A Polymer with the Mesomorphic Order of Liquid Crystalline Phthalocyanines

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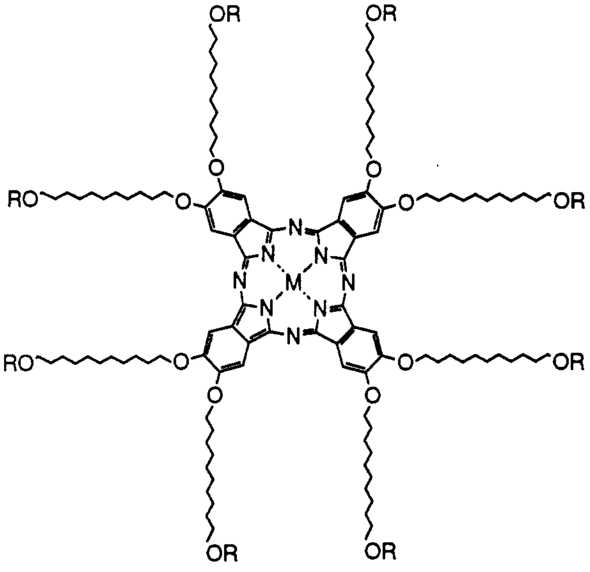
ABSTRACT: Phthalocyanines (Pc) substituted with eight terminally functionalized *n*-alkoxy chains have been synthesized and their mesomorphic properties investigated. Radical polymerization has been carried out in a columnar mesophase of a phthalocyanine that contained an acryloyl or a methacryloyl function at the end of each of its eight alkoxy chains. Polymers with liquid crystalline order were obtained, the structures of which were determined by small-angle X-ray diffraction. Temperature-dependent luminescence measurements (4.2-300 K) have been performed and the results explained in terms of efficient energy migration through the stacked Pc units already at low temperatures. The conductivity of one of the polymers was 5×10^{-5} S/m at 175 °C and increased to 1×10^{-3} S/m after doping with I_2.

Introduction

Since the first report on a discotic mesophase by Chandrasekhar et al.[1] in 1977 it has been shown that thermotropic liquid crystalline behavior occurs in a large number of discotic compounds. Among them are a variety of derivatives of triphenylene,[2] truxene,[3] bis[(3,4-di-*n*-alkoxybenzoyl)methanato]copper(II),[4] and porphyrin.[5] Discotic liquid crystalline main-chain and side-chain polymers based on triphenylene[6,7] and benzene[8] were reported by Ringsdorf's group. A class of thermotropic discotic liquid crystals to which currently much attention is given are the phthalocyanines (Pc's).[9-15] Recently, we reported on the liquid crystalline behavior of peripherally octa-*n*-alkoxy substituted Pc's.[15] In the liquid crystalline state these disclike molecules are stacked in hexagonally arranged ordered columns (Figure 1).

In search of new materials our group is interested in supramolecular, organized structures.[15-19] Such molecular materials might, for example, show interesting properties in the domains of catalysis, electronics, optoelectronics, and transport. The work described in the present paper is concerned with the synthesis of mesomorphic Pc's with a functional group as a handle at the end of the aliphatic chains. In particular, we synthesized compounds with polymerizable groups at the terminal position, the aim being to keep the structure of the mesophase fixed by polymerization.



	M
a	HH
b	Cu
c	Zn
d	Co
e	Ni
f	Pb

	R
1	–H
2	$-C(O)CH_3$
3	$-C(O)CH{=}CH_2$
4	$-C(O)C(CH_3){=}CH_2$

Synthesis and Characterization

Two different synthetic routes were developed to Pc's with eight 11-hydroxyundecoxy chains. These are depicted in Scheme I, in which yields refer to compounds isolated after purification. Following route A catechol was alkylated by treating it with 11-bromo-1-undecanol in DMSO in the presence of potassium carbonate to give **5**. This compound was converted to **6** by bromination with molecular bromine in methylene chloride. In the next step a Rosenmund–Von Braun reaction yielded the dicyanide **7**, which was converted into the corresponding MPc **1** by refluxing in 2-(dimethylamino)ethanol in the presence (M = metal) or absence (M = 2H) of a metal salt. The yields of compound **7** are lower than usually observed for the Rosenmund–Von Braun reaction, probably because of the presence of the hydroxyl groups.

Route B is a more general procedure of synthesizing symmetrical octasubstituted Pc's because the chains are attached in the last step. Octamethoxy-MPc (**8**) was synthesized following the procedure described by Hanack et al.[20] When the Pc is metal free or contains copper, demethylation can be achieved by refluxing in pyridine hydrochloride to give **9** in high yield. In the case of labile complexes like ZnPc, it is necessary to use a milder reagent. Refluxing **8**, M = Zn, in toluene in the presence of $AlCl_3$ gave satisfactory results. Product **9** is a versatile starting material for diversification. Care must be taken that

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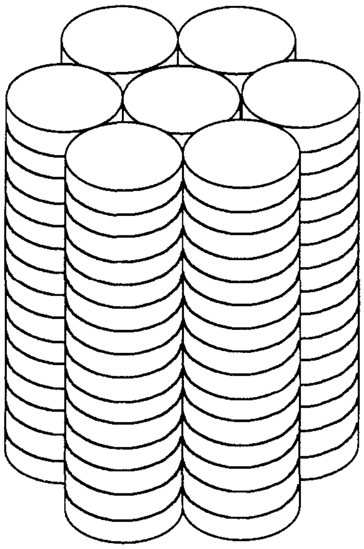


Figure 1. Schematic presentation of a hexagonal ordered columnar (D_{ho}) mesophase.

the product is kept under nitrogen because of its sensitivity toward oxidation. Treatment of the octahydroxy derivative **9** with 11-bromo-1-undecanol in the presence of potassium carbonate in DMSO for approximately 1 week yielded 2,3,9,10,16,17,23,24-octakis(11-hydroxyundecoxy)-MPc (**1**). After treatment in a Soxhlet apparatus, 28–35% of pure product was isolated.

Products **1a–f** are highly soluble in pyridine, DMF, and DMSO, moderately soluble in boiling chloroform and methanol, and insoluble in ether, acetone, and water.

