*Dyes and Pigments*, Vol. 35, No. 3, pp. 269–278, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
PII: S0143-7208(96)00112-X 0143-7208/97 $17.00+0.00

ELSEVIER

# Synthesis and Properties of 1,5-Dithio-3-oxa-pentanediyl Bridged Polymeric Phthalocyanines

Erbil Ağar,[a] Selami Şaşmaz,[a] İbrahim Keskin[a]
and Bünyamin Karabulut[b]

[a]Department of Chemistry, Ondokuz Mayıs University, 55139-Kurupelit, Samsun, Turkey
[b]Department of Physics, Ondokuz Mayıs University, 55139-Kurupelit, Samsun, Turkey

(Received 2 September 1996; accepted 22 October 1996)

## *ABSTRACT*

*Oxa-thio bridged metal-free and metal phthalocyanine polymers were prepared. Metal-free phthalocyanine polymer ($H_2Pc$) and metal phthalocyanine polymers (Ni, Cu, Co, Zn or Fe) carrying dithio-oxa bridged were synthesized from 3,3'-4,4'-tetracyanodiphenyl-1,5-dithiopentanyl-oxa-ether and hydroquinone or the corresponding anhydrous metal salts [$NiCl_2$, $CuCl$, $CoCl_2$, $Zn(CH_3CO_2)_2$ or $Fe(CO)_5$]. The model phthalocyanine compounds were characterized by IR, UV/VIS and DTA. The electrical conductivities of the phthalocyanines measured as gold sandwiches are about $10^{-10}\,S\,m^{-1}$* in vacuo *and in air.*

*Keywords*: Phthalocyanine polymers, dithio-oxa-ether.

## INTRODUCTION

Phthalocyanines are known for their interesting properties, including thermal stability, chemical inertness, semi conductivity, catalytic activity and photoconductivity [1]. Metal containing polymeric phthalocyanines have been described for use as dyes [1] and industrial high-tech materials [2, 3], and are also of additional interest because of their high thermostability [4, 5]. Low-molecular-weight metal phthalocyanines are generally prepared in high yield by cyclotetramerization of phthalic acid derivatives, such as 1,2-benzenedicarbonitrile or benzene-1,2-dicarboxylic anhydrides, with urea and metal salts. Starting with bifunctional reactants, such as 1,2,4,5-benzenetetracarboxylic dianhydrides or 1,2,4,5-benzenetetracarbonitrile, metal polymeric phthalocyanines can be prepared via polytetracyclomerization [6–8].

The synthesis and properties of thio-oxa bridged polymeric phthalocyanines are described.

## RESULTS AND DISCUSSION

Scheme 1 shows the synthesis of the thio-oxa ether-substituted bis(phthalonitrile) compounds used in this investigation. This reaction was carried out at room temperature in dry DMSO with anhydrous $K_2CO_3$ as the base [9]. Cyclotetramerization of bis(phthalonitrile) in the presence of metal salts gave the polymers. The solvents used for these reactions were quinoline for NiII (**3**) and ZnII (**6**), and ethylene glycol for CoII (**5**) and FeII (**7**).

