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Asymmetrically substituted liquid-crystalline phthalocyanines and side-chain polymers derived from them

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SUMMARY:

Asymmetrically substituted, liquid-crystalline phthalocyanines were synthesized. They contain one methoxy, six dodecyloxy and one acryloyloxy- or methacryloyloxydodecyloxy groups. The latter functions were polymerized under free radical conditions to give polymers with molecular weights between 9000 and 47000. The aggregation behaviour of the phthalocyanines in the polymer side chains was studied in solution by absorption and fluorescence spectroscopy. An enhanced intramolecular interaction between the phthalocyanines was observed. In the solid state this interaction is reflected in the spontaneous formation of a columnar structure. The polymers, however, do not display liquid-crystalline behaviour. Temperature-dependent luminescence measurements (at 4,2 – 300 K) were performed and the results are explained by the presence of an efficient energy migration process through the stacked phthalocyanine units.

Introduction

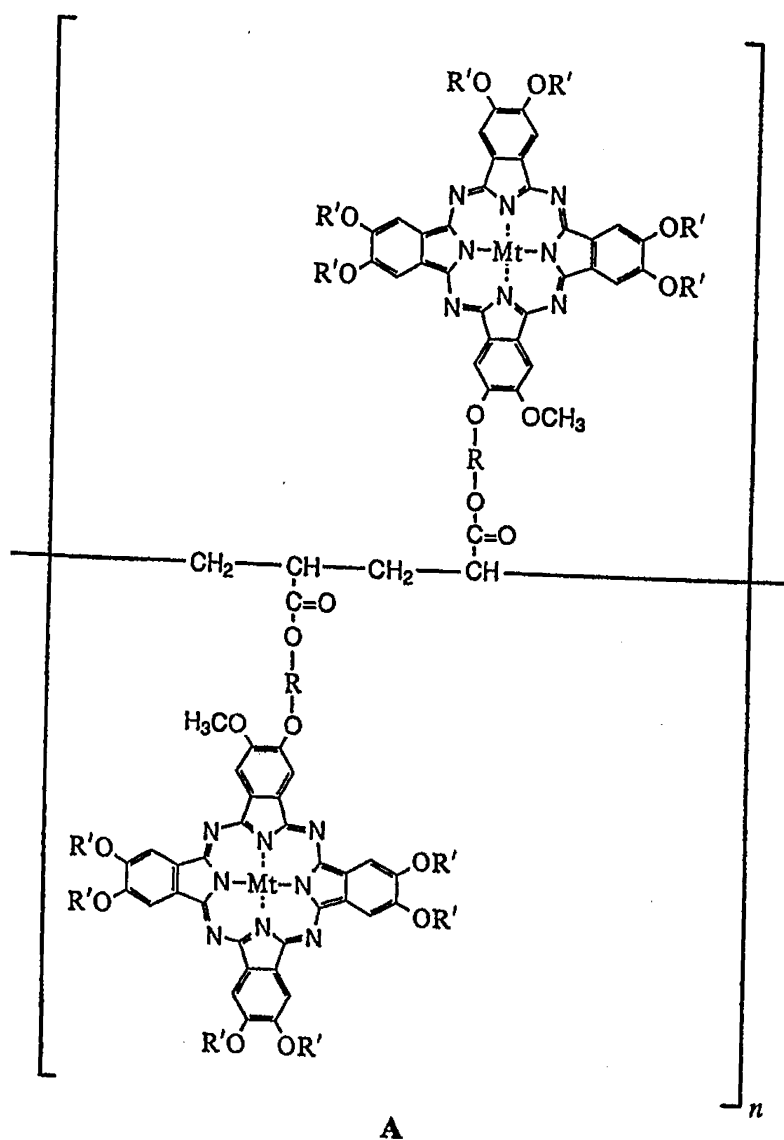
Thermotropic polymeric liquid crystals based on rod-like mesogens have been synthesized and investigated for quite a long time now¹⁾. Both main-chain and side-chain polymers exhibiting (monoaxial and biaxial) nematic^{2,3)}, smectic⁴⁾ and cholesteric⁵⁾ phases are known. In line with the problems encountered in synthesizing asymmetrically substituted disc-like molecules only a few liquid-crystalline polymers based on disc-like mesogens have been reported^{6,7)}. The structural units incorporated in these polymers up to now are triphenylene⁶⁾ and benzene⁷⁾.

Recently, we described the synthesis and mesomorphic properties of low-molecular-weight, peripherally substituted octakis(*n*-alkoxy)phthalocyanine (Pc) derivatives, which appear to exhibit a D_{ho}-phase⁸⁾. We now report on the synthesis and properties of liquid-crystalline Pc monomers which can be polymerized to a homopolymer **A** with Pc as a structural unit in the side chain.

In this polymer the pendant Pc units are connected to the polymer main chain by a flexible spacer. This spacer will partially decouple the motions of the side chains from the polymer main chain, thus allowing the preservation of the liquid-crystalline ordering of the side groups. This spacer concept was first studied systematically by Finkelmann, Ringsdorf et al.⁹⁾ and is generally accepted now.

Incentive of our work is the hope that polymers containing stacked Pc moieties in their side-chains may have interesting electrical properties¹⁰⁾.

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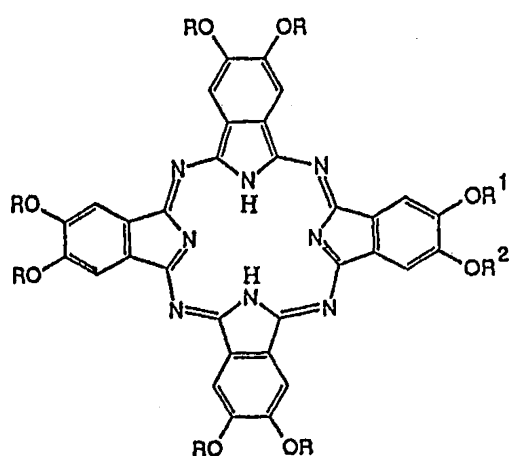


Results and discussion

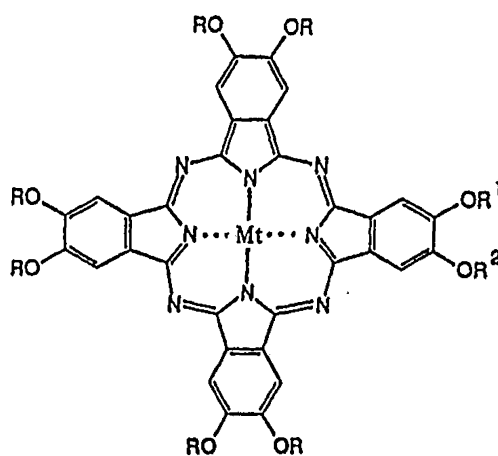
Monomers

Synthesis and characterization

Symmetrically octasubstituted metallo-phthalocyanines (Pc's) exhibit a fourfold symmetry axis and may be synthesized by tetramerization of the appropriately substituted phthalonitriles. Asymmetrically substituted Pc's are more difficult to obtain. The preparation of monofunctionalized Pc's requires the tetramerization of a mixture of phthalonitrile derivatives. In order to facilitate the separation of the different products produced during the reaction, we needed a polar functional group, which afterwards can be used for the introduction of a polymerizable group. A solid phase procedure has been reported in literature¹¹⁾, but it requires at least two extra steps, and the yields are not quite high. Therefore, we preferred the procedure given in *Scheme 1*.



