Functional Metallomacrocycle Derivatives and Their Polymers. Part 23.† Biaxially Orientated Langmuir–Blodgett Films of Substituted Metallophthalocyanines

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Soluble metallophthalocyanine compounds (M = Ni^{II} or Cu^{II}) with alkyloxycarbonyl groups substituted at either the 2 or 3 position of the benzene ring (alkyl = 1- or 2-octyl, or 1-decyl) were synthesized by the reaction of the corresponding metallophthalocyaninetetracarboxyl chlorides with the alkyl alcohols, and monolayers were formed at a water–air interface . All compounds formed stable monolayers at surface pressures higher than *ca.* 15 mN m^{-1}. In the Langmuir–Blodgett films built up from monolayers of the compounds on Pyrex substrates, the orientation of the phthalocyanine rings was shown to be biaxial from the one-dimensional orientation of the phthalocyanine stacked columns, observed by measurement of polarized visible absorption spectra.

Metallophthalocyanines have previously been well known as metal–organic dyes exhibiting high thermal and chemical stabilities. Recently, they have become noted for their optical and electronic properties, such as electronic conductivity, photovoltaic effects, and electrochromism.[1,2] However, metallophthalocyanines are insoluble in most organic solvents. Therefore, it was necessary to prepare soluble phthalocyanine derivatives for these detailed investigations. We have studied the preparation, as well as the chemical function, of some soluble phthalocyaninatometal derivatives containing functional groups on the peripheral benzene rings, and the polymers derived therefrom.[3–9]

The preparation of uniform, well ordered, and defect-free films of metallophthalocyanines is also crucial to the successful use of these materials. In recent years, and for this purpose, the extensive technological possibilities of Langmuir–Blodgett (LB) films of metallophthalocyanine derivatives have been of interest in microelectronic and microbiological fields. For the preparation of phthalocyanine films by the LB technique, metallophthalocyanine derivatives possessing chemical functional groups in the peripheral sites have been studied by many investigators.[9–12]

Recently, we have synthesized some bis- or tetrakis(decyloxycarbonyl)phthalocyaninatometal complexes.[13] This paper is concerned with the formation of Langmuir–Blodgett films of Ni^{II} as well as copper(II) phthalocyanines having alkyloxycarbonyl substituents on either the 2 or 3 position of the peripheral benzene rings, and the orientation of metallophthalocyanine molecules in these built-up multilayer films.

Experimental

Materials.—Tetracarboxyphthalocyaninato-nickel(II) (**1a**), and -copper(II) (**1b**) and the corresponding tetra-acid chlorides were prepared in accordance with the method described previously.[3] Octan-1-ol, octan-2-ol, and decan-1-ol were purified by distillation. The other reagents were of analytical grade from commercial origin and used without further purification.

[*Tetrakis*(*decyloxycarboxyl*)*phthalocyaninato*]*nickel*(II) (**2a**).—Compound (**1a**) (1.00 g, 1.3 mmol) was refluxed in thionyl chloride (20 cm^3) for 1 week. The thionyl chloride was removed under reduced pressure. A mixture of the resulting acid chloride of (**1a**) and decan-1-ol (30 cm^3) was heated at 180 °C for 1 d, followed by refluxing for 1 d. Excess of decan-1-ol was removed and addition of methanol (50 cm^3) to the residue gave a blue-green solid. The crude product was recrystallized from benzene–methanol (1:1) and purified by column chromatography on silica gel using toluene–isopropyl alcohol (2:1) as the eluant. Yield: 0.78 g (46%). Decomposition temperatures: 360 °C (Found: C, 69.90; H, 7.90; N, 8.45; Ni, 4.15. Calc. for $C_{76}H_{96}N_8NiO_8$: C, 69.75; H, 7.40; N, 8.55; Ni, 4.50%). I.r. (KBr): 2 920m, 2 878m, 1 720s ($\nu_{C=O}$), 1 610w ($\nu_{C=C}$), 1 510w, 1 338m, 1 278s, 1 244s, 1 180m, 1 090m, 755w, and 733s cm^{-1}. U.v.–visible [benzene, $\lambda_{max.}$(log ε)]: 339 (4.47), 464(sh) (3.80), 610 (4.47), and 664 nm (sh) (4.26). ^1H N.m.r. (CCl_4): δ 0.90 and 1.23 (br, 84 H). E.s.r. (benzene at 77 K): *g* = 2.000.