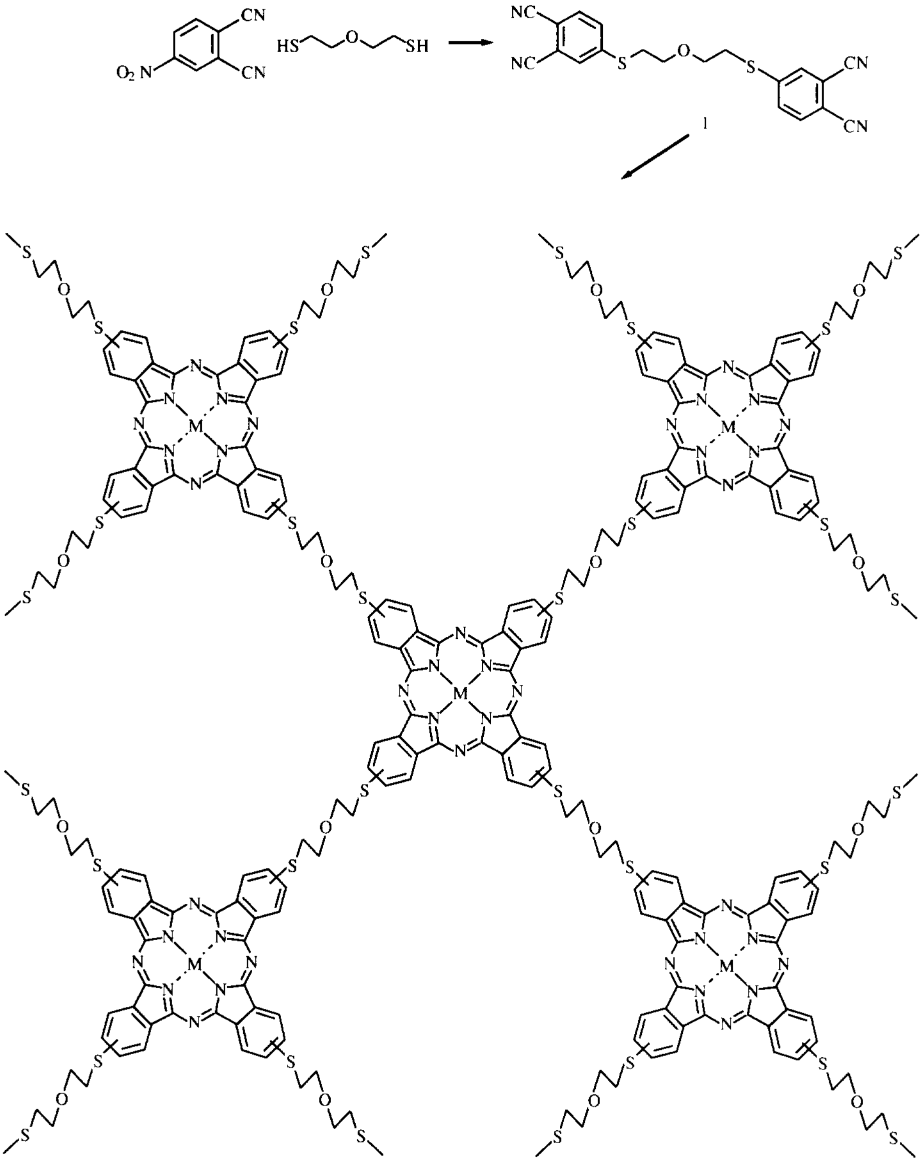
The metal-free phthalocyanine derivative (**2**) was obtained directly from the reaction of the tetracyano compound (**1**) with freshly sublimed hydroquinone in the absence of solvent [1]. Similarly, no phthalocyaninatocopper polymer was detected in a number of trials of the tetracyano compound with CuCl and urea, but the copper phthalocyanine derivative (**4**) was obtained in the presence of the strongly basic *N*,*N*-diaminoethanol at reflux [2]. For the phthalocyanines, the insoluble products were obtained in sufficient purity after successive washings with various solvents.

The molecular weight of the polymers could not be determined either by conventional methods because of poor solubility in organic solvents, or by comparison of the IR absorptions of the end groups with those of the bridging groups [8, 9].

Compound **1** was characterized by IR, $^1H$ and $^{13}C$ NMR and elemental analyses. The polymeric phthalocyanines (**2**–**7**), obtained according to the standard procedure, have cyano end groups together with imide functions, as indicated by the absorptions at 1725 and 1770 $cm^{-1}$, respectively [6, 7].

The IR spectra of polyphthalocyanines provide evidence for the structural skeleton of phthalocyanine and the nature of the end groups. The intense absorpion at 1100 and 1300 $cm^{-1}$, corresponding to vibrations of the pyrrole or benzene rings [10], have been observed in the IR spectra of polyphthalocyanines.

The IR spectrum of **1** clearly indicates the presence of alkyl and ether and CN groups by the intense stretching bands at 2960–2840 (C—H), 1220–1200 (C—O—C), 740 (C—S—C) and 2220 $cm^{-1}$ (CN). The IR spectra of the phthalocyanine polymers (**2**–**7**) are very similar, with the exception of the metal-free phthalocyanine polymer (**2**) showing a NH stretching band at 3270 and 1010 $cm^{-1}$ due to the inner core [11, 12]. These bands are particularly useful for characterization of polymeric metal-free phthalocyanines, as



| Complex | M |
|---|---|
| 2 | 2H |
| 3 | Ni |
| 4 | Cu |
| 5 | Co |
| 6 | Zn |
| 7 | Fe |

**Scheme 1**

there is little frequency dependence on ring substitution and they are not overlapped by strong bis(phthalonitrile) monomer absorptions [6,7]. These bands are absent in spectra of the metal complexes. Metal–N vibrations were expected to appear at 400–100 $cm^{-1}$, but they were not observed in KBr pellets [11, 12].

