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A Structural Model for Square Planar Metal Polymeric Phthalocyanines Synthesized from 3,3',4,4'-Benzophenonetetracarboxylic Dianhydride

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ABSTRACT

A structural model is described for calculating the molecular weight and the number of phthalocyanine rings in two-dimensional metal polymeric phthalocyanines synthesized from 3,3',4,4'-benzophenonetetracarboxylic dianhydride. Using this model, the number of phthalocyanine rings was determined in vanadyl polymeric phthalocyanines with carboxylic acid and ester end groups, and in their low-molecular-weight analogues with imide end groups. The accuracy of this model was supported by titration of carboxylic acid end groups and vapour pressure osmometer measurements.

1 INTRODUCTION

The synthesis of polymeric phthalocyanines from 1,2,4,5-tetracyanobenzene (TCB) and pyromellitic dianhydride (PMDA) has been widely studied.[1–10] Polymeric phthalocyanines synthesized from bifunctional group reactants preferentially form two-dimensional network polymers.[11,12] Because of the poor solubility of these polymers in organic solvents, their molecular weight cannot be determined by conventional methods. To date, studies have been limited regarding the degree of polymerization of polymeric phthalocyanines as correlated with their analytical data. In 1989, Wöhrle proposed a model for polymeric phthalocyanine,[13] in which the degree of polymerization could be calculated when the determination of end groups was possible. This model is therefore useful in calculating the

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molecular weight of polymers with nitrile or carboxylic acid end groups. However, some polymeric phthalocyanines contain end groups such as imides and esters, which cannot be determined quantitatively by IR spectra or titration. In polymers containing these end groups, elemental analysis is required to determine the degree of polymerization.

In this study, we submit a model for calculating the number of phthalocyanine rings in metal polymeric phthalocyanines synthesized from 3,3',4,4'-benzophenonetetracarboxylic dianhydride. The real number of phthalocyanine rings in polymers can be found by comparing experimental C/N values from elemental analysis with calculated values, as determined by equations described later. Our model can be applied to determine the molecular weight of vanadyl polymeric phthalocyanines with imide, carboxylic acid, and ester end groups. The accuracy of this model is supported by titration of carboxylic acid end groups and vapour pressure osmometer measurements.

2 EXPERIMENTAL

2.1 Preparation of vanadyl polymeric phthalocyanines 1, 2, and 3

Methods for the synthesis of two-dimensional vanadyl polymeric phthalocyanines and their derivatives with carboxylic acid and ester end groups are as follows:

Vanadyl polymeric phthalocyanine (poly VOPc **1**) was obtained by reaction of 16·11 g (0·05 mol) 3,3'-4,4'-benzophenonetetracarboxylic dianhydride, 30 g (0·5 mol) urea, 3·94 g (0·025 mol) vanadium chloride, and 0·5 g (0·0004 mol) ammonium molybdate in a sealed ampoule at 150°C for 1 h. The temperature was then raised to 250°C and kept there for 2 h. The low-molecular-weight analogue was then separated by reflux extraction for 24 h using *N,N*-dimethylformamide (DMF) as solvent. Poly VOPc **2** with carboxylic acid end groups was prepared by saponification of 15 g poly VOPc **1** in a solution of 5 g sodium hydroxide and 90 g sodium chloride in 45 ml water at 70°C for 6 h. Poly VOPc **3** with ester end groups was obtained by esterification of 6 g poly VOPc **2** in a solution of 20 ml 2-butyloxyethanol and 2 ml hydrochloric acid at 120°C for 2 h.