[*Tetrakis*(*decyloxycarbonyl*)*phthalocyaninato*]*copper*(II) (**2b**).—Complex (**2b**) was prepared from (**1b**) by the same method as for (**2a**). Yield: 0.89 g (51%). Decomposition temperature: 360 °C (Found: C, 69.80; H, 7.55; Cu, 4.40; N, 8.05. Calc. for $C_{76}H_{96}CuN_8O_8$: Cu, 4.85; C, 69.50; H, 7.90; N, 8.55%). I.r. (KBr): 2 925m, 2 883m, 1 715 ($\nu_{C=O}$), 1 510w, 1 340m, 1 280s, 1 243s, 1 182m, 1 142m, 1 115w, 1 088m, 756w, and 734s cm^{-1}. U.v.–visible [benzene, $\lambda_{max.}$(log ε)]: 335 (4.69), 608 (4.66), and 6.79 nm (4.35). E.s.r. (benzene at 77 K): *g* = 2.068.

[*Tetrakis*(1-*octyloxycarbonyl*)*phthalocyaninato*]*copper*(II) (**2c**).—A mixture of the acid chloride of (**1b**) (1.3 mol) and octano-1-ol (50 cm^3) was refluxed for 2 d. The crude product was purified by column chromatography on silica gel using toluene–isopropyl alcohol (2:1) as the eluant. Yield: 0.89 g (57%). Decomposition temperature: 365 °C (Found: C, 67.65; H, 6.70; Cu, 5.30; N, 9.20. Calc. for $C_{68}H_{80}CuN_8O_8$: C, 68.00; H, 6.70; Cu, 5.30; N, 9.35%). I.r. (KBr): 2 920m, 2 880m, 1 718s ($\nu_{C=O}$), 1 612w ($\nu_{C=C}$), 1 510w, 1 340m, 1 277s, 1 243s, 1 180m, 1 088m, 754w, and 735s cm^{-1}. U.v.–visible [benzene, $\lambda_{max.}$(log ε)]: 335 (4.67), 606 (4.64), and 678 nm (4.31). E.s.r. (benzene at 77 K): *g* = 2.069.

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† Part 22 is ref. 9.

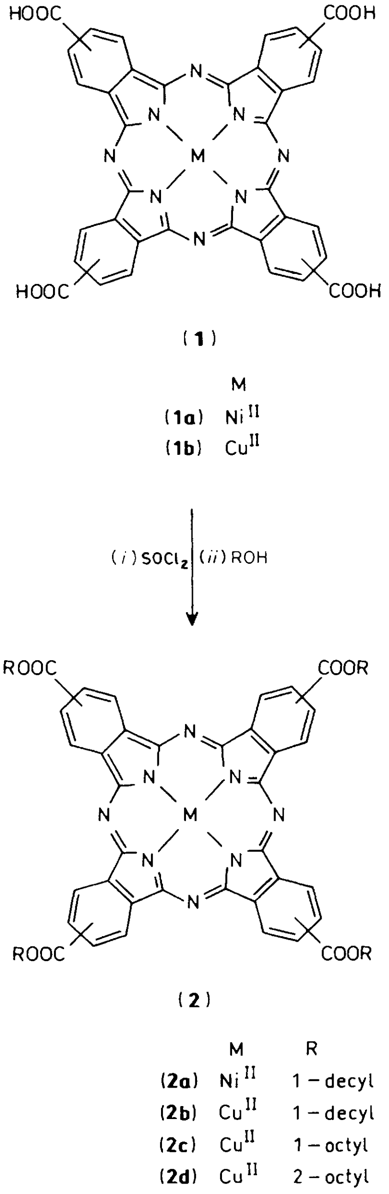

Figure 1. General synthesis and structures of tetrakis(alkyloxycarbonyl)phthalocyaninato–metal complexes

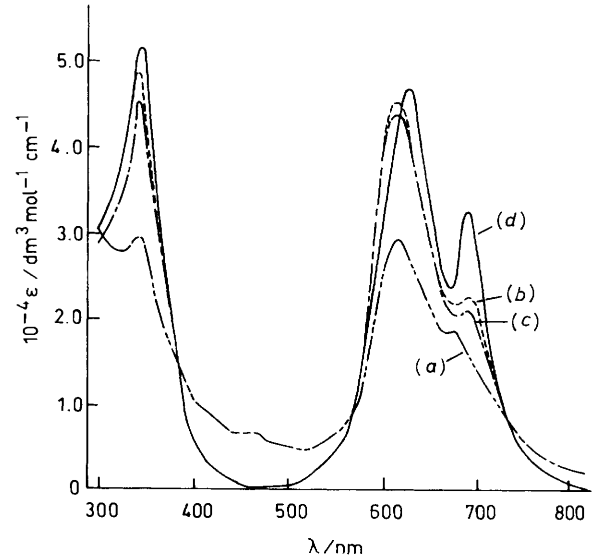

Figure 2. Electronic spectra of the compounds in benzene solutions (*a*) (**2a**), (*b*) (**2b**), (*c*) (**2c**), and (*d*), (**2d**)