Pc **1** was treated with acetic acid anhydride in pyridine or with various acid chlorides in dry chloroform to give, after reaction times of approximately 4 days at room temperature, the terminally substituted products **2–4** in 75–98% yield. These products are completely insoluble in acetone, methanol, DMF, DMSO, and ether but highly soluble in chloroform, benzene, and toluene, the metal containing products being somewhat less soluble than the free ligands. During the reaction with the acid chlorides N-substituted products are also formed as indicated by the formation of an additional band in the UV–vis spectrum at 720 nm.[21] The additional band is only detected when very dry solvent is used. After workup, this band has vanished. With Pb as the central metal (compound **1f**) it was not possible to substitute the protons of the OH groups without losing the central metal ion. Lead(II) Pc's have a limited stability toward solvents because the Pb(II) ion is large compared to the hole inside the Pc nucleus.[22]

In the ^1H NMR spectra of compounds **3a** and **4a** vinylic and ester methylene protons are present as sharp signals around 6.0 and 4.0 ppm, respectively, while aromatic protons and ether methylene protons are visible as broad signals at 8.5 and 4.4 ppm, respectively. Signals due to protons close to the Pc nucleus are expected to be broad as a consequence of aggregation phenomena.[23]

In the IR spectrum of **3a** bands are present at 1715 (C=O) and 1630 cm^{-1} (C=C) due to the acrylic ester groups. Absorptions due to OH groups around 3600 cm^{-1} were not observed.

Aggregation Behavior

We have compared the aggregation behavior of free-base Pc's **1a** and **3a** in various solvents. Visible spectra of compounds **1a** and **3a** in different solvents are shown in Figure 2. In chloroform or tetrahydrofuran, bands are visible at 700, 660, and 600 nm with a shoulder at 640 nm. These bands are attributed to monomeric Pc.[20–25] In polar solvents such as methanol or acetone these bands vanish and a new one appears around 620 nm. This band has been attributed to the presence of dimeric and oligomeric Pc species.[20] In some solvents, however, compounds **1a** and **3a** display contrasting behavior. Thus, while compound **3a** shows the 700 nm band in toluene, chloroform and methylene chloride, **1a** features the 620 nm band in these solvents (Figure 2). In pyridine the situation is reversed. For CuPc **1b** the 620-nm band is observed in chloroform and methylene chloride, whereas in toluene and pyridine qualitatively the same behavior is observed as for **1a**.

These results indicate that the factors determining the aggregation properties are influenced not only by solvent properties—no direct correlation is present between solvent polarity E_T (MeOH > MeCOMe > CH_2Cl_2 > pyridine > $CHCl_3$ > toluene) and aggregation—but also by the nature of the side chains of the Pc core.

Mesomorphic Properties

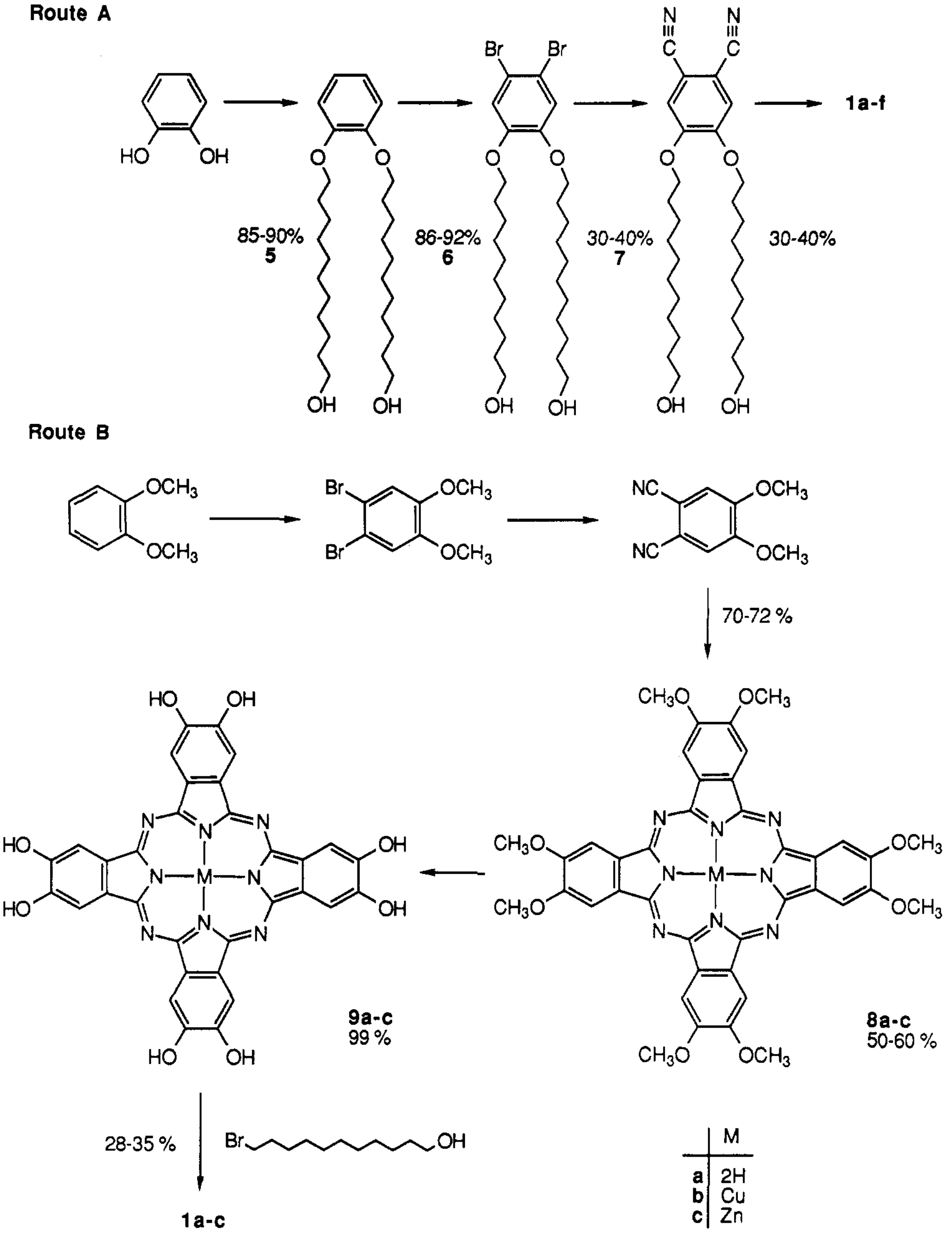
The mesomorphic behavior of the synthesized Pc's has been examined by temperature controlled polarizing microscopy and differential scanning calorimetry (DSC).