When IR spectra in KBr mulls of polymeric phthalocyanines were compared with the metal-free (**2**) and metal–phthalocyanines (**3**–**7**), it was shown that some significant differences existed. There is little shift to longer wavelength numbers in most of the IR bands of metal polymeric phthalocyanines with respect to the metal-free analogues [6, 7].

The $^1H$ NMR spectrum of the bis(phthalonitrile) derivative (**1**) indicates aromatic protons (8.20–7.70 ppm) and $S—CH_2—CH_2—O$ protons (3.82–3.21 ppm). In the $^{13}C$ NMR spectra of **1** the aromatic carbon in the vicinity of oxa-thio ether groups is at the lowest field, 109.85 ppm, while the chemical shifts of the other aromatic carbons and two nitrile carbons appear at 116.20, 115.82 and 115.20 ppm.

The UV/VIS absorption spectra of the phthalocyanine system exhibit characteristic Q and B bands [13]. The results obtained from UV/VIS experiments are given in Table 1.

The phthalocyanine polymers (**2**–**7**) show typical electronic spectra with two strong absorption region, one of them in the UV region at about 300–350 nm (B band) and the other in the visible region at 600–860 nm (Q band). The Q bands, and their overtones were obtained in three transition levels in DMSO and conc $H_2SO_4$. The spectra of phthalocyanines in $H_2SO_4$ also showed bands in the 224–410 nm region. These bands may arise from the phenyl units distant from the phthalocyanines phenyl units. Increasing polymerization of a monomer is responsible for a red shift [14]. The present complexes are soluble in DMSO (**2** and **3**), and $H_2SO_4$ (**4**–**7**) and exhibit absorption coefficients that are typical of phthalocyanines complexes. [1] The lower solubility of the polymers (**4**–**7**) meant that their spectra could be

**TABLE 1**

UV/VIS and First Derivative Spectral Transitions of the Polymeric Phthalocyanines in $H_2SO_4$ and DMSO ($\lambda_{max}$ and $\epsilon$ are in nm and $g^{-1}$ $cm^{-1}$ litre, respectively)

| *Compound* | |
|---|---|
| **2**[a] | 228 (3760), 260 (1361), 297 (2337), 632 (373), 690 (391). |
| **3**[a] | 248 (4200), 265 (4030), 298 (4000), 360 (1210), 406 (800), 731(1100) 770 (1600). |
| **4**[a] | 227 (1210), 398 (1341), 459 (333), 592 (326), 683 (329), 759 (319). |
| **5** | 231 (4320), 252 (4288), 284 (3820), 369 (2173), 753(530), 830 (880). |
| **6** | 226 (4580), 282 (3300), 303 (3215), 401 (1713), 764 (1325), 860 (1576). |
| **7** | 224 (4160), 257 (3100), 384 (2060), 410 (1840), 760 (430), 850 (685). |

[a] In DMSO ($c$:$1 \times 10^{-3}$ g litre).

obtained only in conc $H_2SO_4$. The phthalocyanine ring is a relatively large and symmetrical structure which has a strong tendency to associate in solution [15]. Solvent effects on the UV/VIS characteristics of polymeric phthalocyanines were regular and red shifts of the spectra bands showed systematic changes. For a more precise understanding of solvent effects, more detailed solvent influences must also be taken into consideration [14]. The solvent effect is clearly evident in these spectra with the shift of lower energy absorption to the near-IR region ($\lambda_{max} > 800$ nm).

The UV/VIS spectra of the polymeric phthalocyanines are very similar to those of crown ether [16], alkyl chains [17] and ester-imide [18] substituted phthalocyanine polymers. The experimental UV/VIS bands of the polymeric phthalocyanines were slightly different from theoretical values [19], and from results for mononuclear [20–22], binuclear [23], five nuclear [24] and nonanuclear phthalocyanines [25].

