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Vinyl Polymers Bearing a Pyrrole Ring. II. 5,10,15,20-Tetraphenylporphyrins with a Substituent-Bearing Vinyl Group at the Pyrrole Residue and Their Zinc Complexes

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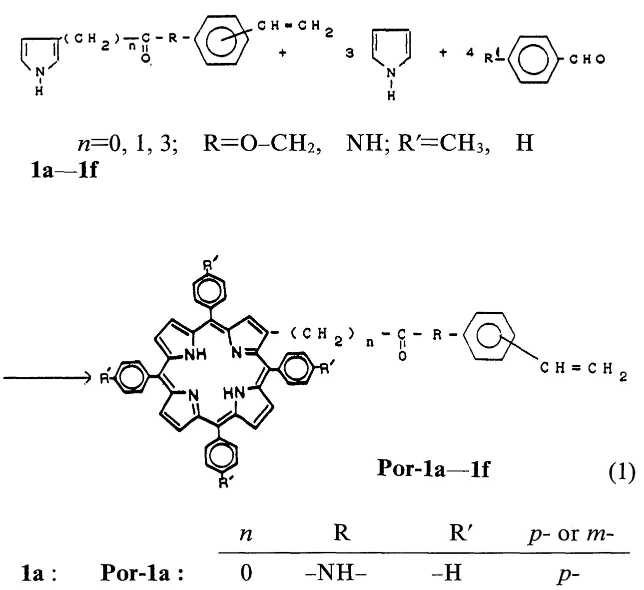
Synopsis. 5, 10, 15, 20-Tetraphenylporphyrins (**Por**) with a styrenic double bond-bearing substituent attached at the pyrrole residue with an amide or ester spacer were synthesized starting with 3-substituted pyrroles. Free radical copolymerization of **ZnPor**, prepared from **Por**, with 1-vinyl-2-pyrrolidone gave more favorable results than did **Por**.

Numerous studies on the preparation of polymers bearing porphyrin or metalloporphyrin units have been reported.1–5) The present note discusses the preparation of novel water-soluble vinyl polymers with pendant porphyrin and zinc porphyrin units. 5, 10, 15, 20-tetraphenylporphyrins with a substituent-bearing vinyl group (**Por**) attached at the pyrrole residue and their zinc complexes (**ZnPor**) were synthesized. Subsequent copolymerizations of these vinyl monomers with 1-vinyl-2-pyrrolidone (VP) produced copolymers soluble in aqueous solvents. For the **Por** monomer synthesis, 3-substituted pyrroles, synthesized as in a previous study,6) were employed as starting materials, as shown in **Methods A** and **B**.

Method A

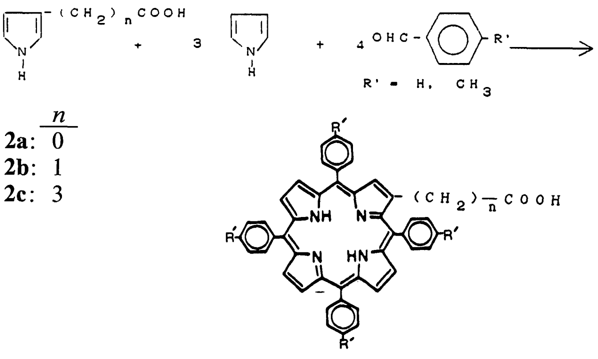


n=0, 1, 3; R=O-CH$_2$, NH; R′=CH$_3$, H
1a—**1f**

Por-1a—**1f** (1)

		n	R	R′	*p*- or *m*-
1a :	**Por-1a** :	0	-NH-	-H	*p*-
1a′:	**Por-1a′**:	0	-NH-	-H	*m*-
1b :	**Por-1b** :	1	-NH-	-H	*p*-
1b′:	**Por-1b′**:	1	-NH-	-H	*m*-
1c :	**Por-1c** :	3	-NH-	-H	*p*-
1c′:	**Por-1c′**:	3	-NH-	-H	*m*-
1d :	**Por-1d** :	0	-OCH$_2$-	-CH$_3$	*p*-
1e :	**Por-1e** :	1	-OCH$_2$-	-CH$_3$	*p*-
1f :	**Por-1f** :	3	-OCH$_2$-	-CH$_3$	*p*-