Observations under a polarizing microscope equipped with a heating and cooling stage showed for all compounds above a certain transition temperature (see also Table I) the presence of a mozaic texture, characteristic of a D_h phase. The terminally unsubstituted octa-*n*-alkoxy-Pc's also have a D_h phase.[15] Therefore, the columnar structure of the mesophase is not appreciably affected by substituents at the end of the aliphatic hydrocarbon chains. Within the series of octa-*n*-alkoxy-Pc's, compounds **1a** and **2a** are the first examples that exhibit a thermodynamically stable isotropic phase, i.e., without simultaneous decomposition. When the isotropic liquid is cooled slowly (2 °C/min), digitate stars appear from the undercooled liquid, which are visible when polarizer and analyzer are parallel. The stars grow slowly and eventually coalesce to large homotropic domains. Sometimes, linear birefringent defects, characteristic of D_{ho} phases, are observed (Figure 3).[15]

Transition temperatures and heats of transition were determined by DSC. The data are summarized in Table I, together with the calculated entropy of transition. It is interesting to note that the transition temperature can be varied by incorporating different substituents at the end of the aliphatic chains. Also a dependence of the central metal ion is recognized. The observed large differences in transition entropy (Table I) indicate an appreciable difference in the degree of order in the LC state, assuming that the degree of order in the solid state is equal. This view is supported by the qualitative observation that compounds with smaller transition entropies have a higher viscosity in their mesophase.

It is well established that when two liquid crystalline compounds are isomorphous, they are miscible in all proportions.[26] In order to establish the phase type of the acrylic monomer **3a**, a temperature–composition phase diagram was constructed from DSC measurements of mixtures of **3a** and 2,3,9,10,16,17,23,24-octa-*n*-dodecoxy-MPc (M = 2H) (**10**). The latter compound is known to exhibit a D_{ho} mesophase.[15] Every mixture showed two transitions, one at a temperature of 80 °C and one at a higher temperature that depended on the composition. These temperatures were used to construct the diagram shown in Figure 4. This phase diagram shows that the

Scheme I



two compounds are miscible in the liquid crystalline state, while they are not miscible in the solid state, which was checked by X-ray diffraction at room temperature of the mixture with composition $x = 0.5$. The fact that the two compounds are miscible in all proportions in the mesophase proves that compound **3a** also has a D_{h_o} phase.

Polymerization Experiments

The aim of this research is to fix the organization in the mesophase by polymerization and thus to conserve the mesophase order when cooling to room temperature. Two techniques have been employed.

Photopolymerization. In principle, photopolymerization has the advantage of being possible at any temperature. For instance, the system could first be ordered in the temperature range of the mesophase and subsequently photopolymerized.[27]

We have performed some experiments on acrylate **3a** in a DSC apparatus described elsewhere[27] equipped with a light source (λ_{max} = 350 nm) under a nitrogen atmosphere in the mesophase at 95 °C in order to follow the formation of heat during polymerization. The compound under investigation was mixed with 1 wt % α,α-dimethoxy-α-phenylacetophenone as photoinitiator, which also has a λ_{max} at 350 nm. Unfortunately, no polymerization took place.

The reason for the fact that no polymerization takes place might be that all photons are absorbed by the Pc-core, which is indicated by the fact that a change in heat flow was detected by DSC upon switching the light on. Furthermore, a strong absorption band is present at 350 nm.

Thermal Polymerization. Polymerization experiments were performed in vacuum on monomers **3a,b** and **4a,b** in the mesophase at a temperature of 93 °C and with 2,2′-azobis(2-methylpropanenitrile) (AIBN) as initiator. Polymers were obtained from which traces of initiator were removed by extraction with ethyl acetate. In contrast to the monomers, the polymers were totally insoluble in organic solvents and concentrated sulfuric acid, indicating that polymerization had indeed taken place.

The morphology of the polymer obtained from **3a** depends on the amount of initiator used: with <0.5 mol % (relative to the acrylic groups) a brittle polymer resulted,

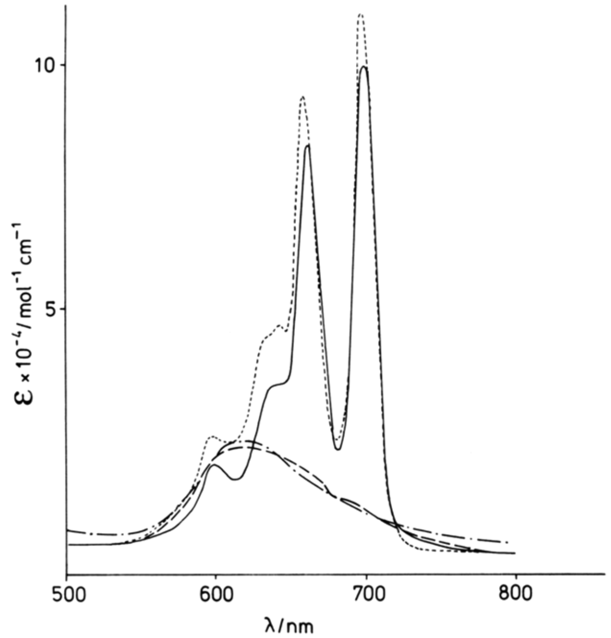


Figure 2. Visible spectra in different solvents: (—) **1a** and **3a** in chloroform, (- · ·) **1a** and **3a** in methanol, (– – –) **1a** in toluene, and (- - -) **3a** in toluene.

Table I
Mesomorphic Properties of Substituted Phthalocyanines: Transition Temperatures and Thermodynamic Parameters[a]

compd	transitions	T_m, °C	ΔH, kJ/mol	ΔS, J/(K·mol)[b]
1a	K → D → I	120 [80], 254	58, 16	148, 31
1b	K → D	134[c] [106]	62	152
1c	K → D	139[c] [111]	62	150
1d	K → D	112[c] [90]	25	65
1e	K → K′ → D	32, 66[c]	2.1, 58	6.8, 170
1f	K → K′ → D	47, 110[c]	4.0, 25	12.4, 60
2a	K → D → I	85 [64], 235	98, 28	274, 55
2b	K → D	75[c] [58]	67	193
2c	K → D	82[c] [55]	60	169
2d	K → D	82[c] [53]	38	107
2e	K → D	63[c] [45]	50	149
3a	K → D	85[c] [65]	105	293
3b	K → D	70[d] [50]	65	190
3c	K → D	77[d] [59]	60	171
3d	K → D	75[d] [57]	72	208
3e	K → D	73[d] [47]	92	266
4a	K → D	54[d] [30]	64	196
4b	K → D	51[d] [25]	65	201
4c	K → D	80[d] [50]	65	185
4d	K → D	85[d] [83]	29	81
4e	K → D	50[d] [29]	92	288

[a] Cited transition temperatures and enthalpies are measured by DSC and observed during the second and subsequent heating runs. Transition temperatures measured during cooling are given in brackets. K and K′ are different crystalline phases, D is a discotic mesophase, and I is the isotropic phase. Heating rate 10 K/min, cooling rate 5 K/min. [b] $\Delta S = \Delta H / T_m$, where T_m is the transition temperature in K. [c] Isotropization at temperatures above 290 °C, the temperature at which, according to TGA, decomposition starts. [d] Polymerization took place at temperatures of 200–225 °C.

whereas with 2 mol % an elastic product was obtained. In both cases the polymer showed birefringence when viewed between crossed polarizers of a polarizing microscope. Esterolysis of the ester groups in refluxing *tert*-butyl alcohol in the presence of potassium *tert*-butoxide gave a soluble compound with a UV–vis spectrum identical with that of Pc **1**, indicating that the Pc nucleus had not been altered by the radicals resulting from the decomposition of AIBN.