1

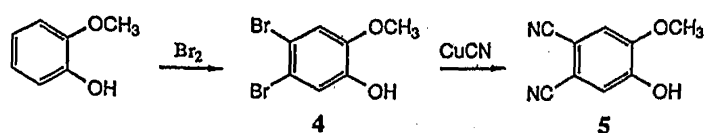


2: Mt = Cu

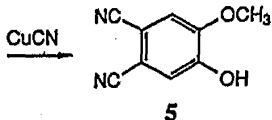
3: Mt = Ni

	R	R ¹	R ²
1a, 2a, 3a	C ₁₂ H ₂₅	C ₁₁ H ₂₂ OC(O)CH=CH ₂	CH ₃
b	C ₁₂ H ₂₅	C ₁₁ H ₂₂ OC(O)C(CH ₃)=CH ₂	CH ₃
c	C ₁₂ H ₂₅	C ₁₁ H ₂₂ OH	CH ₃
d	C ₁₂ H ₂₅	C ₁₀ H ₂₀ CHO	CH ₃
e	C ₁₂ H ₂₅	C ₁₂ H ₂₅	C ₁₂ H ₂₅
f	C ₈ H ₁₇	C ₁₁ H ₂₂ OC(O)CH=CH ₂	CH ₃

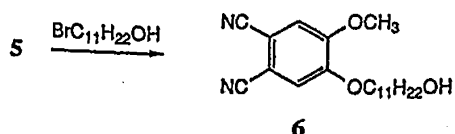
Scheme 1:



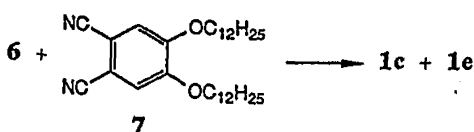
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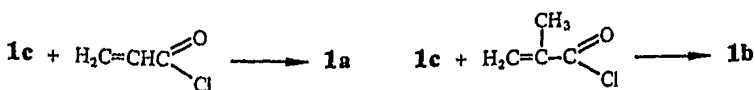
5



6



7



4,5-Didodecyloxyphthalonitrile (7) was synthesized following the procedure reported previously by us⁸). The best route to 4-(11-hydroxyundecyloxy)-5-methoxyphthalonitrile (6) was via 4-hydroxy-5-methoxyphthalonitrile (5). This compound was

prepared from 4,5-dibromo-2-methoxyphenol (**4**) in a Rosenmund-Von Braun reaction, followed by working up with FeCl_3 under acidic conditions¹²). The 11-hydroxyundecyl chain was attached by reacting **5** with 11-bromo-1-undecanol in DMSO in the presence of potassium carbonate. Refluxing a mixture of **7** and **6** in 2-dimethylaminoethanol in a 1:3 mole ratio afforded a mixture of different Pc's which were separated, after Soxhlet extraction, by column chromatography. In the presence of a metal salt the corresponding metallo-Pc's were obtained. A disadvantage of this procedure is the low yield (approx. 4% with respect to the cyanide; 12% of the Pc-products is **1c**) due to the formation of by-products, which are hard to separate from the required monohydroxy Pc. By-products that were isolated are the aldehyde **1d** and the symmetrically substituted Pc **1e** (up to 70% of all Pc-products formed). The formation of aldehyde **1d** can be understood from the mechanism of the reaction. Ring closure of the tetramerized dicyanides requires a reduction step to obtain the Pc. Simultaneously with reduction, an alcohol is oxidized¹³). Normally, this alcohol is 2-dimethylaminoethanol¹⁴), but in our case also the terminal hydroxyl group of dicyanide **6** may be oxidized.

To obtain higher yields of **1c**, we turned to a different route which uses a strong organic base like 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and is performed in low concentrations in an alcohol^{15,16}). The yields of **1c** relative to all Pc-products formed, now approached the statistically expected value of 42,2%.

To our knowledge, this is the highest yield reported so far for the synthesis of Pc's containing one hydroxyl function^{17,18}). Furthermore, the synthesis is quite easy, efficient, versatile and straightforward. Purification is very well possible, due to large differences in R_f -values and the absence of large amounts of Pc-by-products apart from **1e**. Compound **1c** is a dark-green solid at room temperature. The acrylic and methacrylic monomers **1a** and **1b** were obtained by treating **1c** in dry chloroform/triethylamine with acryloyl chloride and methacryloyl chloride, respectively. During this reaction also *N*-substituted products were formed, as was judged from the appearance of an additional band in the UV/Vis-spectrum at 742 nm (Fig. 1)¹⁹). After washing the reaction mixture with water this extra band vanished and the colour changed to light-green, the colour one normally observes for octa-*n*-alkoxy metal-free Pc-derivatives, indicating that the presence of the acryloyloxy or methacryloyloxy groups has no influence on the absorption of the Pc-ring. Similar results were obtained for the corresponding copper and nickel containing Pc's.

Compounds **1a-c**, **2a-c** and **3a-c** were characterized by IR, ^1H NMR, ^{13}C NMR and UV/Vis spectroscopy, except for the CuPc's, which could not be studied by NMR because these compounds are paramagnetic. Their purity was checked by TLC and elemental analysis. All results were in accordance with the proposed structures.

The 200 MHz ^1H NMR spectrum of **1c** [Fig. 2(a)] displays the methylene protons next to the hydroxyl group as a well resolved triplet at $\delta = 3,62$. The protons of the methoxy group are visible as a singlet at $\delta = 4,28$. The asymmetry in the molecule is further reflected by the fact that signals originating from the aromatic protons are present at different shift positions. The fourteen $-\text{CH}_2\text{O-Ar}$ protons are present at $\delta = 4,43$ as a strongly broadened triplet. Signal-broadening of these protons may be

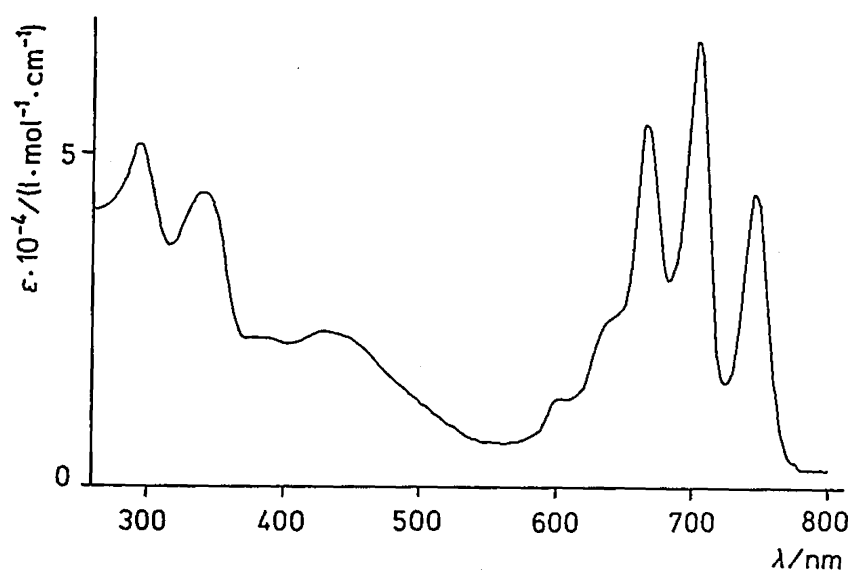


Fig. 1. Vis-spectrum observed during the reaction of 1c with acid chlorides

caused by aggregation of the Pc rings. It is known that Pc's aggregate in relatively concentrated solution¹⁸⁻²¹.

Upon esterifying the hydroxyl group with acryloyl chloride, the triplet at $\delta = 3,62$ shifts 0,53 ppm to lower field. The characteristic coupling pattern of the vinyl group of the product is present between $\delta = 5,7$ and 6,6 [Fig. 2(b)]. The FTIR-spectrum of 1a [Fig. 3(a)] shows the presence of a carbonyl group at 1730 cm^{-1} , while the carbon-carbon double bond is reflected by a weak vibration at 1630 cm^{-1} .