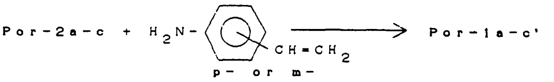
Method B



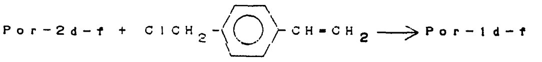
	n
2a:	0
2b:	1
2c:	3

	n	R′
Por-2a:	0	-H
Por-2b:	1	
Por-2c:	3	
Por-2d:	0	-CH$_3$
Por-2e:	1	
Por-2f:	3	

(2)



(3)



(4)

Results and Discussion

Method A consisted of the application of a conventional procedure7) for the preparation of 5, 10, 15, 20-tetraphenylporphyrins from **1a**—**f**, and easily produced the desired products, **Por-1a**—**f** (Eq. 1), which were purified by silica-gel column chromatography.

In **Method B**, carboxyl group-bearing **Por-2a**—**f** were first synthesized using **2a**—**c** (Eq. 2) and then converted to **Por-1a**—**c**, **Por-1a′**—**c′**, and **Por-1d**—**f** with *p*- and *m*-anilines and *p*-vinylbenzyl chloride, respectively, also without any difficulty (Eqs. 3 and 4).

An advantage of **Method B**, compared to **Method A**, was that **Por-2a**—**f** could be separated easily from the byproduct porphyrins bearing no COOH group. Addition of triethylamine (TEA) to the benzene solutions of the crude products neutralized the COOH group and precipitated the resulting salts, thereby facilitaing the purification of the final products **Por-1a**—**f**. The analytical data for the **Por-1a**—**f** synthesized according to **Method B** are given in Table 1. The absorption spectra of **Por-1a**—**f** in chloroform indicated the Soret

Table 1. Analytical Results for **Por-1a**—**f**[a)]

Por	Yield	Element. analysis[b)]			IR[c)]	NMR[d)]
	%	C %	H %	N %	cm^{-1}	δ
1a	21	83.22 (83.79)	4.83 (4.87)	9.19 (9.22)	1650 (Amide), 990, 900 (Vinyl)	5.5 (q), 6.7 (q) (vinyl); 8.9 (s, por.)
1a′	39	83.34 (83.79)	5.06 (4.87)	9.25 (9.22)	1660 (Amide), 990, 900 (Vinyl)	5.6 (q), 6.5 (q) (vinyl); 8.9 (s, por.)
1b	11	83.51 (83.83)	5.12 (5.05)	9.16 (9.06)	1650 (Amide), 990, 910 (Vinyl)	3.4 (s, CH_2); 5.5 (q), 6.7 (q) (vinyl); 9.0 (s, por.)
1b′	32	83.81 (83.83)	4.96 (5.05)	9.35 (9.06)	1660 (Amide), 990, 910 (Vinyl)	3.4 (s, CH_2); 5.4 (q), 6.7 (q) (vinyl); 8.9 (s, por.)
1c	33	83.65 (83.90)	5.44 (5.37)	8.92 (8.74)	1640 (Amide), 990, 900 (Vinyl)	1.0—3.5 (m, CH_{22}); 5.4 (q), 6.7 (q) (vinyl); 8.9 (s, por.)
1c′	28	83.68 (83.90)	5.49 (5.37)	8.35 (8.74)	1650 (Amide), 990, 900 (Vinyl)	1.0—3.5 (m, CH_2); 5.5 (q), 6.8 (q) (vinyl); 8.8 (s, por.)
1d	47	83.40 (83.61)	4.92 (5.03)	7.00 (7.23)	1740 (Ester), 990, 910 (Vinyl)	5.3 (s, CH_2); 5.5 (q), 6.8 (q) (vinyl); 8.9 (s, por.)
1e	44	83.24 (83.65)	5.48 (5.20)	7.08 (7.10)	1740 (Ester), 980, 900 (Vinyl)	3.5 (s, CH_2); 5.3 (s, CH_2); 5.5 (q), 6.6 (q) (vinyl); 8.9 (s, por.)
1f	51	83.51 (83.72)	5.43 (5.51)	7.03 (6.85)	1740 (Ester), 990, 910 (Vinyl)	1.0—3.5 (m, CH_2); 5.1 (s, CH_2); 5.5 (q), 6.7 (q) (vinyl); 8.9 (s, por.)

a) Prepared according to Method B. b) Figures in parentheses indicate calcd values. c) KBr. d) $CDCl_3$; por.=porphyrin ring.