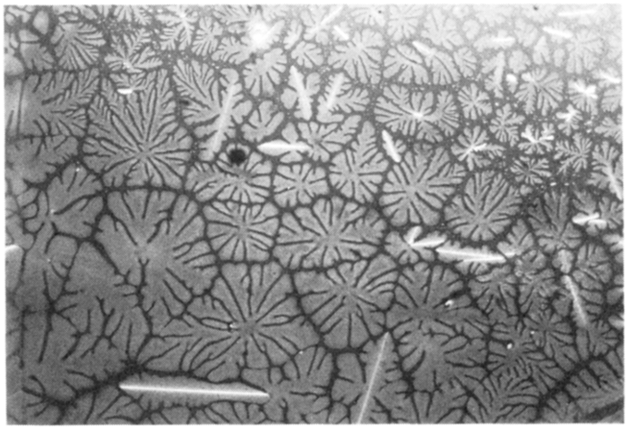


Figure 3. Digitate stars as observed for compounds **1a** and **2a** under a polarizing microscope when the isotropic liquid is cooled slowly (2 °C/min). Analyzer and polarizer are parallel. In addition, some linear birefringent defects are present.

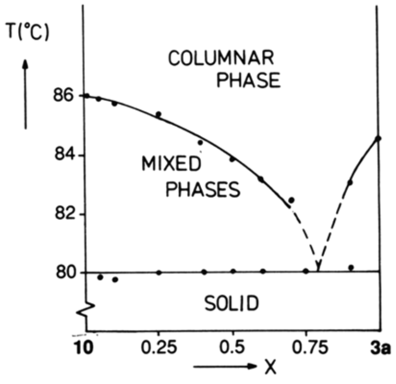


Figure 4. Temperature composition phase diagram for mixtures of **3a** and **10**.

Photoacoustic spectroscopy (PAS) is a valuable method to study insoluble compounds in a pure state. PAS spectra recorded for the monomer and the polymer, are shown in Figure 5. From the fact that a weak absorption at 1620 cm^{-1} is still present, it is apparent that not all acrylic groups have been incorporated into a polymer chain.

DSC did not reveal any phase transition of the polymer, suggesting that a cross-linked network was obtained.

When mixtures of **3a** and **10** were heated in the DSC apparatus up to 225 °C, polymerization of **3a** was achieved. Polymerization of **3a** was checked by comparing the K → M transition enthalpy before and after polymerization. The results of these comparisons are shown in Figure 6a. The decrease in transition enthalpy after polymerization is proportional to the amount of **3a** present in the original mixture. Further, the product obtained has very limited solubility in chloroform, even when low concentrations of **3a** were present in the original mixture. From this and the data presented in Figure 4 it is clear that inclusion of **10** in the polymeric matrix has taken place. The enthalpy effect present after polymerization of **3a** can thus be ascribed to the transition of **10** into its mesophase. The transition temperatures are shown in Figure 6b as a function of composition of the original mixtures. The mean transition temperature has decreased with respect to pure **10**. This decrease could be due either to a stabilizing effect of the polymer or to the polymer behaving as an impurity. The latter explanation seems less probable, however, since a horizontal temperature composition diagram would not be expected.

Small-Angle X-ray Scattering (SAXS)

Preliminary X-ray diffraction experiments were performed on powder samples of compounds **1a**–**4a** in the

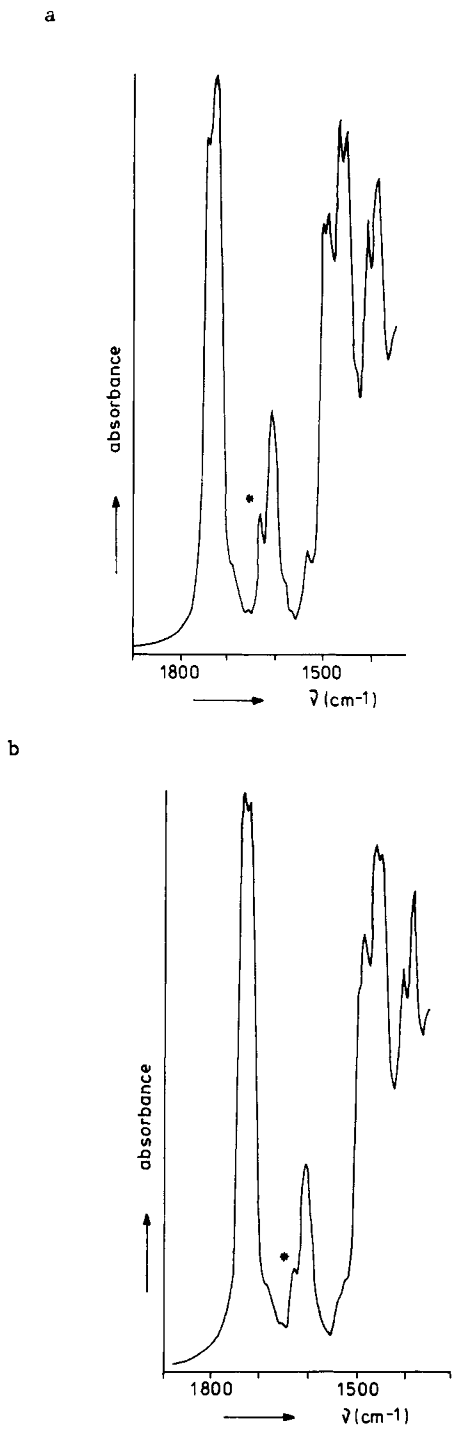


Figure 5. PAS spectra of **3a** (a) and its polymer (b).