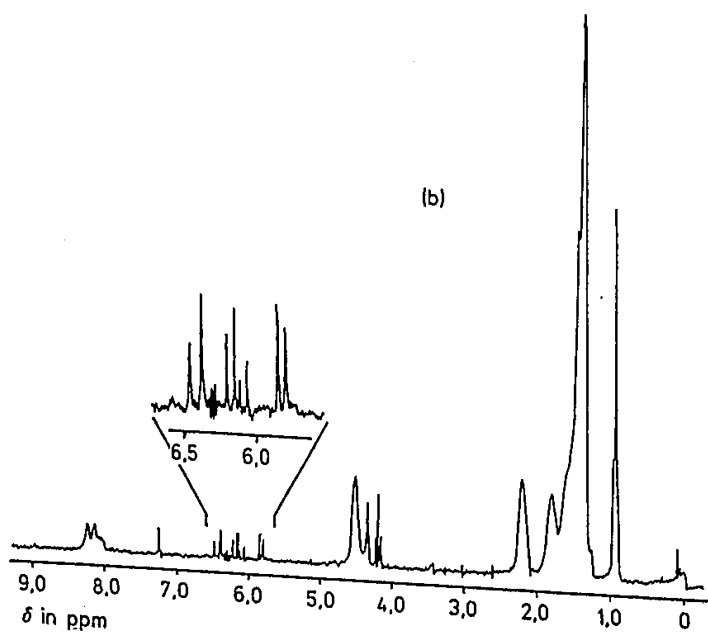
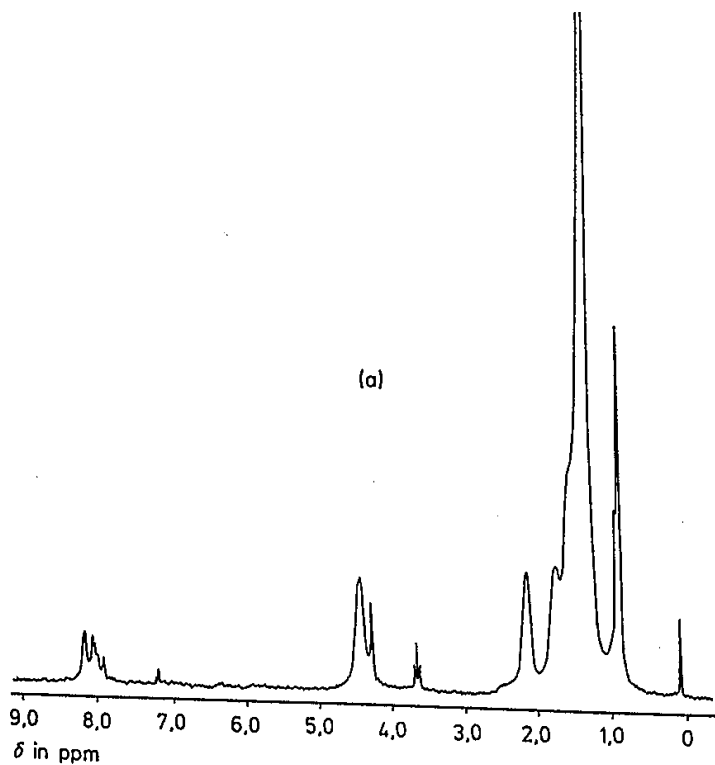
Mesomorphic properties

Phase transition temperatures were determined by DSC and checked by temperature controlled polarizing microscopy. Transitions to the isotropic liquid were not observed until 300°C . The data are presented in Tab. 1 together with the transition enthalpies and calculated entropies. On cooling, the transitions from mesophase to crystal occurred at temperatures approximately 20°C lower than on heating, because of slow nucleation and crystal growth kinetics due to the viscosity of the mesophase. The samples show only one transition upon heating, except for 1a, 3a and 2c. The latter compound shows two transitions. The cooling run reveals only one transition for all these compounds. The thermograms of the metal-free monoacrylate 1a, show an oscillation around 10°C before the main peak appears [Fig. 4(a)]. An oscillation was also observed for nickel Pc, 3a, around 10°C [Fig. 4(b)]. The shape of the oscillation depends on the thermal history of the sample. For the main peak a large difference in enthalpy upon heating (24 J/g) and cooling (10 J/g) was found. This suggests that the oscillation is the result of a transition between on the one hand two metastable phases and on the other hand a thermodynamically stable phase. A similar oscillation has been observed for certain derivatives of linear chain copper(II) alkanoates²².

Polymers

Synthesis and characterization

Anionic polymerization of monomer **1a** with butyllithium in THF did not result in any polymer formation. Therefore, we tried a radical polymerization which was achieved only under very specific conditions i. e. in concentrated oxygen-free benzene



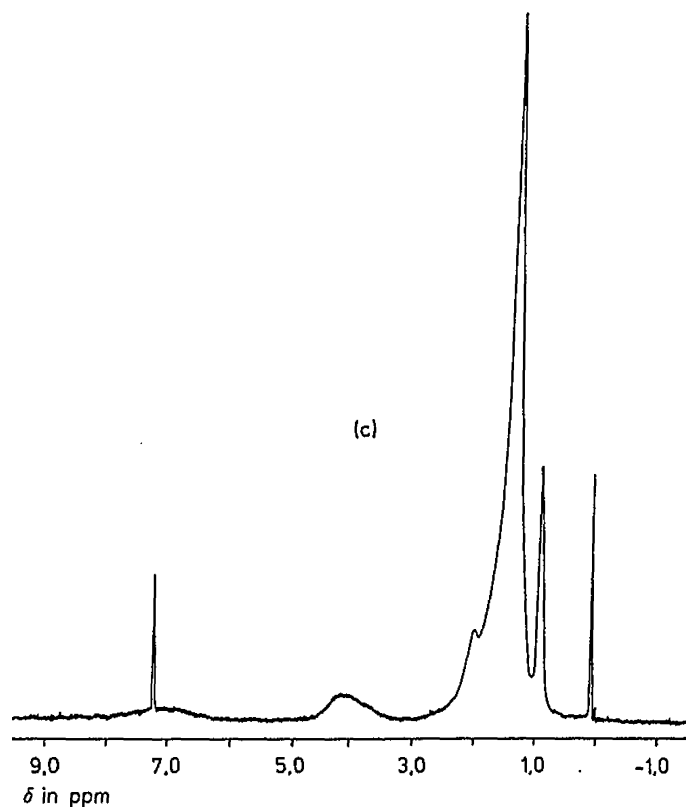


Fig. 2. 200 MHz ¹H NMR spectra of (a): compound 1c, (b): compound 1a, and (c): poly(1a)

solution, at temperatures ranging from 45–60 °C and using a relatively high percentage of the initiator 2,2'-azoisobutyronitrile (AIBN) ($\approx 12\%$). Reaction times were chosen such that a minimum of three half life times of AIBN could elapse.

The results of various polymerization reactions are listed in Tab. 2. The molecular weights of the polymers were markedly influenced by the reaction temperature, monomer concentration and initiator concentration. Monomer concentrations were restricted by the solubility of 1a. As expected, a higher molecular weight polymer is obtained when the concentration of monomer increases, when the ratio initiator/monomer decreases and when the reaction temperature is lowered. The minimum percentage of initiator relative to monomer appeared to be 12. This high value is presumably required because radical impurities are present in molecular materials based on Pc, as was evidenced previously by ESR studies²³). These impurities may partially destroy the initiator, thus setting a lower limit to the ratio initiator/monomer. We found that the highest molecular weights in the polymerization of 1a are obtained under the conditions as given in Tab. 2, Exp. No. 5. Typical GPC runs for monomer 1a, the crude reaction mixture of Exp. No. 5 (Tab. 2) and for the purified polymer sample are shown in Fig. 5. It should be noted that the molecular weights found by GPC are apparent molecular weights. The real molecular weights may differ appreciably from the values in Tab. 2. Higher yields of polymer are obtained in the polymerization of the methacrylic monomer 1b, while also the apparent molecular