[*Tetrakis*(2-*octyloxycarbonyl*)*phthalocyaninato*]*copper*(II) (**2d**).—Complex (**2d**) was prepared from (**1b**) by the same method as for (**2c**). Yield 0.97 g (62%). Decomposition temperature: 311 °C (Found: C, 67.60; H, 6.70; Cu, 5.35; N, 9.30. Calc. for $C_{68}H_{80}CuN_8O_8$: C, 68.00; H, 6.70; Cu, 5.30; N, 9.35%). I.r. (KBr): 2 923m, 2 880m, 1 712s ($\nu_{C=O}$), 1 507w, 1 340m, 1 278s, 1 242s, 1 182m, 1 140w, 1 115w, 1 088m, 755w, and 734s cm^{-1}. U.v.–visible [benzene, $\lambda_{max.}$(log ε)]: 338 (4.71), 619 (4.68), and 682 nm (4.54). E.s.r. (benzene at 77 K): g = 2.067.

Preparation of the Monolayers and Built-up Multilayer Films of Tetra-alkyl substituted Metallophthalocyanines.—The surface pressure (π) *vs.* area (*A*) isotherms were studied using a commercially available Langmuir trough (1 999 cm^2) (Kyowa FACE) equipped with a film balance (Kyowa HBM AP). Triply distilled water was used as the sub-phase; the third distillation was performed under a nitrogen atmosphere. The monolayers were obtained by spreading solutions of the substituted metallophthalocyanines in benzene (spectroscopic grade) at a concentration of 10^{-4} mol dm^{-3}. Isotherms were measured at a compression rate of 16.7 cm^2 min^{-1}. The monolayers were transferred by the Langmuir–Blodgett technique at a surface pressure of 10 mN m^{-1} with a dipping rate of 5 mm min^{-1} onto a Pyrex substrate (6.0 × 4.5 × 0.1 cm) treated with sulphuric acid, followed by distilled water.

Measurements.—I.r. spectra were recorded on a JASCO A-302 spectrophotometer and u.v.–visible spectra on a JASCO UVIDEC-505 apparatus. E.s.r. spectra were measured by a Varian E-line spectrophotometer using *X*-band radiation (9.196 GHz at 123 K) with a microwave power of 100 mW; *g* values were calculated using solid diphenylpicrylhydrazyl (dpph) as the *g* marker. Metal analyses were performed with a Hitachi 170-70 Zeeman-effect atomic absorption spectrophotometer. Decomposition temperatures were determined using a Rigaku TG-DSC-CN 8085E1.

Results and Discussion

Synthesis and Characterization.—The corresponding acid chloride of (**1a**) and (**1b**) were prepared as described in a previous paper.[13] The [tetrakis(1- decyloxycarbonyl)phthalocyaninato]-nickel(II) and -copper(II) complexes [(**2a**) and (**2b**)], [tetrakis(1-octyloxycarbonyl)phthalocyaninato]copper(II) (**2c**), and [tetrakis(2-octyloxycarbonyl)phthalocyaninato]copper(II) (**2d**) were obtained by esterification of (**1a**) or (**1b**) with decan-1-ol, octan-1-ol or octan-2-ol (Figure 1). The structures of (**2a**)—(**2d**) are in accord with the spectral data and analytical results (see Experimental section). These alkoxycarbonyl–metallophthalocyanine derivatives exhibit excellent solubility in organic solvents such as benzene, chloroform, toluene, and *o*-xylene. The i.r. spectra exhibit an ester carbonyl stretching band at 1 712—1 720 cm^{-1}. The phthalocyanine rings show characteristic absorptions in the region 1 500—300 cm^{-1}.