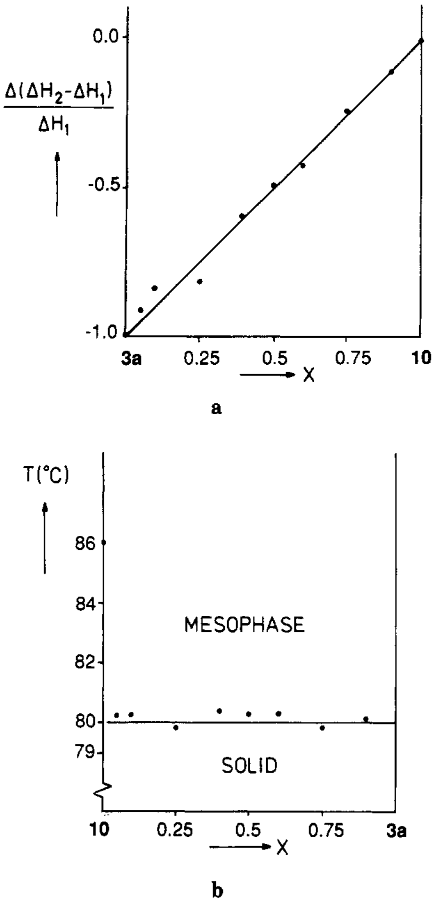


Figure 6. (a) Decrease in transition enthalpy for the transition solid → mesophase, caused by polymerization as a function of molar ratio x. (b) Transition temperature of compound **10** in the polymer matrix as a function of original molar ratio x.

Table II
Structural Parameters at Different Temperatures[a]

compd	temp, °C	D, Å	h, Å	I, Å
3a	100	37.6	3.3	4.6
poly-**3a**	25	36.4	3.3	4.5
poly-**3a**	200	36.4	3.4	4.5
poly-**3b**	25	36.4	3.3	4.5
poly-**3b**	200	36.4	3.4	4.5
4b	100	38.1	3.3	4.6
poly-**4b**	25	37.5	3.3	4.6
poly-**4b**	200	37.5	3.4	4.6

[a] D, distance between the axis of neighboring columns; h, stacking period; I, average interatomic distance between the side chains.

solid state at room temperature. The samples were prepared by heating until the mesophase was reached and subsequent cooling to room temperature. In this way well-organized structures and correspondingly well-resolved diffraction lines were obtained. Reflections are present at both small and wide angles. The wide-angle reflections are clearly indicative of short-range order between molecules, while the ones at small angles indicate a rectangular packing of columns in the solid state.

From the SAXS diffraction patterns of compound **3a** in its liquid crystalline phase at 100 °C the presence of a D_{h_0} structure was inferred. This result confirms the conclusions from the miscibility experiments described above. Structural parameters for **3a** are shown in Table II.

Monomers **3a**, **4a**, and **4b** were polymerized in the liquid crystalline state with 3% AIBN inside an X-ray glass capillary. The presence of a D_{h_0} phase for **3a** in the presence of AIBN was separately checked with X-ray diffraction. For the polymerization a piece of glass ware as shown in Figure 7 was used. A capillary filled with monomer and initiator was placed in compartment A, while compartment B was filled with silicon oil. The vessel was evacuated three times with subsequent admission of nitrogen. The valve was closed and compartment B was placed in an oil bath at a temperature of 96 °C. After 15 min the silicon oil was transferred into compartment A, thus allowing the monomeric compound to reach almost instantaneously its mesophase with as little accompanying polymerization as possible. Next, compartment A was placed in the oil bath. Polymerization was checked by testing the solubility of the resulting polymer after opening a control capillary. The small-angle X-ray diffraction pattern of the resulting polymer at 25 °C is shown in Figure 8. At small angles four lines are present with recip-

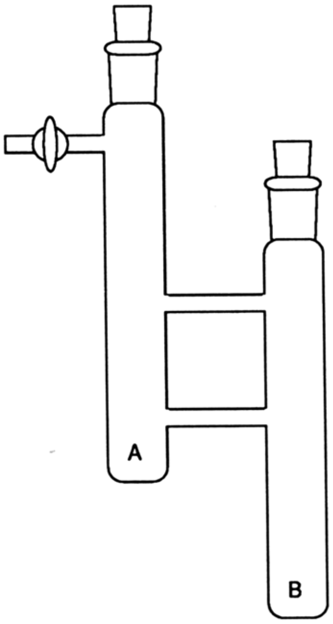


Figure 7. Apparatus used for polymerization in an X-ray glass capillary.

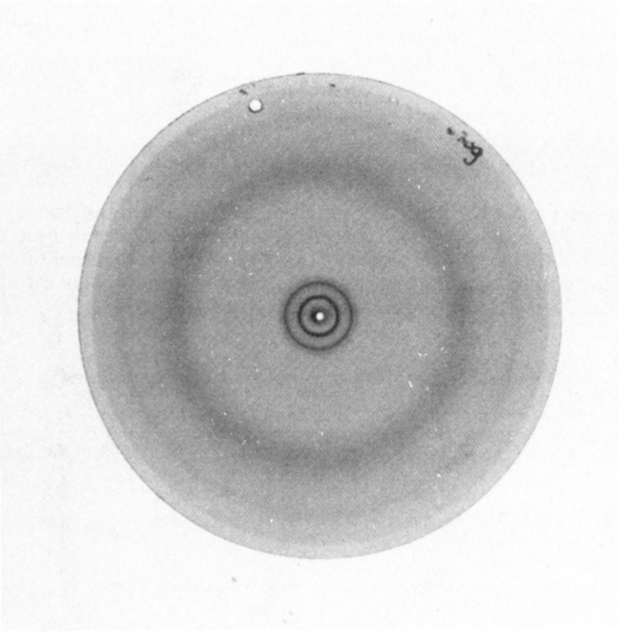


Figure 8. X-ray photograph at 25 °C of the polymer obtained from **3a**.

rocal spacings in the proportion of $1:3^{1/2}:4^{1/2}:7^{1/2}$, characteristic of a hexagonal lattice. At wide angles a very diffuse reflection is present near $2 \sin \theta/\lambda = 1/4.5$ Å^{-1} and a sharper reflection near $2 \sin \theta/\lambda = 1/3.3$ Å^{-1}, assignable to disordered aliphatic chains and the intracolumnar Pc–Pc distance, respectively. The pattern is similar to the diffraction pattern of the monomer in its mesophase (Table II). This unambiguously shows that the structure present in the monomer is maintained in the polymer without change. Thus, a new polymer with mesomorphic order has been obtained. Structural parameters of the polymers at 25 and 200 °C are summarized in Table II. The intercolumnar distance in the polymer appears to be independent of temperature and somewhat smaller than for the monomer, while the stacking period increases somewhat with temperature (Table II).