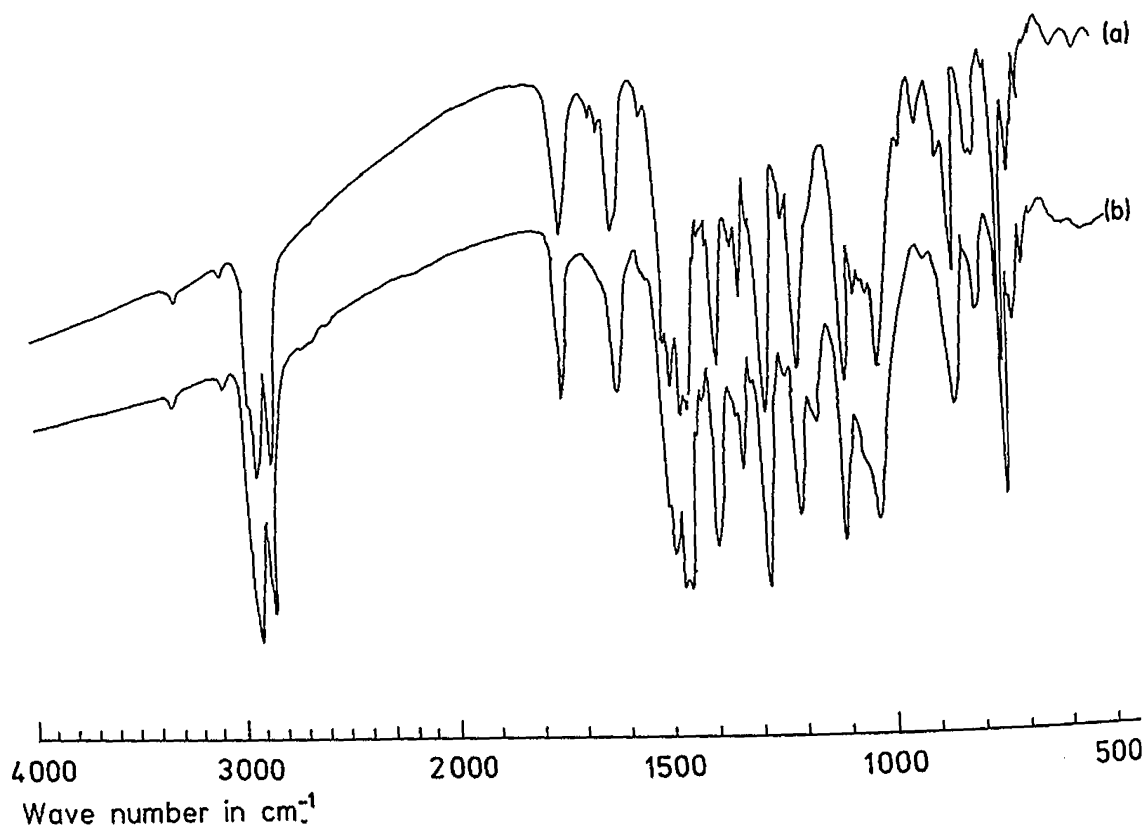


Fig. 3. FTIR spectra of (a): compound 1a, and (b): poly(1a)

Tab. 1. Transition temperatures and thermodynamic parameters^{a)}

Compound	Phase transition temp. in °C K ₁ → K ₂ → M ₁ → M ₂		ΔH /(kJ/mol)	ΔS /(J/mol · K) ^{b)}
1a	10 ^{c)}	52	59 ^{c)}	181 ^{c)}
2a		51	40	123
3a	-2,5 ^{c)}	52	47 ^{c)}	146 ^{c)}
1b		63	56	166
2b		62	44	132
1c		78	57	162
2c		60 112	38, 2,8	114, 7,4
3c		45	39	122

a) Tabulated transition temperatures and enthalpies were observed by DSC during second and subsequent heating runs. Heating rate: 10 K/min. K₁ and K₂ are crystalline phases, M₁ and M₂ are mesophases.

b) $\Delta S = \Delta H/T$, where T is the transition temperature in K.

c) Oscillation (see Fig. 4).

weight is slightly higher (Tab. 2). Polymerization of CuPc 2f yields polymer samples with an apparent molecular weight somewhat lower than the metal-free Pc 1a. The

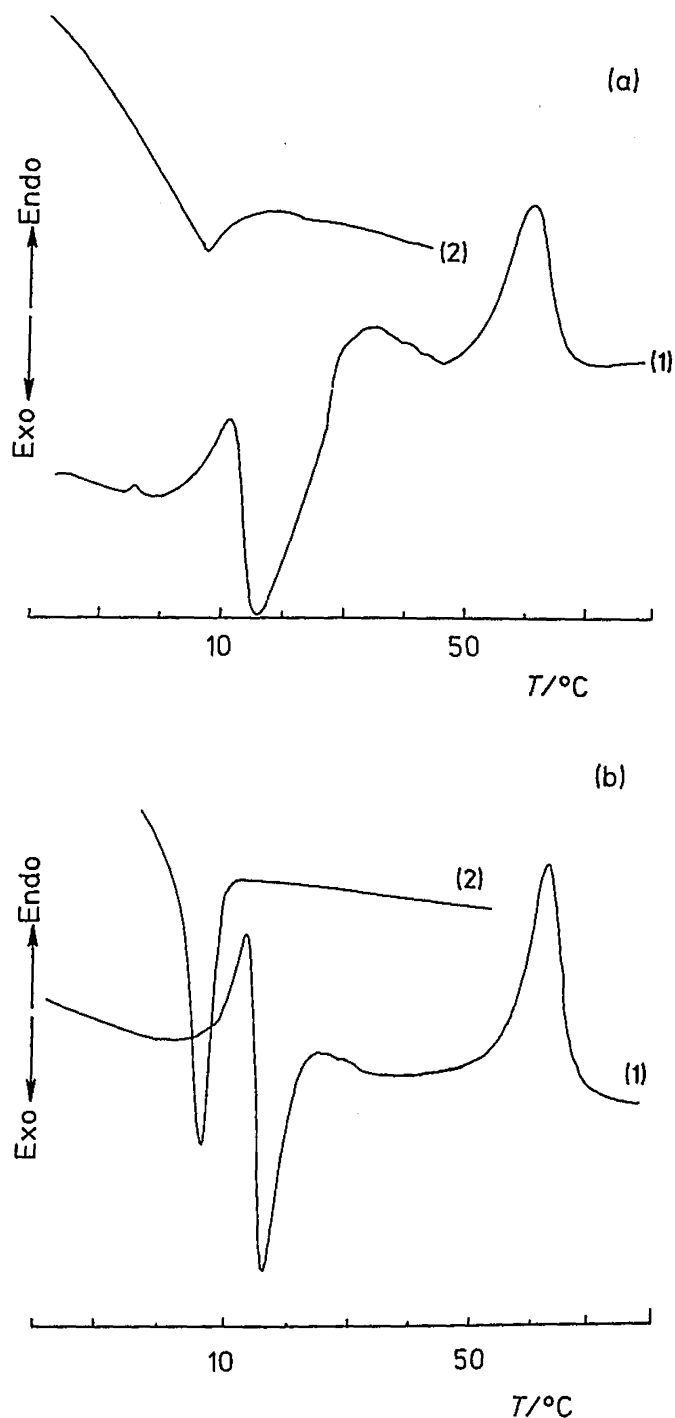


Fig. 4. DSC-thermograms observed for compounds (a): **1a**, and (b): **3a**. Heating (1) and cooling rate (2): 10 K/min

following discussion will concentrate on the polymers obtained from the metal-free monoacrylate **1a**.

The purified polymers are soluble in chloroform, toluene and THF but insoluble in polar solvents such as methanol and DMF.

Fig. 2(c) presents the 200 MHz ^1H NMR spectrum of poly (**1a**). Peaks are observed that are even broader than in the case of the monomer. The aromatic protons are shifted to higher field by as much as 1,5 ppm. This suggests an enhanced intramolecular interaction between the subunits. A similar shift was observed in polymers of

Tab. 2. Results of polymerization reactions in benzene under varying conditions

Exp. No.	Compound	Conc. in mg/cm^3	Amount of AIBN in mol-%	$T/^\circ\text{C}$	t/h	Yield in %	\bar{M} ^{a)}	
1	1a	160	25	60	65	14	9 000	
2			25	50	192	35	11 500	
3			12,5	50	114	48	16 000	
4			320	12,5	50	192	62	27 000
5			320	12,5	45	262	44	45 000
6	1b	320	14,8	50	192	95	47 000	
7	2f	320	12,5	50	192	81	25 000	

a) Apparent \bar{M} values as determined in tetrahydrofuran by gel permeation chromatography. Calibration by polystyrene standards. \bar{M} found for monomer is 2000.

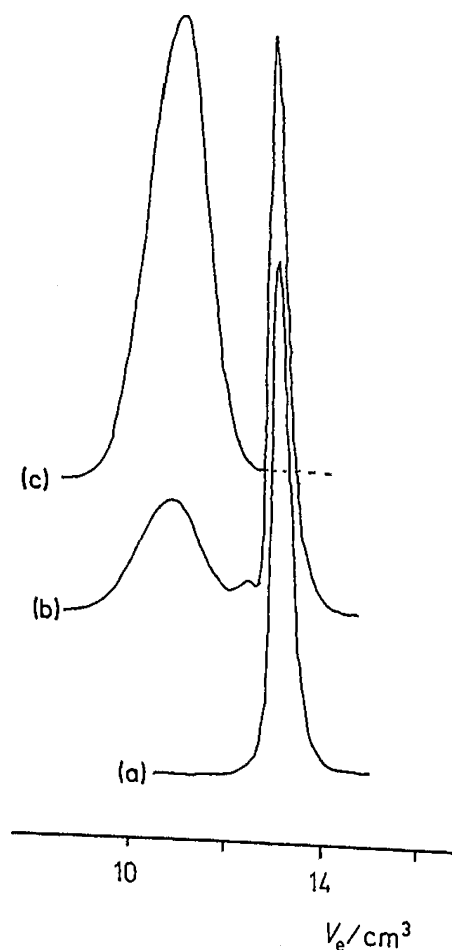


Fig. 5. GPC runs for (a): compound 1a, (b): crude reaction mixture of the polymerization of 1a and (c): purified poly(1a)

dihydroxysilicon-Pc, which could be explained by a classic five-loop-pair ring-current model²⁴. The FTIR spectrum of poly(1a) [Fig. 3(c)] shows a carbonyl vibration that is shifted 20 cm^{-1} to higher frequency as a consequence of the disappearance of conjugation with the acrylic CC double bond. Both the signals due to the acrylic C—H out of plane (1070 cm^{-1}) and the rocking (880 cm^{-1}) vibrations, as well as the signals due to the double bond (1610 cm^{-1}) have disappeared in the spectrum.