Table 2. Copolymerization Behavior of **Por** and **ZnPor** with VP[a)]

Por or **ZnPor**	Conversion	Polymer		
	%	Soret band nm	Content of **Por** or[b)] **ZnPor**/%	$[\eta]$[c)]
Por-1a	26	424.0	3.1	0.12
Por-1a′	31	420.5	0.4	0.09
Por-1b	25	423.0	3.0	0.12
Por-1b′	33	418.5	0.8	0.09
Por-1c	20	418.0	3.5	0.09
Por-1c′	29	419.0	0.6	0.09
ZnPor-1c	84	420.0	13.4	0.23
ZnPor-1c′	67	420.0	15.8	0.27

a) **Por** or **ZnPor**, 0.1 mmol; VP, 5.0 mmol; AIBN, 2%/total monomers; 20% total monomers concentration in DMF; at 80 °C for 4 h under N_2. b) Determined spectrophotometrically employing the Soret band. c) Intrinsic viscosity (dLg^{-1}) in DMF at 25 °C.

band at 418.5—421 nm and had several longer λ_{max} with decreasing, ε_{max}, which was characteristic of a porphyrin structure. The introduction of a Zn atom caused the reversal of the order of λ_{max} around 515 and 550 nm together with slight red λ_{max}-shifts [e. g. λ_{max} (ε_{max}): 515.0 (2.50×10^4 mol^{-1} dm^3 cm^{-1})) and 549.5 (1.09) for **Por-1c**; 517.5 (1.71) and 552.5 (2.13) for **ZnPor-1c**].

The results obtained by subjecting **Por-1a**—**c′** and **ZnPor-1c,c′** to conventional free-radical copolymerization with VP are summarized in Table 2. As Table 2 shows, copolymerization of **Por-1a**—**c′** without Zn gave poor results; both the conversions and the values of the intrinsic viscosity of the polymer were low and **Por**-contents in the polymer were also much lower than those (>10%) in the initial monomer mixture.

IR-spectra indicated, however, that the vinyl absorptions around 990—980 and 910—900 cm^{-1} (Table 1) no longer existed and a strong C=O absorption around 1650 cm^{-1} (attributable to the VP portion) appeared, indicating that water-soluble polymers of low molecular weights were obtained by this procedure.

ZnPor-1c and **-1c′** gave, on the other hand, larger values of conversion, **ZnPor**-content, and intrinsic viscosity, indicating a satisfactory process of copolymerization. Particularly, the values of the **ZnPor**-content in the copolymer were close to that (13.5%) in the initial monomer mixture. Visible absorption spectra for polymers made from **Por-1a**—**c′** were somewhat deformed, whereas those for polymers made from **ZnPor-1c** and **-1c′** indicated no signs of deformity. From these observations, especially as regards **Por-1a**—**c′**, we suppose that the porphyin ring may participate in free-radical polymerization. The applications of these polymers, e. g. as redox catalysts, will be the subject of another study.

Experimental

N-[*p*- and *m*-Vinylphenyl)-1*H*-pyrrole-3-carboxamides (**1a**,**a′**), -3-acetamides (**1b**,**b′**), and -3-butyramides (**1c**,**c′**), and *p*-vinylbenzyl 1*H*-pyrrole-3-carboxylate (**1d**), -3-acetate (**1e**), and -3-butyrate (**1f**) were synthesized via the respective carboxylic acids (**2a**—**c**) according to the methods described in a previous study.[6]

5,10,15,20-Tetraphenylporphyrins (Por-1a—f). Method A: Pyrroles bearing the vinylphenyl group [**1a**—**f** (2 mmol)], pyrrole (0.40 g, 6 mmol), and benzaldehyde or *p*-tolualdehyde (8 mmol) were dissolved in propionic acid (5 mL). The resulting solution was added to refluxing propionic acid (50 mL), followed by further refluxing for 30 min, with hydroquinone (0.1 g) added. Upon standing at room temperature overnight, the resulting crystals were washed thoroughly with hot water and subjected to silica-gel column chromatography.