Luminescence and Energy Migration in the Solid State

In a previous study[28] it was concluded that for compound **10** the exciton migration rate depends on the stacking of the Pc units in the columns. The highest one-dimensional migration rate is observed when the molecular planes are perpendicular to the axis of the stack. The luminescence of the polymer of acrylate **3a** has been investigated in the solid state down to 4.2 K. The luminescence measurements were performed by 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 is approximately 4%. This behavior is in contrast with that of compound **10**.[28] This compound shows a high q at 4.2 K and two emission bands with maxima at 795 (intrinsic emission) and 820 nm (extrinsic emission).

In the present polymer the stacking at low temperatures is similar to that of the mesophase of **10**, i.e., energy migration through the Pc stacks is fast. Therefore, the excitation energy is likely to reach a quenching site (CuPc), and the quantum efficiency is low. Efficient energy migration is also expected to give rise to an enhanced visiting probability of extrinsic, or slightly disturbed, molecules. The 830-nm emission is ascribed to these molecules. The linear decrease in 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**2a** and of **10**[28] are comparable, since trapping by extrinsic sites is expected to be less important then.

Electrical Conductivity

The electrical properties of the polymer derived from **3b** were determined by preliminary complex impedance spectroscopy measurements as described elsewhere.[29] The value of the electrical conductivity (σ) at 175 °C was 1×10^{-5} S/m, 2 orders of magnitude higher than that of CuPc-$(OC_{12}H_{25})_8$.[30] The conductivity activation energy (E_a) was determined to be 0.4 eV. After doping with I_2, σ_{25} and E_a amounted to 5×10^{-5} S/m and 0.2 eV, respectively. According to TGA 60–70% of the I_2 evaporates between 100 and 120 °C, which is accompanied by a sudden decrease in conductivity and an increase in activation energy of conduction in this temperature range. At 175 °C, σ and E_a of the doped sample amounted to 1×10^{-3} S/m and 0.6 eV, respectively.

Conclusion

The columnar order present in the mesophase of 2,3,9,10,16,17,23,24-octakis[(acryloyloxy)undecoxy]-Pc (>85 °C) is retained on cooling to room temperature when the compound is polymerized above its transition temperature. Efficient energy migration is shown to occur in the polymer. The conductivity of the polymer was shown to be 2 orders of magnitude higher than that of the corresponding unpolymerized phthalocyanine.

Experimental Section

Catechol was recrystallized three times from toluene and stored at 4 °C under nitrogen. 11-Bromo-1-undecanol, bromine, and CuCN were used as received. DMSO and DMF were stored on molecular sieve (4 Å). Methylene chloride and chloroform were distilled from $CaCl_2$ before use. ^1H NMR spectra were recorded on Varian EM-360 and Bruker WP-200 instruments. Chemical shifts are given in parts per million relative to TMS. Infrared and UV–vis spectra were taken on a Perkin-Elmer 283 and a Perkin-Elmer 555 spectrometer, respectively. Solid-state luminescence measurements were performed by 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 differential scanning calorimeter. FAB mass spectra were recorded on a VG ZAB 2F spectrometer. X-ray diffraction measurements were performed with a Guinier-Lenné camera (Ni filtered Cu Kα radiation). Abbreviations used are as follows: s, singlet; t, triplet; m, multiplet; br, broad; v br, very broad; sh, shoulder.

Route A (Scheme I), Typical Procedure. 1,2-Bis(11-hydroxyundecoxy)benzene (5). A solution of 13.2 g (0.12 mol) of catechol and 63.2 g (0.25 mol) of 11-bromo-1-undecanol in 150 mL of DMSO was evacuated three times and nitrogen was let in. After the addition of 58 g (0.42 mol) of K_2CO_3 and evacuating again, the mixture was heated at 100 °C in a dry nitrogen atmosphere while stirring magnetically. According to TLC (SiO_2; eluent $CHCl_3/MeOH = 10/1$; $R_f(\mathbf{5}) = 0.4$) on samples from which DMSO had been removed by evaporation, the reaction was complete after 8 h. Subsequently, 500 mL of water and 200 mL of methylene chloride were added and the mixture was stirred until two clear layers were obtained. The aqueous layer was extracted three times with chloroform. The combined organic extracts were washed with water (3 × 200 mL) and dried over $MgSO_4$ and the solvent was evaporated. The remaining solid was dissolved in boiling acetone (approximately 20 mL/g). The product crystallized at 4–7 °C. Yield 48.2 g (89%) of a white solid; mp 83 °C; FAB MS *m/z* 451 ($[M + 1]^+$); IR (KBr) 3300 (O–H), 1220 (Ar–O), 1050 (ArO–C), 750 (ortho-substituted benzene) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (br s, 36 H, CH_2), 1.4 (s, 2 H, OH), 3.65 (t, 4 H, CH_2OH), 3.95 (t, 4 H, $ArOCH_2$), 6.85 (s, 4 H, Ar H).

1,2-Dibromo-4,5-bis(11-hydroxyundecoxy)benzene (6). 1,2-Bis(11-hydroxyundecoxy)benzene (5) (40.0 g, 88.9 mmol) was dissolved in 600 mL of dry chloroform. As catalyst, 1 mL of a solution of BF_3 (50% in ether) was added. To this solution 12 mL (0.38 mol) of Br_2 in 100 mL of chloroform was added in about 1 h, the first half at 0 °C, the second half at room temperature. The mixture was stirred for an additional 2 h at the same temperature to complete the reaction. The reaction mixture was washed subsequently with 10% aqueous $NaHCO_3$, 10% aqueous $NaHSO_3$, and water. The organic layer was colorless now. The extract was evaporated to dryness. Recrystallization from methylene chloride yielded a white powder. Yield 37.8 g (94%); mp 86 °C; FAB MS *m/z* 606/608/610 (M^+), 607/609/611 ($[M + 1]^+$); IR (KBr) 3300 (O–H), 650 (ArBr), 1050 (C–OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (br s, 36 H, CH_2), 1.7 (s, 2 H, OH), 3.65 (t, 4 H, CH_2OH), 3.93 (t, 4 H, $ArOCH_2$), 7.07 (s, 2 H, Ar H).

1,2-Dicyano-4,5-bis(11-hydroxyundecoxy)benzene (7). To a mixture of 15 g (0.17 mol) of CuCN and 19 mL of pyridine was added a suspension of 30.0 g (0.049 mol) of 1,2-dibromo-4,5-bis(11-hydroxyundecoxy)benzene (6) in 170 mL of DMF. After it was evacuated, the mixture was heated under reflux for 6 h under an atmosphere of dry nitrogen. After it was cooled, the reaction mixture was poured into 1.5 L of concentrated ammonium hydroxide and air was allowed to flow through the solution for 18 h. The remaining solid was suction filtered over sintered glass. The residue was washed with 10% aqueous ammonia until the filtrate was colorless and subsequently with water until the washings were neutral. The dry product was purified by flash chromatography (SiO_2; eluent $CHCl_3$). Two yellow bands appeared, after which the product was eluted until no fluorescence could be detected on TLC. The purity of the product could be checked with TLC (SiO_2: eluent $CHCl_3$; $R_f(\mathbf{7}) = 0.5$). Yield 9.7 g (38%); mp 136.5 °C; FAB MS *m/z* 501 ($[M + 1]^+$); IR (KBr) 3330 (O—H), 2220 (C≡N), 1090 (ArO—C), 1050 (C—OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (br s, 38 H, CH_2OH), 3.65 (t, 4 H, CH_2OH) 4.00 (t, 4 H, OCH_2), 7.17 (s, 2 H, Ar H).