DSC did not reveal any phase or glass transition in the polymers; they are obviously not liquid-crystalline. Hot stage polarizing microscopy shows that the polymers do not flow; they display a uniform birefringence. This birefringence increases when the temperature is raised.

Structure

We performed X-ray diffraction measurements on poly (1a) and poly (1b). At room temperature a sample of the material, as it is obtained in the polymerization reaction, gives rise to a number of reflections. At small angles a strong reflection corresponding to approximately 29 Å and a vague reflection between 14 and 17 Å are present. At larger angles reflections show up corresponding to $d = 4,5$, 3,3 and 7,1 Å. These observations indicate that the polymer is partially crystalline and that the structure consists of a two-dimensional hexagonal array of ordered columns. As the temperature increases the vague band between 17 and 14 Å sharpens to two sharp reflections at $d = 16,7$ and 14,5 Å. The other reflections present remain essentially unchanged. Cooling down to room temperature does not change this diffractogram. The intercolumnar distance is 33,4 Å, being somewhat smaller than the value of 35,0 Å, found for Pc(OC₁₂H₂₅)₈⁸⁾. The distance between the Pc-units corresponds to 3,32 Å. The broad reflection around 4,5 Å is indicative of disordered, non-crystallized paraffinic chains. Our observations indicate that upon increasing the temperature the columnar arrangement of the Pc units becomes more perfect. Thus, although no first order transition or macroscopic mobility of the polymer is observed, the Pc-units apparently have some ability to move on a molecular scale. No glass transition is present, which shows that the mobility of the main chain polymer segments is strongly hindered. A similar behaviour was found for main-chain polymers containing triphenylene units²⁵⁾.

The polymers do not exhibit a liquid-crystalline phase. Obviously, the inter-Pc forces in the polymer are too strong to allow this at elevated temperature. This may partially be caused by the long aliphatic substituents, since the Van-der-Waals interactions between the side chains play an important role in determining mesomorphic properties. Somewhat shorter side-chains might give liquid crystalline polymers. Therefore, the polymer obtained from 2f was studied. This polymer did not show liquid-crystalline behaviour either. Its structure fully corresponds to the D_{ho}-structure found in liquid-crystalline phases of the low-molecular-weight analogues⁸⁾. This implies a non-tilted stacking in columns and the possibility of interesting one-dimensional transport properties.

Aggregation behaviour in solution

Absorption spectroscopy

A sensitive probe for the presence or absence of coupling between two or more Pc-units is the electronic absorption spectrum²²⁻²⁴⁾. In the absence of coupling, metal-free Pc shows two sharp bands at 664 (log $\epsilon = 5,1$) and 700 nm (log $\epsilon = 5,2$), called

the *Q*-bands, and two weaker vibrational components at the higher energy side of the main absorption [Fig. 6(a)]. With a central metal ion present, e.g. as in **2a** the symmetry increases from D_{2h} to D_{4h} and the splitting of the *Q*-band disappears [Fig. 6(b)]. When coupling of Pc-units occurs the peaks at 664 and 700 nm decrease in intensity, and a new absorption at 625 nm appears^{26,27}. The absorption spectra have been explained both in terms of molecular orbital overlap²⁸) and in terms of exciton coupling due to the close approach of two Pc-rings^{29,30}). The polymer synthesized from **1a** shows a broader and less intense ($\log \epsilon_{625} = 4,6$) absorption band than the monomer in the 610–650 nm region and weak shoulders at 664 and 700 nm. These shoulders point to the presence of some residual monomer, which must be in equilibrium with the aggregated species [Fig. 6(a)]. A more pronounced shoulder at 680 nm is visible in the spectrum of poly(**2a**) [Fig. 6(b)]. The polymer obtained from compound **1b** exhibits the same absorption spectrum as poly(**1a**), indicating that the nature of the polymer backbone has no influence on the aggregation of the side-chains. To exclude that the observed UV/Vis-spectra are due to compounds formed in chemical reactions with initiating or propagating radicals during the polymerization, a control experiment was performed with **1e** and an excess of AIBN at 60 °C in benzene. No changes in the absorption spectrum occurred during this experiment. Accordingly, the change in position and intensity of the band, relative to the mononuclear species, is a direct indication of coupling between Pc units. The spectra do not change upon dilution, suggesting that the coupling is intramolecular in nature. It might be anticipated that the repeating units in the polymer exist in various conformations which are in dynamic equilibrium. A solution of the polymer at room temperature would likely contain a selection of species ranging from strongly coupled to uncoupled, and the electronic spectrum would be a composite of the absorption spectra of these species. For some binuclear Pc's³⁰), such a composite spectrum has indeed been observed. In our case, however, only a very weak shoulder at 700 nm might originate from some uncoupled Pc units, indicating that virtually all Pc units are aggregated. This result is in contradiction to the assumption in Ref.²⁹) that with long spacers, overlap between different Pc units is zero. It is noteworthy that the absorption spectra of our polymers very much resemble those of cofacial dimers of 'crowned' phthalocyanines^{31,32}).

Fluorescence emission spectroscopy

For mononuclear metal-free Pc species fluorescence emission from the lowest π^* -state is common³³). In chloroform solution mononuclear $H_2Pc(OC_{12}H_{25})_8$ (**1e**) exhibits a strong emission band at $\lambda = 707$ nm. Furthermore, bands are observed at $\lambda = 675$, 740 and 790 nm (Fig. 7, at 10^{-6} mol/dm³). Whereas for this compound the absorption spectrum is not conspicuously altered by dilution, the emission characteristics are strongly dependent on concentration (Fig. 7). At $6 \cdot 10^{-4}$ mol/dm³ only one band is observed ($\lambda = 790$ nm). On dilution to $3 \cdot 10^{-4}$ mol/dm³ this band becomes weaker, while the band at 740 nm increases in intensity³⁴). Upon further dilution the 740 nm band loses most of its intensity, while new bands appear at 675 and 707 nm. The same behaviour was observed for $H_2Pc(CH_2OC_{12}H_{25})_8$ by Knoesel et al. in benzene

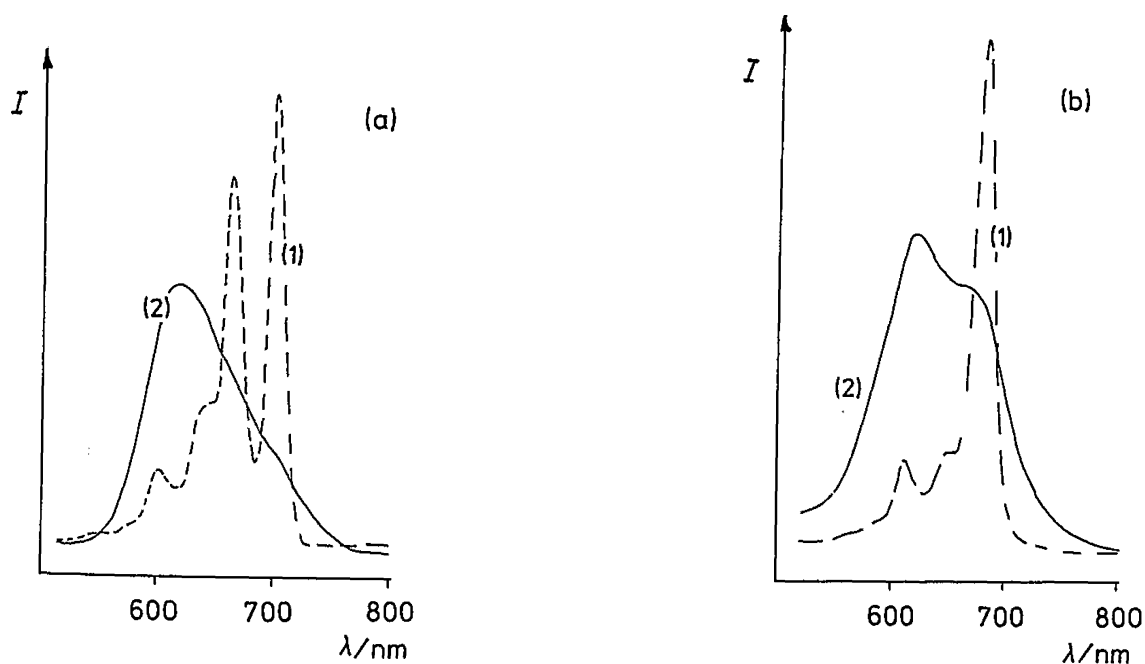


Fig. 6. UV/Vis spectra of (a): mononuclear (1) and polymeric (2) 1a, (b): mononuclear (1) and polymeric (2) 2a