The electronic spectra of the tetraesters (**2a**)—(**2d**) were measured in benzene solution, Figure 2. All compounds exhibit absorption bands at 606—682 and 335—339 nm which may be attributed to the *Q* band [$a_{1u}(\pi) \longrightarrow e_g(\pi^*)$] and Soret band [$a_{2u}(\pi) \longrightarrow e_g(\pi^*)$], respectively.[14] The molar absorption coefficients of the nickel(II) complex were lower than those of the copper(II) complexes. The $\lambda_{max.}$ of the *Q* band shifted to longer

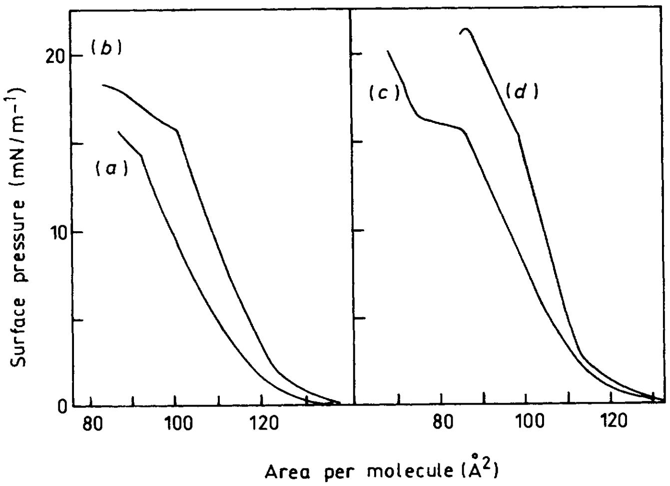

Figure 3. Surface pressure *vs.* area isotherms for the compounds on the water sub-phase at 15 °C: (*a*) (**2a**), (*b*) (**2b**), (*c*) (**2c**), and (*d*) (**2d**)

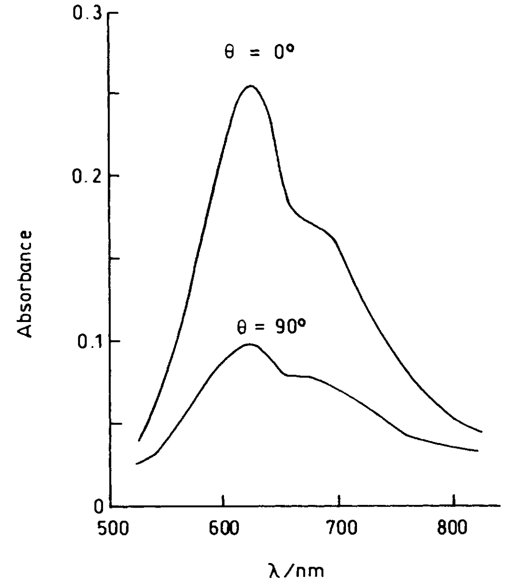

Figure 4. Polarized electronic absorption spectra for the built-up film of 30 layers on a glass substrate from complex (**2b**), monolayer at a surface pressure of 20 mN m^{-1} on the 15 °C sub-phase. θ is the angle between the dipping direction and the polarizing direction of the incident radiation

wavelength in the order (**2d**) > (**2c**) > (**2b**). This may be due to the difference in the solvation energies of the excited states based on the solubility of alkoxycarbonyl groups.[13] The absorption coefficient (ε) at 682 nm of complex (**2d**) is higher than those of (**2b**) and (**2c**). This suggests that the aggregation of phthalocyanine rings is sterically hindered by the α-methyl groups on the alkoxy chain.

The e.s.r. spectra of complexes (**2a**) and (**2d**) in benzene at −140 °C were measured. Complex (**2a**), which is square-planar d^8 and low spin, was diamagnetic. Therefore, the appearance of an e.s.r. signal was not expected. However, a signal at $g = 2.000$ was observed. This may be assigned to a cation radical of the phthalocyanine ring which occurred by partial oxidation. The e.s.r. spectrum of the copper(II) complex (**2d**) was also measured. In the case of a typical square-planar d^9 copper(II) complex, a four-line hyperfine structure (h.f.s.) is expected based on the nuclear spin (^{63}Cu, ^{65}Cu; $I = \frac{3}{2}$).[15] However, a broader spectrum with a centre at $g = 2.067$ was observed. This may be due to the stacking structure of phthalocyanine in benzene solution.