Anal. Calcd for $C_{30}H_{48}N_2O_4$ (MW = 500.72): C, 71.96; H, 9.66; N, 5.60; O, 12.78. Found: C, 71.75; H, 9.64; N, 5.28; O, 13.33.

2,3,9,10,16,17,23,24-Octakis(11-hydroxyundecoxy)phthalocyanine (1a). A solution of 2.0 g (1.0 mmol) of 1,2-dicyano-4,5-bis(11-hydroxyundecoxy)benzene (7) in 3.0 mL of 2-(dimethylamino)ethanol was heated under reflux for 78 h under a nitrogen atmosphere. After it was cooled, the mixture was diluted with 10 mL of chloroform and dropped into 150 mL of acetone. The precipitate was filtered over a sintered glass funnel. The residue was treated in a Soxhlet apparatus with acetone for 24 h. The residue was solubilized with chloroform. After the mixture was cooled to 5 °C, the precipitate was removed by filtration and recrystallized from methanol. Yield 720 mg (36%) of dark green powder. K → M, 120 °C; M → I, 254 °C. FAB MS (matrix 4-nitrobenzyl alcohol/MeOH) *m/z* 2002 (M^+), 2003 ($[M + 1]^+$); IR (KBr) 3330 (O–H), 3290 (N–H), 2840/2905 (C–H), 1272 (Ar–O), 1095 (ArO–C), 1030 (C–OH), 1120 (N–H), 740 (skeletal C–H) cm^{-1}; ^1H NMR (200 MHz, pyridine-d_5) δ −4.1 to −3.8 (v br, 2 H, NH), 1.3–2.0 (144 H, CH_2), 2.27 (br t, 16 H, OCH_2CH_2), 3.98 (t, 16 H, CH_2OH), 4.22 (br t, 16 H, $ArOCH_2$), 5.88 (br s, 8 H, OH), 8.07 (br s, 16 H, Ar H); UV–vis ($CHCl_3$) λ_{max} ($\log \epsilon/(L\cdot mol^{-1}\cdot cm^{-1})$) 700 (5.07), 660 (5.03), 640 (sh), 600 (4.32), 412 (4.60), 344 (4.96), 290 (5.03) nm.

Anal. Calcd for $C_{120}H_{194}N_8O_{16}$ (MW = 2004.91): C, 71.89; H, 9.75; N, 5.59; O, 12.77. Found: C, 70.49; H, 9.83; N, 5.56; O, 14.12.

Route B, Typical Procedure. 2,3,9,10,16,17,23,24-Octamethoxymetallophthalocyanines (M = H, Cu, Zn) (8a,b,c) were synthesized following a procedure analogous to the one described in ref 20.

2,3,9,10,16,17,23,24-Octahydroxymetallophthalocyanines (9a,b) (M = H, Cu). The corresponding 2,3,9,10,16,17,23,24-octamethoxymetallophthalocyanine (8) (150 mg) was heated under reflux in 4.0 g of pyridine hydrochloride on a metal bath for half an hour. The reaction mixture was diluted with 40 mL of 10% aqueous HCl and stirred for 1 h. After the solution was filtered and the residue was washed with water and acetone under a nitrogen atmosphere, the product was dried in vacuum. The yield was 99% of a black powder. The products were directly used in the next step. **9a**: IR (KBr) 3300 (v br O–H), 1280 (Ar–OH), 740 (skeletal C–H) cm^{-1}; UV–vis (DMSO/pyridine = 1/20) λ_{max} ($\log \epsilon/(L\cdot mol^{-1}\cdot cm^{-1})$) 700 (4.65), 660 (4.57), 640 sh (3.94), 600 (3.92), 412 (4.21) nm.

Compounds **9a** and **9b** were also synthesized according to the procedure given for (2,3,9,10,16,17,23,24-octahydroxyphthalocyaninato)zinc (**9c**).

(2,3,9,10,16,17,23,24-Octahydroxyphthalocyaninato)zinc (9c). (2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)zinc (**8c**) (640 mg, 0.78 mmol) was heated under reflux in 60 mL of toluene together with 2.09 g (16 mmol) of $AlCl_3$ for half an hour. After the solution was cooled to room temperature, 100 mL of 10% HCl was added and the mixture stirred for 1 h. The solid was filtered off, washed with water and acetone, and dried. IR (KBr) as for **9a**. UV–vis (pyridine) λ_{max} ($\log \epsilon/(L\cdot mol^{-1}\cdot cm^{-1})$) 675 (5.20), 644 sh (4.47), 608 (4.45), 362 (4.89) nm.

2,3,9,10,16,17,23,24-Octakis(11-hydroxyundecoxy)phthalocyanine (1a). 2,3,9,10,16,17,23,24-Octahydroxy-Pc (**9a**) (150 mg, 0.2 mmol) was solubilized with 0.44 g (1.8 mmol) of 11-bromo-1-undecanol in 7.0 mL of DMSO and evacuated. To this mixture was added 0.24 g (1.8 mmol) of K_2CO_3. The mixture was evacuated again and heated at 100 °C for 1 week. The reaction mixture was boiled with 40 mL of water, filtered, and washed with water and ether. After it was dried the residue was treated (48 h) in a Soxhlet apparatus with acetone and chloroform. Recrystallization from chloroform yielded the desired product in 30–40% yield. Analytical data are given above.

Anal. Calcd for $C_{120}H_{194}N_8O_{16}$ (MW = 2004.91): C, 71.89; H, 9.75; N, 5.59; O, 12.77. Found: C, 71.18; H, 9.70; N, 5.67; O, 13.44.