solution²¹). These authors interpreted these changes in terms of aggregate formation. Aggregation is, however, not indicated by the absorption spectra.

Fig. 8 shows that the 707 nm emission band of compound 1e partially overlaps with the absorption band, while the bands at 740 and 790 nm do not. The change in the emission spectrum (Fig. 7) when going to higher Pc concentration, therefore, can be explained by reabsorption of emission intensity instead of aggregation. The results from this work are in line with those from fluorescence experiments on aggregation behaviour upon increasing solvent polarity³⁴).

The acrylic polymer, poly(1a), exhibits its main emission band at 702 nm, somewhat blue-shifted relative to the monomer emission. Satellites are present at the same wavelength positions as in the mononuclear spectrum of 1e and 1a. As compared to 1e the emission intensity has decreased to 6%. It has been suggested³⁰) that the weaker intensity of the emission spectrum of binuclear Pc's reflects intramolecular selfquenching through several possible mechanisms including relaxation to triplet states and non-radiative vibrational relaxation. The minor blue shift observed in poly(1a) is probably caused by a somewhat less polar environment of the emitting species in the polymer than in the mononuclear species, where the polarity is determined by the solvent. The excitation spectra of the polymer emission at 702 nm and its vibrational satellites, are similar to the absorption spectrum of the mononuclear species, indicating that the aggregated species do not emit. The residual emission intensity is due to the small amount of non-aggregated species in equilibrium with the aggregated ones, in agreement with the observed absorption spectra.

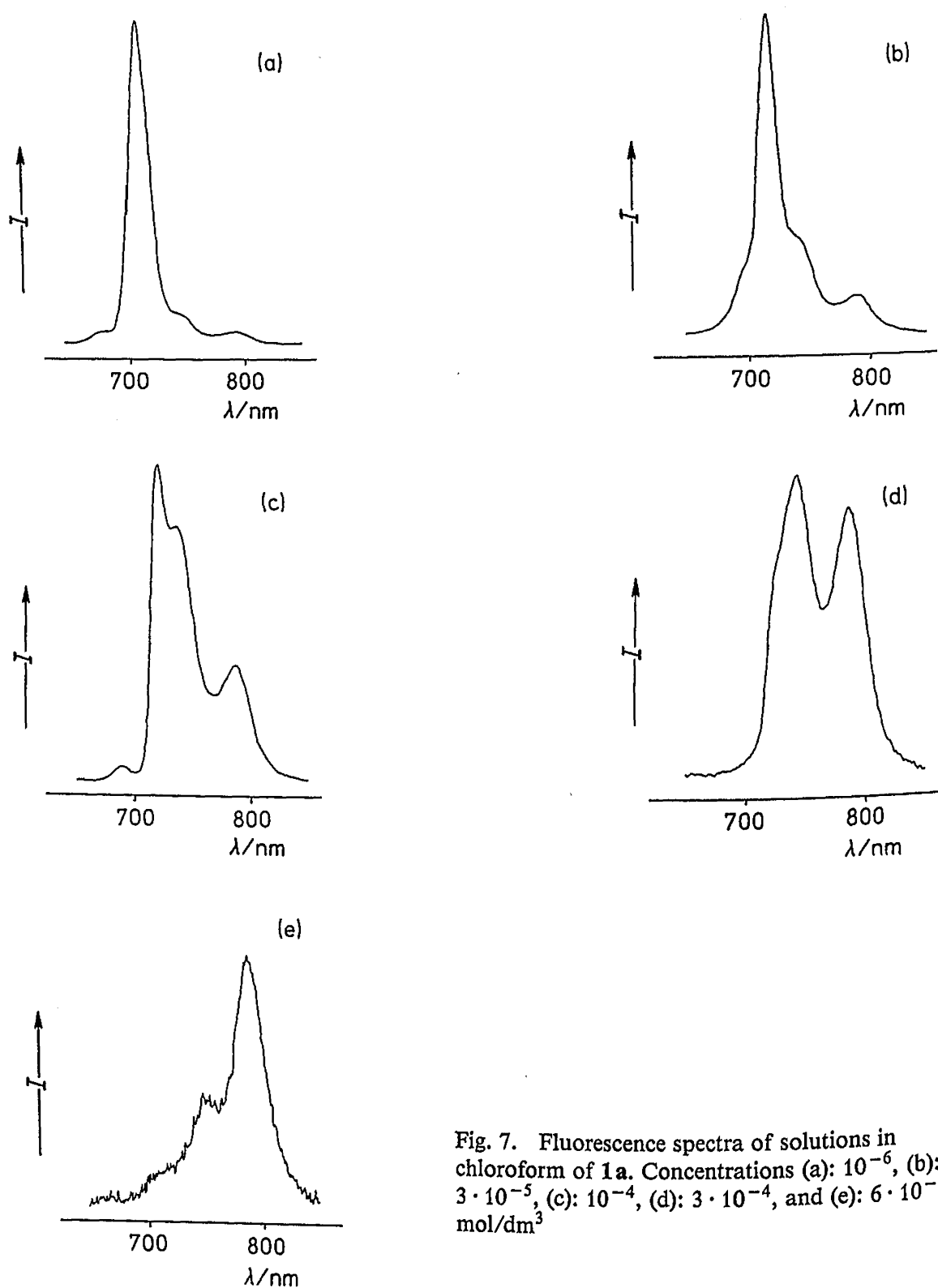
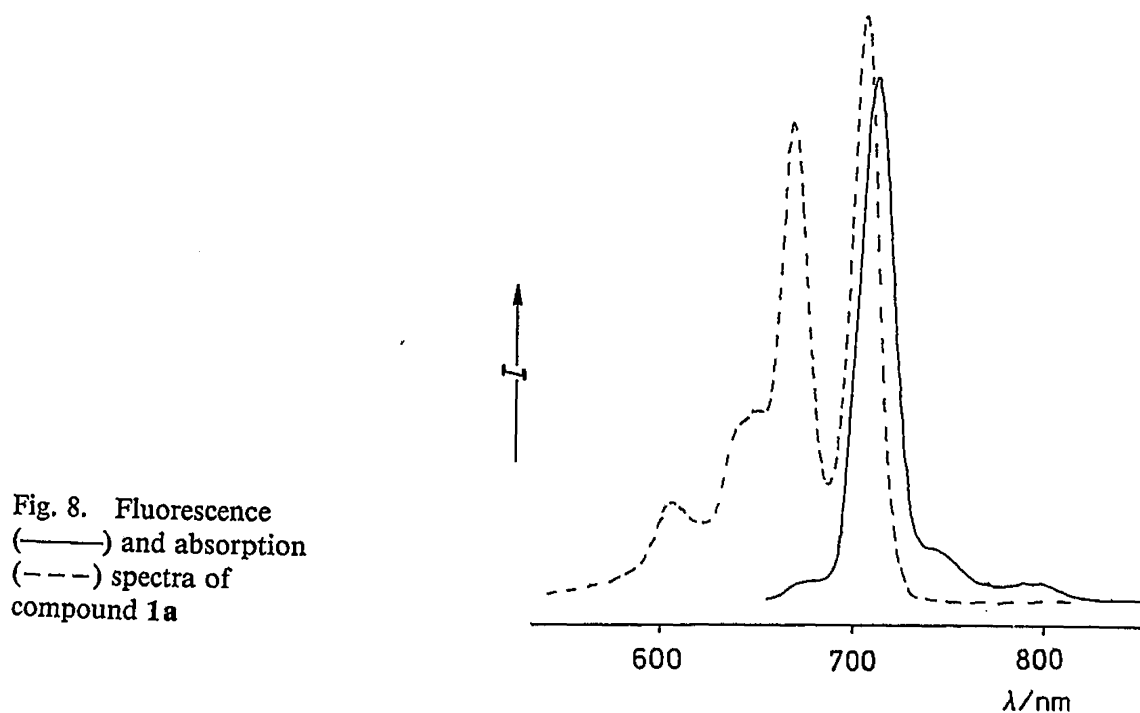