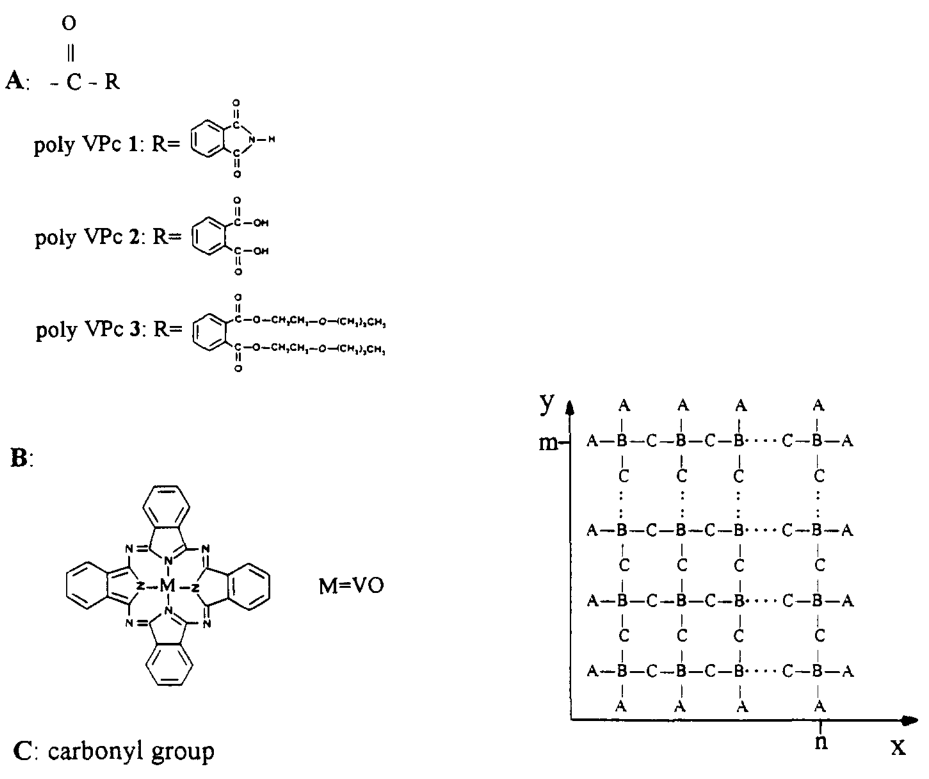
2.2 General

Elemental analyses were performed with a Perkin-Elmer 240C. Titration of carboxylic acid end groups was carried out with a Jenco model 6071 microcomputer pH meter. Molecular weight measurements were made with a Knauer vapour pressure osmometer, using DMF as solvent.

3 RESULTS AND DISCUSSION

3.1 Structural model for two-dimensional metal polymeric phthalocyanines

Polymeric phthalocyanines from bifunctional reactants formed two-dimensional polymers or random arrangement polymers. To simplify the model for polymeric phthalocyanines, we discuss only the two-dimensional polymer in its square arrangement. The structure of polymeric phthalocyanines can be divided into three repeating units: (A) end groups of polymeric phthalocyanines, (B) phthalocyanine rings, and (C) carbonyl groups for linking phthalocyanine rings. The structure of polymeric phthalocyanines can be expressed according to the model in Fig. 1.



(a) (b)

Fig. 1. Structural model for two-dimensional metal polymeric phthalocyanines: (a) A, B, and C are the repeating units of polymeric phthalocyanines A: end groups, B: phthalocyanine rings, C: carbonyl groups; (b) The square arrangement for polymeric phthalocyanines n: number of rows on the x-axis, m: number of rows on the y-axis.

3.2 Determination of the molecular weight of two-dimensional metal polymeric phthalocyanines

The molecular weight of polymeric phthalocyanines can be expressed by eqn (1):

$$W = n_1 B + n_2 A + n_3 C + n_4 M \tag{1}$$

In this equation, W is the molecular weight of the polymer, n_1 is the number of phthalocyanine rings, n_2 is the number of end groups, n_3 is the number of carbonyl groups, and n_4 is the number of metal ions. The values of n_1, n_2, n_3, and n_4 can be calculated according to eqns (2)–(5), where n is the number of rows in the abscissa, and m is the number of rows in the ordinate:

$$n_1 = n * m \tag{2}$$

$$n_2 = 2[(n - 2) + (m - 2)] + 8 = 2n + 2m \tag{3}$$

$$n_3 = [(n - 1)m + (m - 1)n] \tag{4}$$

$$n_4 = n * m \tag{5}$$

In the square model, $n = m$, so eqns (2)–(5) can be replaced by eqns (6)–(9):

$$n_1 = n^2 \tag{6}$$

$$n_2 = 4n \tag{7}$$

$$n_3 = 2(n - 1)n \tag{8}$$

$$n_4 = n^2 \tag{9}$$

The numbers of phthalocyanine rings, end groups, carbonyl groups, and metal ions for polymeric phthalocyanines with $n = 1$–10 are listed in Table 1.

The molecular weight of polymeric phthalocyanines can be expressed by eqn (10):

$$W = (B + 2C + M)n^2 + (4A - 2C)n \tag{10}$$

The molecular weights of B, C, and M are the same in poly VOPc **1**, poly VOPc **2**, and poly VOPc **3**: $B = 508{\cdot}5$ g/mole, $C = 28$ g/mole, $M = 66{\cdot}94$ g/mole. Equation (10) therefore can be replaced by eqn (11):

$$W = 631{\cdot}44n^2 + (4A - 56)n \tag{11}$$

In this equation, A represents the molecular weight of end groups in each polymer: 174 g/mole for poly VOPc **1**, 193 g/mole for poly VOPc **2**, and 393 g/mole for poly VOPc **3**.