Further Derivatization. 2,3,9,10,16,17,23,24-Octakis(11-acetoxyundecoxy)phthalocyanine (2a). One hundred milligrams of 2,3,9,10,16,17,23,24-octakis(11-hydroxyundecoxy)phthalocyanine (**1a**) was treated with 1.5 mL of acetic acid anhydride in 3.0 mL of pyridine for 24 h at room temperature. The completion of the reaction was checked by TLC (SiO_2; eluent $CHCl_3$; $R_f(\mathbf{2a}) = 1$) and MeOH was added. After 1 h the reaction mixture was evaporated to dryness and the residue subjected to flash chromatography (SiO_2; eluent $CHCl_3$). Yield 100 mg (98%). K → M, 85 °C; M → I, 235 °C. FAB MS m/z 2338 (M^+); IR (KBr) 3290 (N—H), 2840/2905 (C—H), 1740 (s, C═O), 1272 (Ar—O), 1095 (ArO—C), 740 (skeletal C—H) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ −2.0 to −1.6 (v br, 2 H, NH), 1.3–2.0 (144 H, CH_2), 2.00 (s, 24 H, C(O)CH_3), 2.27 (br t, 16 H, $\mathrm{OCH_2C}H_2$), 4.00 (t, 16 H, CH_2OC(O)), 4.41 (br t, 16 H, ArOCH_2), 8.52 (br s, 16 H, Ar H); UV–vis ($CHCl_3$) λ_{max} (log ϵ/(L·mol^{-1}·cm^{-1})) 700 (5.00), 660 (4.98), 640 (sh), 600 (4.27), 412 (4.59), 344 (4.91), 290 (4.75) nm.

Anal. Calcd for $C_{136}H_{210}N_8O_{24}$ (MW = 2341.21): C, 69.77; H, 9.04; N, 4.79; O, 16.40. Found: C, 69.84; H, 9.34; N, 4.75; O, 16.07.

2,3,9,10,16,17,23,24-Octakis[11-(acryloyloxy)undecoxy]phthalocyanine (3a). One hundred milligrams of 2,3,9,10,16,17,23,24-octakis(11-hydroxyundecoxy)phthalocyanine (**1a**) was treated with 0.4 mL of acryloyl chloride in 2.0 mL of dry chloroform at room temperature for 48 h. K_2CO_3 (25 mg) was added to neutralize the acid formed. In the beginning the reaction was heterogeneous. The reaction mixture turned brown to black. The completion of the reaction was checked by TLC (SiO_2; eluent $CHCl_3$; R_f(**3a**) = 1). After extraction with chloroform, water was added. (In the case of **3e** and **4e** it was necessary to evaporate the reaction mixture to dryness before further work up. The reason was cleavage of the C–O–C(O) bond by the addition of water. This was indicated by the disappearance of the C═O vibration in the IR and of the triplet near 4.5 ppm in the ^{1}H NMR, while a new resonance at 1.0 ppm became visible.) The organic layer was washed with water, dried over $MgSO_4$, evaporated to dryness, and dried for 24 h under vacuum. Yield 85–95%. K → M, 85 °C; IR (KBr) 3290 (N—H), 2840/2905 (C—H), 1740 (s, C═O), 1660 (C═C), 1270 (Ar—O), 1095 (ArO—C), 740 (skeletal C—H) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −2.6 to −2.2 (v br, 2 H, NH), 1.2–1.8 (128 H, CH_2), 2.17 (br, t, 16 H, $ArOCH_2CH_2$), 4.12 (t, 16 H, $-CH_2OC(O)-$), 4.41 (br, t, 16 H, $ArOCH_2-$), 5.50–6.50 (m, 24 H, CH═CH_2), 8.57 (br s, 16 H, Ar H); UV–vis ($CHCl_3$) as for **2a**.

Anal. Calcd for $C_{144}H_{210}N_8O_{24}$ (MW = 2437.30): C, 70.96; H, 8.69; N, 4.60; O, 15.75. Found: C, 70.53; H, 8.91; N, 4.58; O, 15.98.

2,3,9,10,16,17,23,24-Octakis[11-(methacryloyloxy)undecoxy]phthalocyanine (4a) was synthesized from 2,3,9,10,16,17,23,24-octakis(11-hydroxyundecoxy)phthalocyanine (**1a**) and methacryloyl chloride as described for **3a**. Yield 75–85%. K → M, 54 °C. IR (KBr) 3290 (N—H), 2840/2905 (C—H), 1740 (s, C═O), 1660 (C═C), 1270 (Ar—O), 1095 (ArO—C), 740 (skeletal C—H) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −2.6 to −2.2 (v br, 2 H, NH), 1.2–1.8 (128 H, CH_2), 1.90 (s, 24 H, C(CH_3)═C), 2.17 (br t, 16 H, $\mathrm{ArOCH_2C}H_2$), 4.12 (t, 16 H, CH_2OC(O)), 4.41 (br t, 16 H, ArOCH_2), 5.42 and 5.98 (m, 16 H, C═CH_2), 8.57 (br s, 16 H, Ar H); UV–vis ($CHCl_3$) as for **2a**.

Anal. Calcd for $C_{152}H_{226}N_8O_{24}$ (MW = 2549.51): C, 71.61; H, 8.94; N, 4.39; O, 15.06. Found: C, 71.06; H, 9.08; N, 4.29; O, 15.56.

Polymerization. **3a** (75 mg, 30.8 mmol) was dissolved in 0.5 mL of a solution of AIBN (18.4 mmol/L) in $CHCl_3$. The solvent was evaporated and the vessel evacuated three times. After each evacuation nitrogen was admitted. The vessel was placed under vacuum in an oil bath at a temperature of 93 °C. After 2.5 h the mixture was allowed to cool to 25 °C. Impurities in the product were extracted with EtOAc and the product was collected by centrifugation. The polymer was dried under vacuum. PAS (neat) 3290 (N—H), 2840/2905 (C—H), 1740 (s, C═O), 1270 (Ar—O), 1095 (ArO—C), 740 (skeletal C—H) cm^{-1}.

Anal. Calcd for $(C_{144}H_{210}N_8O_{24})_n$ ($MW_{momomer}$ = 2437.30): C, 70.96; H, 8.69; N, 4.60; O, 15.75. Found: C, 69.79; H, 8.92; N, 4.62; O, 16.68.

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Registry No. **1a**, 123934-41-8; **2a**, 123934-42-9; **3a**, 123934-43-0; **3a** (homopolymer), 123962-97-0; **3b**, 123934-47-4; **3b** (homopolymer), 123934-48-5; **4a**, 123934-44-1; **5**, 123934-38-3; **6**, 123934-39-4; **7**, 123934-40-7; **8a**, 121258-16-0; **8b**, 123934-45-2; **8c**, 104507-32-6; **9a**, 121244-81-3; **9b**, 123934-46-3; **9c**, 121322-70-1; I_2, 7553-56-2; catechol, 120-80-9; 11-bromo-1-undecanol, 1611-56-9.

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