Fig. 7. Fluorescence spectra of solutions in chloroform of **1a**. Concentrations (a): 10^{-6} , (b): $3 \cdot 10^{-5}$, (c): 10^{-4} , (d): $3 \cdot 10^{-4}$, and (e): $6 \cdot 10^{-4}$ mol/dm³

Luminescence and energy migration in the solid state

Exciton migration has been shown to occur in solid, unsubstituted H₂Pc^{35, 36} and in the solid phase and columnar mesophase of compound **1e**³⁷. For compound **1e** it was concluded that the exciton migration rate depends on the stacking of the H₂Pc units



in the columns. The highest one-dimensional migration rate is observed when the molecular planes are perpendicular to the axis of the stack³⁷). The luminescence of the polymer of monomethacrylate **1b** was investigated in the solid state down to 4,2 K. The measurements were performed using exciting radiation with a wavelength of 590 nm, i. e. excitation occurs in the lowest absorption band (*Q*-band). The emission spectrum consists of a single broad band with a maximum at 830 nm. The quantum efficiency q at 4,2 K is approximately 15% and decreases more or less linearly with temperature. At 300 K it amounts to approximately 4%. This behaviour is in striking contrast with that of compound **1e**³⁷), which shows a high q value at 4,2 K and two emission bands with maxima at 795 (intrinsic emission) and 820 nm (extrinsic emission; an extrinsic site is present in a slightly disturbed part of the stack). The energy migration model used to explain these results³⁷) can also account for the present results.

In poly(**1b**) the stacking at low temperatures is similar to that of the mesophase of **1e**, and energy migration through the Pc-stacks is fast. Therefore, the excitation energy is likely to reach a quenching site (traces of CuPc), and the quantum efficiency is low. However, in the present polymer the Pc stacking will be somewhat more disturbed than in the mesophase of **1e**, so that the concentration of extrinsic Pc-molecules is higher. The 830 nm emission is ascribed to these molecules. The decreasing luminescence intensity upon increasing temperature is ascribed to temperature activated detrapping of the energy of the excited extrinsic molecules followed by energy migration to quenching sites. It is satisfying to find that at 300 K the quantum efficiencies of poly(**1b**) and of compound **1e**³⁷) are comparable, since trapping by extrinsic sites is less important then.

Our interpretation is confirmed by the fact that the spinal columnar polymer of 2,3,9,10,16,17,23,24-octadodecyloxydihydroxysilicon Pc ($\bar{M} = 200\,000 \pm 32\,000$

g/mol by small angle X-ray scattering) does not show luminescence, not even at 4,2 K³⁸). In this polymer the Pc planes are well oriented on top of each other and the excitation energy can run smoothly to the quenching sites.

Experimental part

Catechol was recrystallized three times from toluene and stored at 4 °C under nitrogen. Triethylamine was distilled from CaH₂ and stored at 4 °C under nitrogen. Methylene chloride and chloroform were distilled from CaCl₂ before use. Guajacol, 11-bromo-1-undecanol, bromine and CuCN were used as received. DMSO and DMF were stored on molecular sieve (4 Å).

4,5-Didodecyloxyphthalonitrile (7) was synthesized according to the procedure given in Ref. ⁸). ¹H NMR spectra were recorded on Varian EM-360 and Bruker WP-200 instruments. Chemical shifts are given in ppm relative to TMS. Abbreviations used are as follows; s, singlet; t, triplet; m, multiplet; br, broad; v br, very broad; sh, shoulder. Infrared, UV-Vis and fluorescence spectra were taken on a Perkin-Elmer 283, a Perkin-Elmer 555, and a Perkin-Elmer 650-40 Fluorescence Spectrophotometer equipped with a Xe lamp, respectively. Solid state luminescence measurements were performed using a Perkin-Elmer spectrofluorometer MPF-44 equipped with a Xe lamp, a red-sensitive photomultiplier (Hamamatsu R928) and a liquid-helium flow cryostat (Oxford Instruments).

DSC thermograms were determined on a Perkin Elmer DSC 2 Differential Scanning Calorimeter.

FAB mass spectra were recorded on a VG ZAB 2F spectrometer.

X-ray diffraction measurements were performed with a Kiessig camera (Ni filtered Cu-K α radiation).

Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands.

4,5-Dibromo-2-methoxyphenol (4): Guajacol (2-methoxyphenol), (62,1 g; 0,5 mol) was dissolved in 200 cm³ of dry methylene chloride. As catalyst 1 cm³ of a solution of BF₃ (50% in ether) was added. To this solution 176 g (56,8 cm³; 1,1 mol) of bromine in 100 cm³ of chloroform was added during approximately 1 h at 0 °C. The mixture was stirred for an additional 3 h at room temperature to complete the reaction. The reaction mixture was washed subsequently with 10% aqueous NaHCO₃, 10% aqueous NaHSO₃ and water, and dried over MgSO₄. The extract was evaporated to dryness. Recrystallization from hexane/chloroform (vol. ratio 8/1) yielded pure product; m. p. 93,8 °C. Yield: 112 g (79%).

FAB MS *m/z* 280/282/284 (*M*⁺), 265/267/269 ([*M* - CH₃]⁺).

IR (KBr): 3400 (O—H), 2820 (OCH₃), 1430 (ArOH), 645 (ArBr), 1050 cm⁻¹ (C—OH).

¹H NMR (CDCl₃): δ = 3,85 (s; 3 H, —OCH₃), 5,55 (s; 1 H, OH), 7,05 (d; 2 H, ArH).

4-Hydroxy-5-methoxyphthalonitrile (5): 15,49 g (53 mmol) of 4,5-dibromo-2-methoxyphenol (4) was dissolved in 300 cm³ of DMF. 14,32 g (0,16 mol) of CuCN was added. After being evacuated the mixture was refluxed for 7 h under an atmosphere of dry nitrogen. Initially, the mixture turned brown and a slightly coloured compound precipitated, which dissolved after approx. 15 min. After being cooled, the reaction mixture was poured into 3 dm³ of a solution of 37 g (0,16 mol) of FeCl₃ in 5% aqueous HCl. This mixture was heated to 80 °C while stirring. A crude product was obtained by extraction with ethyl acetate. The organic layer was washed with 5% aqueous HCl and water, and dried over MgSO₄. After filtration the ethyl acetate was evaporated and the remaining solid treated in a Soxhlet apparatus subsequently with hexane (6 h) toluene (2 days) to collect the product. The brownish residue was recrystallized from 175 cm³ acetone/water (vol. ratio 3/4); m.p. 234 °C. Yield: 4,3 g (45%).

FAB MS *m/z* 174 (*M*⁺).

IR (KBr): 3250 (O—H), 2935/2840 (OCH₃), 2220/2210 (C≡N), 1083 cm⁻¹ (ArOC).

¹H NMR (DMSO-*d*₆): δ = 3,97 (s; 3 H, OCH₃), 7,64 (d; 2 H, ArH), 11,1 (br; 1 H, OH).

4-(11-Hydroxyundecyloxy)-5-methoxyphthalonitrile (6): A mixture of 4,4 g (24 mmol) of 4-hydroxy-5-methoxyphthalonitrile (5), 6,9 g (25 mmol) of 11-bromo-1-undecanol in 150 cm³ of DMF and 4,0 g (30 mol) of K₂CO₃ was stirred at 90 °C in a dry nitrogen atmosphere for 7 h. Subsequently, 300 cm³ of water and 200 cm³ of methylene chloride were added and the mixture was stirred until two clear layers were obtained. The aqueous layer was extracted three times with methylene chloride. The combined organic extracts were washed with 5% aqueous NaHCO₃ and water (3 × 100 cm³) and dried over MgSO₄; the solvent was evaporated. Chromatographic separation (SiO₂; eluent: chloroform/ethyl acetate (vol. ratio 4/1) gave a white solid; m.p. 107,4 °C. Yield: 7,1 g (50%).