TABLE 1
Number of Phthalocyanine Rings (n_1), End Groups (n_2), Carbonyl Groups (n_3), and Metals (n_4) for 2-D Metal Polymeric Phthalocyanines with n = 1–10

Number of rows in x-axis (n)	*2-D square model*			
	n_1	n_2	n_3	n_4
1	1	4	0	1
2	4	8	4	4
3	9	12	12	9
4	16	16	24	16
5	25	20	40	25
6	36	24	60	36
7	49	28	84	49
8	64	32	112	64
9	81	36	144	81
10	100	40	180	100

3.3 Calculation of the C/N ratio in two-dimensional metal polymeric phthalocyanines

The ratio of C, H, and N in poly VOPc **1** is:

$$C\% = [(32n_1 + 9n_2 + n_3) * 12/W] * 100\% = [34n(n+1)*12/W] * 100\% \quad (12)$$

$$H\% = [(12n_1 + 4n_2)/W] * 100\% = [4n(3n+4)/W] * 100\% \quad (13)$$

$$N\% = [(8n_1 + n_2) * 14/W] * 100\% = [4n(2n+1) * 14/W] * 100\% \quad (14)$$

The ratio of C, H, and N in poly VOPc **2** is:

$$C\% = [(32n_1 + 9n_2 + n_3) * 12/W] * 100\% = [34n(n+1) * 12/W] * 100\% \quad (15)$$

$$H\% = [(12n_1 + 5n_2)/W] * 100\% = [4n(3n+5)/W] * 100\% \quad (16)$$

$$N\% = (8n_1 * 14/W) * 100\% = (8n^2 * 14/W) * 100\% \quad (17)$$

The ratio of C, H, and N in poly VOPc **3** is:

$$C\% = [(32n_1 + 21n_2 + n_3) * 12/W] * 100\% = [2n(17n+41) * 12/W] * 100\% \quad (18)$$

$$H\% = [(12n_1 + 29n_2)/W] * 100\% = [4n(3n+5)/W] * 100\% \quad (19)$$

$$N\% = (8n_1 * 14/W) * 100\% = (8n^2 * 14/W) * 100\% \quad (20)$$

Using eqns (11)–(20), the ratio of C, H, and N in the polymeric phthalocyanines can be calculated, and the results are listed in Tables 2–4.

TABLE 2
Calculated Results for Poly VOPc **1**

Number of rows in x-axis (n)	*Number of phthalocyanine rings (n_1)*	*Elemental analyses (calc.[a])*				*Molecular weight*
		C (%)	*H (%)*	*N (%)*	*C/N*	*W^b (g/mole)*
1	1	64·20	2·20	13·22	4·86	1 271
2	4	64·34	2·10	14·72	4·37	3 805
3	9	64·40	2·05	15·47	4·16	7 603
4	16	64·44	2·02	15·92	4·05	12 663
5	25	64·47	2·00	16·22	3·97	18 986
6	36	64·49	1·99	16·44	3·92	26 571
7	49	64·51	1·98	16·60	3·89	35 420
8	64	64·52	1·97	16·73	3·86	45 532
9	81	64·53	1·96	16·83	3·83	56 907
10	100	64·53	1·96	16·91	3·81	69 544

[a] Calculated according to eqns (12)–(14) and (21).
[b] Calculated according to eqn (11).

The experimental values obtained from the elemental analysis of the polymeric phthalocyanines are shown in Table 5. Compared with the calculated values, the experimental carbon and nitrogen values are lower and the hydrogen content is higher. These differences are due to absorbed water (about 10% of total polymer weight) in the polymer.[12] Even so, the values of C/N are not influenced and these values can be used to

TABLE 3
Calculated Results for Poly VOPc **2**

Number of rows in x-axis (n)	*Number of phthalocyanine rings (n_1)*	*Elemental analyses (calc.[a])*					*Molecular weight*
		C (%)	*H (%)*	*N (%)*	*C/N*	*COOH (%)*	*W^b (g/mole)*
1	1	60·58	2·38	8·31	7·29	27·05	1 347
2	4	61·85	2·22	11·32	5·46	18·49	3 958
3	9	62·53	2·15	12·87	4·86	14·05	7 803
4	16	62·93	2·10	13·82	4·55	11·33	12 967
5	25	63·21	2·07	14·46	4·37	9·49	19 363
6	36	63·40	2·04	14·92	4·25	8·17	27 028
7	49	63·55	2·02	15·26	4·16	7·17	35 953
8	64	63·67	2·01	15·54	4·10	6·38	46 140
9	81	63·76	2·00	15·75	4·04	5·76	57 591
10	100	63·84	1·99	15·93	4·00	5·24	70 304

[a] Calculated according to eqns (15)–(17) and (22).
[b] Calculated according to eqn (11).