Resuls of thermogravimetric analyses of the polymers under nitrogenous conditions for initial and main decompositions are shown in Table 2. The phthalocyanine polymers containing heteroatoms (**2**–**7**) can also be considered as non-substituented phthalocyanine polymers of high thermal stability [5]. The initial decomposition temperatures of the compounds synthesised during this work varied between 240 and 465°C (Table 2). The thermal stability of metal phthalocyanine polymers is higher than that of the corresponding substituent-containing (crown ether [13], ester-imide [4], sulphonyl chain [26, 27] and alkyl thio [17]) and transition metal phthalocyanine polymers.

The dc electrical conductivities of the polyphthalocyanines **2**–**7** measured at room temperature in air and vacuum as a sandwich type are also given in Table 2. Althought an increase in the conductivitiy is observed for the measurements in air, the values are of the same order (Table 2). The higher values are comparable with those of monoazacrown ether substituted polyphthalocyanines [28].

A new synthesic route has thus been developed for the synthesis of the above type of polymers. The method appears to be very good for the synthesis

**TABLE 2**
Thermal and Electrical Properties of the Polymeric Phthalocyanines

| *Compound* | *Initial decomp. temp./°C* | *Main decomp. temp./°C* | *Conduct. in vacuum ($\sigma dc/S\,m^{-1}$)* | *Conduct.in air ($\sigma dc/S\,m^{-1}$)* |
|---|---|---|---|---|
| **2** | 240 | 455 | $2.30\times10^{-10}$ | $2.21\times10^{-10}$ |
| **3** | 245 | 460 | $3.34\times10^{-10}$ | $5.61\times10^{-10}$ |
| **4** | 265 | 465 | $1.10\times10^{-10}$ | $1.13\times10^{-10}$ |
| **5** | 250 | 460 | $2.01\times10^{-10}$ | $2.04\times10^{-10}$ |
| **6** | 255 | 455 | $1.94\times x10^{-10}$ | $2.05\times10^{-10}$ |
| **7** | 250 | 465 | $7.10\times10^{-11}$ | $8.63\times10^{-11}$ |

of heat-stability metal-free (**2**) and metal (**3**–**7**) phthalocyanine polymers in almost quantitative yield and these reactions could also be used not only to synthesise polymers of other metal phthalocyanines, but also, with suitable modifications, other materials.

## EXPERIMENTAL

Routine IR spectra were recorded on a Mattson 1000 FTIR spectrometer as KBr pellets. Electronic spectra were recorded on a Unicam UV/VIS spectrometer. Thermogravimetric analyses were obtained on a Rigaku TG 8110 simultaneous thermal analyser combined with a TAS 100 at 10°C $\text{min}^{-1}$ in a nitrogen flow. $^1$H NMR and $^{13}$C NMR studies were made on a Bruker AC-200 FT-NMR spectrometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of TÜBİTAK Gebze Research Center. 4-Nitrophthalonitrile was synthesized according to the reported procedure [29].

### Synthesis of 3,3′-4,4′-tetracyanodiphenyl-1,5-dithiopentanyl-oxa-ether (1)

2-Mercaptoethyl ether (3.19 g, 23.11 mmol) was dissolved in dry dimethyl sulphoxide (50 ml) under nitrogen and 4-nitrophthalonitrile (8.0 g, 46.22 mmol) was added. After stirring for 10 min, finely ground anhydrous potassium carbonate (6.38 g, 46.22 mmol) was added portionwise over 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 24 h. Water was then added and the product filtered off, washed with water until neutral, and then refluxed in methanol, filtered, and finally washed with hot methanol, ethyl acetate, ethyl ether and dried. Yield: 8.0 g (88.8%). This compound was soluble in chloroform, dichloromethane, DMF and DMSO, mp 158–159°C. IR $\upsilon_{\text{max}}$ ($\text{cm}^{-1}$): 2960–2840 ($CH_2$), 2220 (CN), 1580, 1540, 1480, 1420,1410, 1355, 1280, 1220–1200, 1125–1110, 1070, 1020, 960, 910, 880, 850–830, 740, 715, 705, 530. $^1$H NMR ($CDCl_3$-$d_6$): $\delta$8.20–7.70 (*m*, 6H, arom.), 3.82–3.61 (*t*, 4H, O—$CH_2$), 3.52–3.21 (*t*, 4H, S—$CH_2$) ppm. $^{13}$C NMR ($CDCl_3$-$d_6$): 146.52, 133.55, 133.50, 130.20, 130.15, 116.20, 115.82, 115.20, 109.85, 68.55, 30.80. Elemental analyses for **1**: Molecular formula $C_{20}H_{14}S_2N_4O$. Calc: C 61.54%, H 3.59%, N 14.35%; S 16.41%. Found: C 61.55%, H 3.56%, N 14.38%, S 16.46%.