FAB MS m/z 344 ($[M + 1]^+$).

IR (KBr): 3560 (free O—H), 3400 (O—H), 2220 (C≡N), 1455 (CH₂—OH), 1220 (Ar OC), 1050 cm⁻¹ (ArOC).

¹H NMR (CDCl₃): δ = 1,3 (br, s; 18H, CH₂), 2,0 (s; 21H, —OH), 3,6 (t; 2H, CH₂OH), 3,9 (t; 4H, OCH₃), 4,0 (ArOCH₂), 7,15 (s; 2H, ArH).

2-(11-Hydroxyundecyloxy)-3-methoxy-9,10,16,17,23,24-hexakis(dodecyloxy)phthalocyanine (1c)

Method A: A mixture of 4,5-dodecyloxyphthalonitrile (7) (3,7 g; 7,4 mmol) and 4-(11-hydroxyundecyloxy)-5-methoxyphthalonitrile (6) (0,9 g; 2,5 mmol) in 4,5 cm³ of 2-dimethylaminoethanol was refluxed for 72 h under a nitrogen atmosphere. After being cooled the mixture was diluted with 10 cm³ of chloroform and dropped into 150 cm³ of acetone. The precipitate was filtered over a sintered glass funnel (G4). The residue was treated in a Soxhlet apparatus with acetone (24 h), methanol (4 h) and diethyl ether (4 h). The remaining solid was solubilized with chloroform. Yield of crude product: 1,66 g (36%). TLC (SiO₂) eluent CHCl₃/acetone (vol. ratio 10/1: R_f (1c) = 0,2; R_f (1e) = 0,8). The desired product was isolated by column chromatography over SiO₂ (eluent: chloroform). Yield: 194 mg (4,2%) of pure 1c.

IR (KBr): 3400 (OH), 3280 (NH), 2840/2955 (CH), 1272 (ArO), 1095 (ArOC), 740 cm⁻¹ (ArCH).

¹H NMR (200 MHz; CDCl₃): δ = -4,1 to -3,8 (v br; 2H, NH), 1,0 (t; 18H, CH₃), 1,1–1,9 (br; 123H, CH₂ + OH), 2,2 (br, t; 14H, OCH₂CH₂), 3,65 (t; 2H, CH₂OH), 4,35 (s; ArOCH₃), 4,50 (br, t; 14H, ArOCH₂), 7,9–8,4 (m; 8H, ArH).

¹³C NMR (CDCl₃): δ = 14, 23, 26, 27, 29, 30, 33, 34, 57, 63, 70, 103, 104, 105 (CH₂), 129, 130, 148, 152 (ArC).

UV/Vis (CHCl₃): λ_{\max} [$\log \epsilon / (l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$] = 701 [5,18], 664 [5,09], 648 (sh), 603 [4,41], 412 [4,65], 344 [5,01] 290 nm [5,08].

C ₁₁₆ H ₁₈₆ N ₈ O ₉ (1836,8)	Calc.	C 75,85	H 10,21	N 6,10	O 7,84
	Found	C 75,63	H 10,26	N 6,30	O 7,81

Method B: A mixture of 263 mg (0,8 mmol) of 4-(11-hydroxyundecyloxy)-5-methoxyphthalonitrile (6), 1,2 g (2,4 mmol) of 4,5-didodecyloxyphthalonitrile (7) and 208 mg (3,1 mmol) DBN and 7,5 cm³ of absolute ethanol was heated under reflux for 40 h. After being cooled the mixture was diluted with 10 cm³ of chloroform and dropped into 300 cm³ of vigorously stirred acetone. The precipitate was suction filtered, washed with acetone and dried. The crude product was further purified in a Soxhlet apparatus with acetone³⁹⁾ (24 h) and solubilized with chloroform. Yield of crude product: 527 mg (36%). Column chromatography over SiO₂ (eluent: 5% acetone in CHCl₃) yielded 196 mg (13,4% with respect to dicyanide, 37% with respect to crude product) of 1c. Also 190 mg (13,0 and 36%, respectively) of H₂Pc(OC₁₂H₂₅)₈ was isolated. For analytical data see method A.

2-(11-Acryloyloxundecyloxy)-3-methoxy-9,10,16,17,23,24-hexakis(dodecyloxy)phthalocyanine (1a): To a solution of 250 mg (136 μmol) of phthalocyanine 1c and 100 mm³ of triethylamine in 3 cm³ of dry chloroform in a Schlenk vessel was added 550 mm³ (681 mmol) of acryloyl chloride at 0 °C. After stirring for 48 h at room temperature the formation of product was checked with TLC (SiO₂; eluent 5% acetone in chloroform; R_f (1a) = 0,8). 300 mm³ of water was added and

the reaction mixture was evaporated to dryness. The residue was dissolved in chloroform and the solution was washed with 10% NaHCO₃-solution in water, dried over MgSO₄, filtered, and concentrated under vacuum. A final purification by column chromatography over silica (eluent 1% acetone in chloroform) yielded 244 mg (95%) of 1a.

IR (KBr): 3300 (NH), 2850/2920 (CH), 1272 (ArO), 1095 (ArOC), 1730 (C=O), 1635 (C=C), 745 cm⁻¹ (ArCH).

¹H NMR (200 MHz; CDCl₃): δ = -4,1 to -3,8 (v br; 2H, NH), 0,95 (t; 18H, CH₃), 1,1-1,9 (br; 122H, CH₂), 2,2 (br, t; 14H, OCH₂CH₂), 4,20 (t; 2H, CH₂OC(O)), 4,35 (s; 3H, ArOCH₃), 4,50 (br, t; 14H, ArOCH₂), 5,8-6,5 (m; CH=CH₂), 8,0-8,4 (m; 8H, ArH), UV/Vis (CHCl₃): λ_{max} [log ε/l · mol⁻¹ · cm⁻¹] = 702 [5,16], 664 [5,07], 645 (sh), 602 [4,38], 412 [4,62], 344 [4,99], 290 nm [5,05].

C ₁₁₉ H ₁₈₈ N ₈ O ₁₀ (1890,9)	Calc.	C 75,59	H 10,02	N 5,93	O 8,46
	Found	C 75,46	H 10,20	N 5,96	O 8,38

Poly-2-(11-acryloyloxundecyloxy)-[3-methoxy-9,10,16,17,23,24-hexakis(dodecyloxy)phthalocyanine] [poly (1a)]: In a typical experiment (Tab. 2, Exp. No. 5) 80 mg (42 μmol) of 1a and 2 cm³ of a solution of AIBN in chloroform (2,6 μmol/cm³) were mixed in an Schlenk vessel. The chloroform was evaporated, 250 mm³ of dry benzene (p. a.) was added and the mixture was homogenized. The solution was deoxygenized by three freeze-thaw cycles and the mixture stirred for 262 h at 45 °C under a dry nitrogen atmosphere. The reaction mixture was evaporated to dryness. The polymer was isolated by Gel Exclusion Chromatography over a Sephadex LH-60 column (i. d. 30 mm, high 330 mm, 23 g Sephadex), eluent: THF. After a second purification over Sephadex 61 mg (73%) of very pure polymer, \bar{M} = 45 000 (by GPC), was obtained.

IR (KBr): 1735 (C=O), 737 (ArCH) cm⁻¹.

¹H NMR 200 MHz (CDCl₃): δ = 0,95 (br.; 18H CH₃), 1,1-2,2 (br.; 136H, CH₂), 4,2 (br.; 19H, 7,0 (br.; 8H, ArH).

UV-Vis (CHCl₃) λ_{max} [log ε/(l · mol⁻¹ · cm⁻¹)] = 696 sh, 665 sh, 630 [4,63], 404 [4,39], 335 [4,80], 292 nm [4,87].

(C ₁₁₉ H ₁₈₈ N ₈ O ₁₀) _n (1890,9) _n	Calc.	C 75,59	H 10,02	N 5,93	O 8,46
	Found	C 75,49	H 10,10	N 5,98	O 8,43

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