TABLE 4
Calculated Results for Poly VOPc **3**

Number of rows in x-axis (n)	*Number of phthalocyanine rings (n_1)*	*Elemental analyses (calc.[a])*				*Molecular weight W^b (g/mole)*
		C (%)	*H (%)*	*N (%)*	*C/N*	
1	1	64·83	5·96	5·22	12·44	2 147
2	4	64·77	5·04	8·06	8·04	5 558
3	9	64·74	4·46	9·85	6·57	10 231
4	16	64·72	4·06	11·08	5·84	16 167
5	25	64·71	3·77	11·98	5·40	23 366
6	36	64·70	3·54	12·67	5·11	31 828
7	49	64·69	3·37	13·21	4·90	41 553
8	64	64·68	3·23	13·64	4·74	52 540
9	81	64·67	3·11	14·00	4·62	64 791
10	100	64·67	3·01	14·30	4·52	78 304

[a] Calculated according to eqns (18)–(20) and (23).
[b] Calculated according to eqn (11).

determine the molecular weight of the polymers. The C/N values can be calculated according to eqns (12)–(20):

$$\text{C/N value of poly VOPc } \mathbf{1} = 7{\cdot}286(n + 1)/(2n + 1) \tag{21}$$

$$\text{C/N value of poly VOPc } \mathbf{2} = 3{\cdot}64 + 3{\cdot}64/n \tag{22}$$

$$\text{C/N value of poly VOPc } \mathbf{3} = 3{\cdot}64 + 8{\cdot}786/n \tag{23}$$

3.4 Results of analyses

The plots of calculated C/N values versus the number of phthalocyanine rings are shown in Fig. 2. The C/N values decreased as the number of

TABLE 5
Composition of Synthesized Polymeric Phthalocyanines and Their Derivatives

Polymer	*Elemental analyses (found)*				*Content of COOH (%)*	*VPO W (g/mole)*	*Number of Pc rings (n_1)*
	C (%)	*H (%)*	*N (%)*	*C/N*			
Poly VOPc **1** (high-M.-W.)	55·75	3·27	15·18	3·67	—	—	>30
Poly VOPc **1** (low-M.-W.)	49·78	2·71	12·64	3·94	—	—	30
Poly VOPc **2**	54·14	3·28	12·48	4·34	9·12	—	28
Poly VOPc **3**	59·51	4·08	8·89	6·69	—	8 500	8

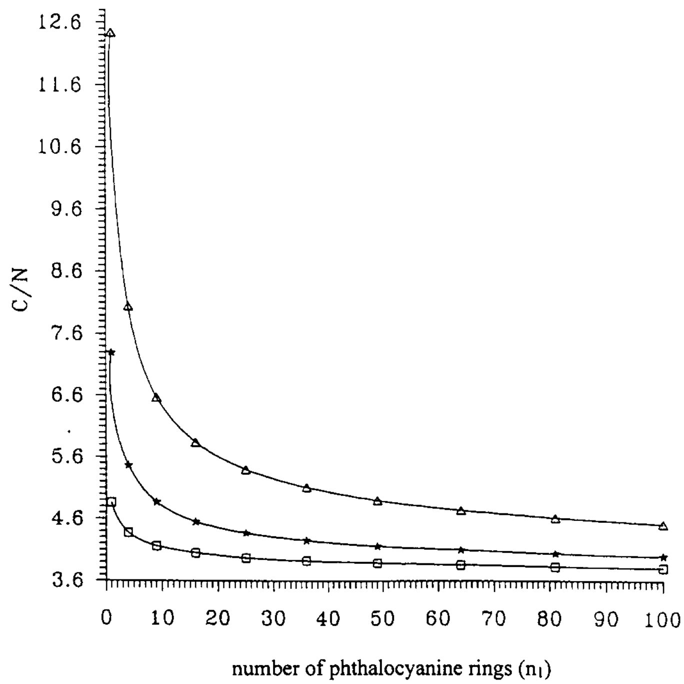


Fig. 2. Calculated results of C/N values for 2-D metal polymeric phthalocyanines vs. the number of phthalocyanine rings (□) poly VOPc **1**; (★) poly VOPc **2**; (△) poly VOPc **3**.