### Metal-free polymer (2)

A mixture of **1** (1.17 g, 3.0 mmol) and hydroquinone (0.33 g, 0.75 mmol) (purified by sublimation) was gently heated under nitrogen in a sealed tube and then cooled. This mixture was then heated to 200°C under an nitrogen atmosphere and held at this temperature for 1 h. After cooling to room temperature, it was diluted with hot ethanol and the product filtered. The green product was then refluxed in chloroform, filtered, washed with chloroform and then successively with hot ethyl acetate, dichloromethane, methanol, acetone and diethyl ether and dried *in vacuo* at 100°C. This polymer was soluble in DMF and DMSO. Yield: 0.80 g. IR $\nu_{max}$ ($cm^{-1}$): 3400–3200 (NH), 2960–2820 ($CH_2$), 2210 (CN), 1770, 1725, 1605–1580, 1510, 1450, 1420, 1380, 1350, 1290, 1210–1200, 1095, 1060, 1010, 930, 890, 860, 820, 750–740, 685, 510. Elemental analyses for **2**: Molecular formula $C_{80}H_{58}N_{16}O_4S_8Ni$. Calc for monomeric phthalocyanine (for CN end groups), C 61.46%, H 3.71%, N 14.34%, S 16.39%. Found: C 59.15%, H 4.02%, N 12.21%, S 13.62%.

### Ni-containing polymer (3)

A mixture of **1** (1.17 g, 3.0 mmol) and $NiCl_2$ (0.10 g, 0.75 mmol) and anhydrous quinoline (30 ml) was heated and stirred at 220°C for 5 h under nitrogen. After cooling, the reaction mixture was diluted with methanol and the precipitate was filtered off. It was treated with boiling methanol twice to dissolve any unreacted metal salts. The dark green product was refluxed in chloroform, filtered, washed with chloroform and then successively with ethyl acetate, dichloromethane, methanol, acetone and diethyl ether and dried in vacuo at 100°C. This polymer was soluble in DMF and DMSO. Yield: 0.75 g. IR $\upsilon_{max}$ ($cm^{-1}$): 3330 (imide), 2960–2820 ($CH_2$), 2210 (CN), 1770, 1725, 1600–1580, 1530, 1480, 1450, 1410–1390, 1350, 1310–1290, 1210–1200, 1100–1090, 1040, 930, 900–890, 860, 820–800, 750–740, 690, 520. Elemental analyses for **3**: Molecular formula $C_{80}H_{56}N_{16}O_4S_8Ni$. Calc. for monomeric phthalocyanine (for CN end groups), C 59.30%, H 3.45%, N 13.84%, S 15.82%. Found: C 57.53%, H 3.71%, N 15.43%, S 13.75%.

### Cu-containing polymer (4)

A mixture of **1** (1.17 g, 3.0 mmol) and CuCl (0.075 g, 0.75 mmol) and *N*,*N*-diethylaminoethanol (30 ml) was heated and stirred at 145–150°C for 4 h under nitrogen. After cooling, the reaction mixture was diluted with methanol and filtered off. The dark green product was washed with $NH_4OH$ (24%, 50 ml) and then with water until the filtrate became neutral. The green product was digested in DMF and chloroform, and the product refluxed, filtered, washed with DMF and then successively with chloroform, ethyl acetate, dichloromethane, methanol, acetone and diethyl ether and dried *in vacuo* at 100°C. This polymer was slightly soluble in hot DMSO. Yield:

0.86 g. IR $\upsilon_{max}$ (cm$^{-1}$): 3340 (imide), 2960–2820 ($CH_2$), 2210 (CN), 1770, 1725, 1605–1580, 1530, 1480, 1450, 1420, 1390, 1350, 1310–1290, 1210–1200, 1100–1090, 1040, 935, 900–890, 860, 820–800, 750–740, 670, 520. Elemental analyses for **4**: Molecular formula $C_{80}H_{56}N_{16}O_4S_8Cu$. Calc. for monomeric phthalocyanine (for CN end groups), C 59.13%, H 3.45%, N 13.80%, S 15.77%. Found: C 57.91%, H 4.57%, N 15.02%, S 14.01%.