Monolayer Formation.—Monolayer films of (alkyloxycarbonylphthalocyaninato)-nickel(II) or -copper(II) were spread on the air–water interface from benzene solution. Figure 3 shows isotherms of surface pressure *vs.* area per molecule (π *vs.* A) for alkyloxycarbonylphthalocyaninato-metal complexes at 15 °C. The monolayers of these soluble metallophthalocyanines on water were stable to film pressures at 5—15 mN m^{-1}. The limiting surface area per molecule obtained from the isotherm of each compound was about 115 [for (**2a**)], 120 [(**2b**)], 113 [(**2c**)], and 113 Å^2 [**2d**)], respectively. These values were affected by the molecular forms, the chain length, and the chain branching of alkyl groups on the metallophthalocyanine rings. The area occupied by a molecule, *ca.* 113—120 Å^2, was reasonable for tetra-alkyloxycarbonylphthalocyaninato-nickel(II) or -copper(II) molecules which stand on the water surface with their molecular face slanted with respect to the perpendicular. Each monolayer collapses at a surface pressure of 14 mN m^{-1} and a molecular-occupied area of 90 Å^2.

Transfer of Monolayers onto Substrates and the Langmuir–Blodgett Film Characterization.—The transfer of a monolayer of alkoxycarbonylphthalocyaninato-nickel(II) or -copper(II) onto hydrophilic Pyrex substrates was carried out at 15 and 20 °C. Multilayers could be built up on Pyrex substrates by repeated insertions and withdrawals through the compressed monolayer on the water surface. In these cases, once the first layer was deposited, the phthalocyanine derivative continued to transfer in a *Z*-type fashion. The transfer ratio with each insertion and withdrawal of the substrate was constant at 1.0. The monolayers of the phthalocyanine derivatives could be transferred to the substrates at a surface pressure of 10 mN m^{-1} a compression rate of 16.7 cm^2 min^{-1}, and at a dipping rate of 5 mm min^{-1}. LB films of alkoxycarbonylphthalocyaninato-nickel(II) or -copper(II) on hydrophilic Pyrex substrates appeared blue under transmitted light. The electronic absorption spectra of multilayers of phthalocyanine derivatives built up on a Pyrex slide were measured. The spectra display maxima at 615 nm, accompanied by shoulders at about 690 nm. The strong absorptions at 615 and 690 nm could be assigned to a phthalocyanine ligand-centred π–π^* transition $(a_{1u} \longrightarrow e_g)$, similar to that in benzene solution. The absorbances at both wavelengths varied linearly with the number of layers on the substrate, indicative of a fairly constant transfer ratio.

Typical polarized electronic spectra of 30 layers of complex (**2b**) are shown in Figure 4. It is instructive to use polarized light to help identify the preferred orientation of the molecules relative to the LB films. A schematic diagram showing a typical deposition profile is given in Figure 5. If the faces of the phthalocyanine molecules lie perpendicular to the substrate and are orientated along the dipping direction, then the electric field vector of the radiation would couple with an allowed transition only when the incident beam is polarized parallel to the dipping direction ($\theta = 0°$, where θ is the angle between the dipping direction and the polarizing direction of incident radiation). However, if the molecular faces lie perpendicular to both the substrate and dipping direction, the strong absorption would take place only when the incident radiation is polarized perpendicular to the dipping direction ($\theta = 90°$). However, it should be remembered that the optical data will represent average orientation of the molecules with respect to the substrate and the dipping direction. From Figure 4, it was clear that the absorbances of the polarized light parallel to the dipping direction ($\theta = 0°$) at 615 and 690 nm were greater than for that perpendicular ($\theta = 90°$). The absorption ratio (A_0 divided by A_{90}) at $\lambda_{\text{max.}}$ values for 30 layers of complexes (**2b**),

Table. The absorption ratios of the LB films of copper(II)–phthalocyanine derivatives *

Compound	Absorption ratio
(2b)	2.6
(2c)	2.4
(2d)	2.2

* Thirty built-up layers at 15 °C.

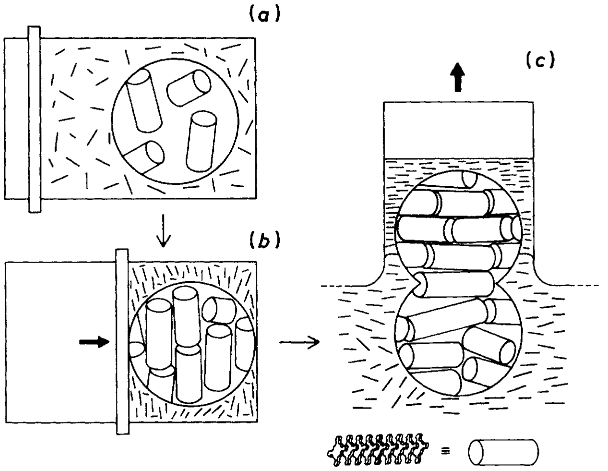

Figure 5. A schematic diagram showing the typical depositon profile of the compounds. (*a*) The plan view of the Langmuir trough before compression of the monolayer; (*b*) the plan view of the trough with the compressed monolayer at the surface pressure of 10 mN m^{-1}; (*c*) the side view at the processes of withdrawing the substrate through the compressed monolayer on the water surface