phthalocyanine rings increased. The number of phthalocyanine rings in the polymeric phthalocyanines can be found by comparing the C/N values in Table 5 with Fig. 2. Poly VOPc **1**, synthesized from 3,3',4,4'-benzophenonetetracarboxylic dianhydride, contained a high-molecular-weight polymer, and one of low molecular weight. These two components were separated by extracting the polymers with DMF for 24 h. In the high-molecular-weight polymer, a small amount of nitrile end groups was detected by IR analysis. Our model, therefore, cannot be used to determine the number of phthalocyanine rings in this polymer. However, the low-molecular weight analogue contains imide end groups and no absorption of nitrile end groups was detected by IR; the molecular weight of this component can be determined by our model. The C/N value of low-molecular weight analogue is 3·94. Comparing the value with the C/N value in Fig. 2, we found that the number of Pc rings in the low-molecular analogue was approximately 30. The molecular weight of the poly VOPc **2** was determined by combining data obtained from elemental analysis and titration of carboxylic acid end groups. The C/N value of poly VOPc **2** is 4·34. Comparing the value with the C/N value in Fig. 2, we found that the number of Pc rings in poly VOPc **2** was approximately 28. The content of the carboxylic acid end groups of poly VOPc **2** is 9·12%. Comparing the value with the content of carboxylic acid end groups in Table 3, we found that the results of the end group titration corresponded to the results of the elemental analysis. The molecular weight of poly VOPc **3** was determined by elemental analysis, and the results were supported by vapour pressure osmometer measurements. The C/N value of poly VOPc **3** is 6·69. Comparing the value with the C/N value in Fig. 2, we found that the number of Pc rings in poly VOPc **3** was approximately eight. The results of VPO measurements showed that the molecular weight of poly VOPc **3** was 8500 g/mole. Comparing the value with the molecular weight in Table 4, we found that the results of VPO measurements corresponded to the results of elemental analysis. The results of analyses showed that poly VOPc **3** was partly decomposed during esterification, resulting in the number of Pc rings apparently decreasing.

4 CONCLUSION

A structural model is described for the two-dimensional metal polymeric phthalocyanines synthesized from 3,3',4,4'-benzophenonetetracarboxylic dianhydride. This model offers a new method for characterizing the structure of polymeric phthalocyanines. The uniformity of end groups of high-molecular-weight polymeric phthalocyanines will be investigated in future studies in order to refine the model.

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REFERENCES

1. Venkatachalam, S., Rao, K. V. C. & Manoharan, P. T., *Synthetic Metals*, **26** (1988) 237.
2. Walton. T. R., Griffith, J. R. & Reardon, J. P., *J. Appl. Polym. Sci.*, **30** (1985) 2921.
3. Achar, B. N., Fohlen, G. M., Parker, J. A. & Keshavayya, J., *J. Polym. Sci. Polym. Chem.*, **25** (1987) 443.
4. Hongsheng Chen, Mang Wang, Linxian Feng & Shilin Yang, *J. Polym. Sci. Polym. Chem.*, **31** (1993) 1165.

5. Davies, C., Petty, D. M. & Willies, M. R., *Synthetic Metals*, **28** (1989) C775.
6. Couves, J. W. & Wright, J. D., *Synthetic Metals*, **29** (1984) F77.
7. Achar, B. N., Fohlen, G. M. & Parker, J. A., *J. Appl. Polym. Sci.*, **29** (1984) 353.
8. Wöhrle, D., *Adv. in Polym. Sci.*, **50** (1983) 106.
9. Li, H., & Guarr, T. F., *J. Electroanal. Chem.*, **297** (1991) 169.
10. Venkatachalam, S., Rao, K. V. C. & Manoharan, P. T., *J. Polym. Sci. Polym. Phys.*, **32** (1994) 37.
11. Wöhrle, D., *Adv. in Polym. Sci.*, **50** (1983) 99.
12. Wöhrle, D. & Preubner, E., *Makromol. Chem.*, **186** (1985) 2189.
13. Knothe, G. & Wöhrle, D., *Makromol. Chem.*, **190** (1989) 1573.