### Co-containing polymer (5)

A mixture of **1** (1.17 g, 3.0 mmol) and $CoCl_2$ (0.10 g, 0.75 mmol) and ethylene glycol (30 ml) was heated and stirred at 220–230°C for 4 h. under nitrogen. After cooling to 100°C, the product was filtered and washed with hot ethylene glycol. The dark-blue product was washed successively with DMF, chloroform, ethyl acetate, dichloromethane, methanol, acetone and diethyl ether and dried *in vacuo* at 100°C. This polymer was slightly soluble in hot DMSO. Yield: 0.82 g. IR $\upsilon_{max}$ (cm$^{-1}$): 3320 (imide), 2960–2820 ($CH_2$), 2210 (CN), 1770–1725, 1600–1580, 1530, 1485, 1460, 1420, 1390, 1350, 1300–1290, 1210–1200, 1100–1090, 1040, 935, 900–890, 870, 825–805, 750–740, 680, 530. Elemental analyses for **5**: Molecular formula $C_{80}H_{56}N_{16}O_4S_8Co$. Calc. for monomeric phthalocyanine (for CN end groups), C 59.30%, H 3.46%, N 13.84%, S 15.81%. Found: C 57.61%, H 4.10%, N 15.21%, S 13.05%.

### Zn-containing polymer (6)

A mixture of **1** (1.17 g, 3.0 mmol) and anhydrous $Zn(CH_3CO_2)_2$ (0.135 g, 0.75 mmol) and anhydrous quinoline (30 ml) was heated and stirred at 200–210°C for 5 h under nitrogen. After cooling, the reaction mixture was diluted with methanol and the precipitate was filtered off. The green product was filtered off and then washed with hot methanol several times. Purification was carried out as described for 5. This polymer was slightly soluble in hot DMSO. Yield: 0.90 g. IR $\upsilon_{max}$ (cm$^{-1}$): 3330 (imide), 2960–2820 ($CH_2$), 2210 (CN), 1770–1725, 1600–1580, 1530, 1485, 1460, 1420, 1395, 1350, 1305–1290, 1210–1200, 1105–1090, 1040, 930, 900–890, 865, 825–800, 750–740, 675, 520. Elemental analyses for **6**: Molecular formula $C_{80}H_{56}N_{16}O_4S_8Zn$. Calc. for monomeric phthalocyanine (for CN end groups), C 59.05%, H 3.45%, N 13.78%, S 15.75%. Found: C 57.95%, H 4.32%, N 15.52%, S 13.21%.

### Fe-containing polymer (7)

A mixture of **1** (1.17 g, 3.0 mmol) and ethylene glycol (30 ml) under nitrogen and rapidly heated and stirred at 200°C. At this temperature, (0.1 ml, 0.75 mmol) of $Fe(CO)_5$ was added slowly by means of a syringe. The mixture was heated at 200°C for 4 h and after cooling, the reaction mixture was diluted with methanol and filtered off. Purification was carried out as described for **5**. This polymer was slightly soluble in hot DMSO. Yield: 0.85 g. IR *vmax* ($cm^{-1}$): 3310 (imide), 2960–2820 ($CH_2$), 2210 (CN), 1770–1725, 1600–1580, 1530, 1480, 1460, 1420, 1395, 1350, 1310,1290, 1210–1200, 1100–1090, 1040, 930, 900–890, 860, 820–800, 750–740, 670, 530. Elemental analyses for **7**: Molecular formula $C_{80}H_{56}N_{16}O_4S_8Fe$. Calc. for monomeric phthalocyanine (for CN end groups), C 59.40%, H 3.46%, N 13.86%, S 15.84%. Found: C 57.40%, H 3.84%, N 15.35%, S 14.05%.

## ACKNOWLEDGEMENTS

This work was supported by the research fund of the Ondokuz Mayis University.

