, 14609-54-2; Por-D1, 119111-77-2; Por–D2, 119111-83-0; Por–D3, 119111-78-3; Por–D4, 119111-79-4; Por–D5, 119111-80-7; Por–D6, 119111-81-8; Mg Por-D1, 119145-94-7; Mg Por-D2, 119145-96-9; Mg Por-D3, 119145-92-5; Mg Por-D4, 119145-88-9; Mg Por-D6, 119145-93-6; Por-D1/VP (copolymer), 119111-82-9; Por-D2/VP (copolymer), 119111-84-1; Por-D3/VP (copolymer), 119111-85-2; Por-D4/VP (copolymer), 119111-86-3; Por-D5/VP (copolymer), 119111-87-4; Por-D6/VP (copolymer), 119111-88-5; Mg Por-D1/VP (copolymer), 119145-95-8; Mg Por-D1/VP (copolymer), 119145-97-0; Mg Por-D3/VP (copolymer), 119182-72-8; Mg Por-D4/VP (copolymer), 119145-89-0; Mg Por-D6/VP (copolymer), 119145-98-1; VP, 88-12-0; $NH_2CH_2NH_2$, 2372-88-5; $NH_2(CH_2)_2NH_2$, 107-15-3; $NH_2(CH_2)_3NH_2$, 109-76-2; $NH_2(CH_2)_4NH_2$, 110-60-1; $NH_2(CH_2)_5NH_2$, 462-94-2; $NH_2(CH_2)_6NH_2$, 124-09-4; *p*-$MeC_6H_4CH_2Br$, 104-81-4; *p*-$CH_2{=}CHC_6H_4CH_2Cl$, 1592-20-7.

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Synthesis of Syndiotactic Poly-1,2-(4-methyl-1,3-pentadiene)

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ABSTRACT: A homogeneous catalyst which promotes syndiotactic polymerization of styrene has been tested in the polymerization of 1,3-butadiene, isoprene, and 4-methyl-1,3-pentadiene. The first two monomers afford essentially 1,4 cis polymers; from the last monomer the 1,2 syndiotactic polymer is obtained. Catalytic hydrogenation of syndiotactic poly-1,2-(4-methyl-1,3-pentadiene) affords crystalline poly(4-methyl-1-pentene) melting at 186 °C.

Several homogeneous catalytic systems, consisting of titanium or zirconium compounds and methylalumoxane, promote syndiotactic specific polymerization of styrene and substituted styrenes.[1-3] As reported in a previous paper by our laboratory,[4] the same catalytic systems can also promote partially isotactic specific polymerization of propene. However, it has been observed that the organometallic species promoting syndiotactic polymerization of styrene are probably unrelated to those coexisting in the catalytic system, which promote isotactic polymerization of propene.[4-6]

Considering the conjugation of the vinyl group of aromatic monomers in comparison with α-olefins, the next obvious step was to test polymerization of conjugated diolefins, in the presence of a typical catalyst for syndiotactic polymerization of styrene, e.g., tetrabenzyltitanium (IV)/methylalumoxane ($Ti(bz)_4$/MAO). We have polymerized 1,3-butadiene, isoprene, and 4-methyl-1,3-pentadiene in the presence of this catalyst. Polymerizations have been performed, as described in the Experimental Section, under conditions very similar to those usually used for styrene polymerization, excepting we used a milder temperature, which was lowered in order to minimize any chance of cross-linking.

All the diolefins tested gave some polymer, and in Figure 1 are reported the ^{13}C NMR spectra of the three polymers. Comparison of the spectrum of poly(1,3-butadiene) (Figure 1A) with the spectra reported in the literature[7] shows that