Method B: Pyrroles bearing a carboxyl group [**2a**—**c** (5 mmol)], pyrrole (1.0 g, 15 mmol), and benzaldehyde or *p*-tolualdehyde (20 mmol) were refluxed in propionic acid (50 mL) for 30 min, as in **Method A**. Upon cooling, the resulting crystals were dissolved in benzene (50 mL). TEA (10 mL) was added to the benzene solution to precipitate out the TEA-salts of **Por-2a**—**f**, which were washed thoroughly with benzene. Methyl chloroformate (0.2 g, 2 mmol) was added with vigorous shaking to a solution of the salt (2 mmol) in tetrahydrofuran (THF; 15 mL) at −15—15 °C. After stirring for 20 min, the mixture was cooled to below 0 °C and a solution of *p*- or *m*-vinylaniline (0.24 g, 2 mmol) and TEA (0.3 mL) in $CHCl_3$ (15 mL) was added dropwise. Stirring was continued for one hour at this temperature and then overnight at 20 °C. The reaction mixture was extracted with H_2O (200 mL) and $CHCl_3$ (500 mL). The organic layer was washed successively with aq $NaHCO_3$ and H_2O and worked up. Silica-gel column chromatography ($CHCl_3$–acetone; 5 : 1 v/v) gave purified products (**Por-1a**—**c′**). To prepare **Por-1d**—f, *p*-vinylbenzyl chloride (0.6 g, 4 mmol) was added to solutions of the TEA-salts of **Por-2d**—**f** (2 mmol) and TEA (0.3 g, 3 mmol) in DMF (10 mL) and the mixtures were stirred at 20 °C for 24 h and kept moisture-free. The reaction mixtures were poured into water and extracted with ether (150 mL). The organic layers were worked up and silica-gel column chromatography gave purified products. The analytical data for **Por-1a**—f prepared by **Method A** were almost identical to the data for **Por-1a**—**f** prepared by **Method B**.

Introduction of a Zn-Atom into Por-1a—f. The application of the conventional procedure[8] provided crude products, which were purified by SiO_2 column chromatography.

Copolymerization of Por or ZnPor with 1-Vinyl-2-pyrrolidone (VP). In a typical example, a solution of **Por** or **ZnPor** (0.1 mmol), VP (0.5 g, 5.0 mmol), and α,α-azobisisobutyronitrile (AIBN; 1 mg) in DMF (2.5 mL) was put into a glass ampule, which was sealed under N_2 in a conventional manner and kept at 80 °C for 4 h. The contents of the ampule were then poured into ether to precipitate the polymerization product. All polymers produced by this method were soluble in aqueous solvents. IR (KBr) 1650, [1700 (for polymers of **Por**- and **ZnPor-1d**—**f**)] cm.$^{-1}$

References

1) W. Lautsch, W. Broser, W. Biedermann, and S. Gnichtel, *J. Polym. Sci.*, **17**, 479 (1955).

2) H. Kamogawa, *Polym. Lett.*, **10**, 711 (1972); H. Kamogawa, *J. Polym. Sci.*, **12**, 2317 (1974); H. Kamogawa, H. Inoue, and M. Nanasawa, *ibid.*, **18**, 2209 (1980); H. Kamogawa, S. Miyama, and S. Minoura, *Macromolecules*, **22**, 2123 (1989).

3) K. Kamachi, H. Akimoto, and S. Nozakura, *Polym. Lett.*, **21**, 693 (1983); M. Kamachi, X. S. Cheng, T. Kida, A. Kajiwara, M. Shibasaka, and S. Nagata, *Macromolecules*, **20**, 2665 (1987); H. Aota, H. Fujii, A. Harada, and M. Kamachi, *Chem. Lett.*, **1990**, 823.

4) D. Woehrle, G. Krawezyk, and M. Patiuras, *Makromol. Chem.*, **189**, 1001 (1988).

5) E. Tsuchida, H. Nishide, M. Yuasa, T. Baba, and M. Fukuzumi, *Macromolecules*, **22**, 66 (1989).

6) H. Kamogawa, T. Nakata, S. Ohori, and S. Komatsu, *Bull. Chem. Soc. Jpn.*, **64**, 1066 (1991).

7) A. D. Adler, F. R. Rongo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).

8) J. E. Falk, "Porphyrins & Metalloporphyrins," Elsevier, Amsterdam (1964).