## REFERENCES

1. Moser, H. and Thomas, L., *The Phthalocyanines*. CRC Press, Boca Raton, Florida, 1983.
2. Schramm, C. J., Scaringe, R. P., Stojakovic, D. R., Hoffmann, B. M., Ibers, J. A. and Marks, T. J., *Journal of the American Chemical Society*, **102** (1980) 6702.
3. Diehl, B. N., Inabe, T., Lyding, J. W., Schoch, K. F., Kannewurf, C. R. and Marks, T. J., *Journal of the American Chemical Society*, **102** (1983) 1551.
4. Archar, B. N., Fohlen, G. M. and Parker, J. A., *Journal of Applied Polymer Science*, **29** (1984) 353.
5. Wöhrle, D. and Schulte, B., *Makromolekulare Chemie*, **186** (1985) 2229.
6. Wöhrle, D. and Preubner, E., *Makromolekulare Chemie*, **186** (1985) 2189.
7. Wöhrle, D., Marouse, U. and Knoop, R., *Makromolekulare Chemie*, **186** (1985) 2209.
8. Wöhrle, D. and Schulte, B., *Makromolekulare Chemie*, **186** (1988) 1167.
9. Chavez, F. and Sherry, A. D., *Journal of Organic Chemistry*, **54** (1989) 2990.
10. Wöhrle, D. and Hundorf, U., *Makromolekulare Chemie*, **186** (1985) 2177.
11. Avram, M. and Mateescu, M., *Infrared Spectroscopy*. Wiley-Interscience, New York, 1966.
12. Nakomato, K., *Infrared Spectra of Inorganic and Coordination Compounds*. John Wiley, New York, 1970.
13. Ahsen, V., Yilmazer, E., Gül, A. and Bekaroğlu, Ö., *Makromolekulare Chemie, Rapid Commun.*, **8** (1987) 243.
14. Jaffe, H. H. and Orchin, M., *Theory and Applications of Ultraviolet Spectroscopy*. John Wiley, London, 1962.
15. Snow, A. W. and Jarvis, N. L., *Journal of the American Chemical Society*, **106** (1984) 4706.
16. Özdemir, M. and Ağar, E., *Spectroscopy Letters* (1991).
17. Ahsen, V., Özdemir, M., Öztürk, Z. Z., Gül, A. and Bekaroğlu, Ö., *Journal of Chemical Research*, S (1993) 348.
18. Achor, B. N., Follen, G. M. and Parker, J. A., *Journal of Polymer Science*, **23** (1995) 1677.

19. Orti, E. and Bredas, J. L., *Journal of Chemical Physics*, **92**(2) (1990) 1228.
20. Ağar, E., Şaşmaz, S., Bati, B. and Özdemir, M., *Synthetic Reactions in Inorganic and Metal-Organic Chemistry*, **25**(7) (1995) 1165.
21. Ağar, E., Şaşmaz, S., Gümrükçüoğlu, İ. E. and Özdemir, M., *Synthetic Reactions in Metal-Organic and Inorganic Chemistry*, **26** (1996) 1243.
22. Şaşmaz, S., Ağar, E. and Akdemir, N., *Bulletin of the Belgium Society*, in press.
23. Vight, S., Lam, H., Janda, P., Lever, A. B. P. and Leznoff, C. C., *Canadian Journal of Chemistry*, **68** (1991) 1457.
24. Gürek, A., Ahsen, V., Gül, A. and Bekaroğlu, Ö., *Journal of the Chemical Society, Dalton Transactions* (1991) 3367.
25. Ağar, E., Bati, B., Erdem, E. and Özdemir, M., *Journal of Chemical Research*, S (1995) 16.
26. Gürol, Ý., Ahsen, V. and Bekaroğlu, Ö., *Journal of the Chemical Society, Dalton Transactions* (1994) 497.
27. Gürek, A. G. and Bekaröğlu, Ö., *Journal of the Chemical Society, Dalton Transactions* (1994) 1419.
28. Musluoğlu, E., Öztürk, Z. Z., Ahsen, V., Gül, A. and Bekaroğlu, Ö., *Journal of Chemical Research*, S (1993) 6–7.
29. Young, J. G. and Onyebuagu, W., *Journal of Organic Chemistry*, **55** (1990) 2155.