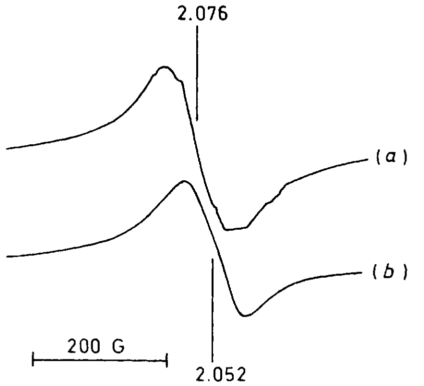

Figure 6. E.s.r. spectra for compound (**2d**); (*a*) in the dip-coated film from benzene solution and (*b*) the 30 layers built-up film on glass rods at ambient temperature (G = 10^{-4} T)

(**2c**), and (**2d**) are shown in the Table. These absorption ratios are within the range 2.2—2.6. The spectra in the LB films displayed absorption maxima at 615 nm, accompanied by shoulders at about 690 nm, similar to that in benzene solution, suggesting stacking of columns of the aggregated tetra-alkoxycarbonylmetallophthalocyanines. These optical data suggest that the stacked columns of molecules are aligned parallel to the substrate and perpendicular to the dipping direction, *i.e.* biaxial orientation. The e.s.r. spectra of complex (**2d**) in the dip-coated film from the benzene solution and in the LB film, 30 layers on Pyrex rod, are shown in Figure 6. The e.s.r. spectra in both solid states exhibit very broad signals at around g = 2.076 and 2.052, respectively, similar to that in benzene solution. This also suggested that (**2d**), in both solid states, is in some aggregated form.

These spectroscopic data support the suggested structure in Figure 5 which shows stacking arrangements of phthalocyanine derivatives in the monolayers on the water sub-phase and the biaxial orientation of the molecules in the built-up multilayers.

Acknowledgements

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References

1 F. H. Moser and A. L. Thomas, 'The Phthalocyanines,' CRC Press, 1983.
2 H. Shirai and K. Hanabusa, *Kagaku Kogyo*, 1987, **38**, 332.
3 H. Shirai, K. Kobayashi, Y. Takemae, A. Suzuki, and O. Hirabaru, *Makromol. Chem.*, 1979, **180**, 2073.
4 S. Shirai, S. Higaki, K. Hanabusa, N. Hojo, and O. Hirabaru, *J. Chem. Soc., Chem. Commun.*, 1983, 751.
5 K. Kobayashi, M. Koshiyama, K. Funayama, T. Osa, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, 1983, 913.
6 O. Hirabaru, T. Nakase, K. Hanabusa, H. Shirai, K. Takemoto, and N. Hojo, *J. Chem. Soc., Chem. Commun.*, 1983, 481.
7 O. Hirabaru, T. Nakase, K. Hanabusa, H. Shirai, K. Takemoto, and N. Hojo, *J. Chem. Soc., Dalton Trans.*, 1984, 1485.
8 N. Kobayashi, H. Shairai, and N. Hojo, *J. Chem. Soc., Dalton Trans.*, 1984, 2107.
9 H. Itoh, S. Kondo, E. Masuda, K. Hanabusa, H. Shirai, and N. Hojo, *J. Polym. Sci., Polym. Lett. Ed.*, 1987, **25**, 413.
10 S. Baker, M. C. Petty, G. G. Roberts, and M. V. Twigg, *Thin Solid Films*, 1982, **99**, 53.
11 S. Baker, G. G. Roberts, and M. C. Petty, *Proc. Inst. Electr. Eng.*, 1983, Part A, **130**, 260.
12 M. Hanack and M. Rein, *Philos. Mag., B*, 1986, **53**, 105.
13 H. Shirai, K. Hanabusa, M. Kitamura, E. Masuda, O. Hirabaru, and N. Hojo, *Makromol. Chem.*, 1984, **185**, 2537.
14 P. Day, G. Scregg, and R. J. P. Williams, *J. Phys. Chem.*, 1963, **38**, 2778.
15 H. Itoh, S. Kondo, E. Masuda, K. Hanabusa, and H. Shirai, *Makromol. Chem., Rapid Commun.*, 1986, **7**, 585.

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