9028 J. Am. Chem. Soc. 1992, 114, 9028–9034

prior to placement in the evaporation chamber.

Preparation of $Cu/S(CH_2)_nCH_3$. Chromium (200 Å) and copper (2000 Å) were evaporated in sequence at 5 Å/s onto Si(100) wafers in a cryogenically-pumped chamber (base pressure $\approx 8 \times 10^{-8}$ Torr; operating pressure $\approx 1 \times 10^{-6}$ Torr) using an electron beam; the resulting copper films are polycrystalline but have a predominant crystallographic orientation that is (111).[10] After evaporation, the chamber was backfilled with argon (Med-tech; 99.998%, <5 ppm O_2), and the wafers were transferred under a positive flow of argon to 1 mM deoxygenated isooctane solutions of the *n*-alkanethiols that were brought into the evaporation chamber. The available area between the opened chamber door and the chamber itself for diffusion of air into the chamber was reduced to the minimum needed for transfer of adsorption solutions into the chamber by blocking these regions with sheets of polyethylene; this procedure minimized the oxidation of the copper films prior to their placement into the solutions containing the thiols.[42] After 1 h in solution, the wafers were removed from solution, rinsed with hexanes, and blown dry with N_2; we have described the procedure used in forming these SAMs previously.[10,43] After various intervals of exposure of the wafers to atmosphere (temperature = ~20 °C; relative humidity ≤30%), two slides (~1 × 3 cm^2) were cut from the wafer, and one each was characterized by wetting and XPS.

Wetting. Advancing and receding contact angles, θ_a and θ_r, respectively, were measured using a Ramé–Hart goniometer on both sides of static drops that had been caused to advance or recede using a Matrix Technologies electro-pipette (~1 μL/s); the pipet tip remained in the drop during the measurements. Data in Figure 6 are typically the average of three drops (six measurements).

X-ray Photoelectron Spectroscopy (XPS). XPS spectra were obtained with a Surface Science X-100 spectrometer using a monochromatized Al Kα X-ray source (spot diameter = 600 μm) and a concentric, hemispherical analyzer (pass energy = 100 eV). Samples were mounted with metal clips onto a stage and rotated sequentially into the X-ray beam under computer control. Under these conditions, the spectral focus of the sample could not be assured; the spectra presented in Figures 2 and 3 have been sized vertically for presentation purposes. Our analysis did not require the samples to be in optical focus as we rely on the relative intensities of peaks having similar binding energies. Copper and sulfur spectra were accumulated over ~30 min (10 scans; 50-eV window) and ~1 h (40 scans; 20-eV window), respectively. The spectra were fitted by using symmetrical 70% Gaussian/30% Lorentzian profiles and a Shirley background.[44] Previous reports have observed reduction of oxidized copper species during the XPS measurement (exposure times as short as 30 min) using nonmonochromatized X-ray sources.[45] We examined sequential spectra obtained on highly oxidized samples in our spectrometer and found little reduction occurring in our samples over the timescale of our accumulations. We believe this difference is due to our use of a monochromatized X-ray source that does not contain the Bremmstrahlung associated with nonmonochromatized sources.[7]

Registry No. Cu, 7440-50-8; $C_{16}H_{34}$, 544-76-3; Si, 7440-21-3; $CH_3(CH_2)_{21}SH$, 7773-83-3; Cr, 7440-47-3; $CH_3(CH_2)_{10}SH$, 5332-52-5; $HO(CH_2)_{11}SH$, 73768-94-2; $CH_3(CH_2)_{11}SH$, 112-55-0; $CH_3(CH_2)_{15}SH$, 2917-26-2; $CH_3(CH_2)_{17}SH$, 2885-00-9; $CH_3(CH_2)_7SH$, 111-88-6.

---

(42) Related experiments using copper films prepared in a diffusion-pumped evaporation chamber (base pressure $\approx 1 \times 10^{-6}$ Torr) by resistive heating of a copper-coated tungsten filament and less rigorous procedures for the transfer of the copper films to the adsorption solution resulted in SAMs that were not as ordered as the SAMs used in this study. The ability of these less ordered SAMs to retard the oxidation of the copper surface was diminished by the disorder (by >50%). The longer SAMs did, however, slow the oxidation of the copper better than the shorter SAMs.

(43) Laibinis, P. E.; Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1991**, *95*, 7017–7021.

(44) Shirley, D. A. *Phys. Rev. B* **1972**, *5*, 4709–4714.

(45) (a) Frost, D. C.; Ishitani, A.; McDowell, C. A. *Mol. Phys.* **1972**, *24*, 861–877. (b) Reference 15.

Radiation-Induced Conductivity in Polymerized and Nonpolymerized Columnar Aggregates of Phthalocyanine

Pieter G. Schouten,[*,†] John M. Warman,[†] Matthijs P. de Haas,[†] Johan F. van der Pol,[‡] and Jan W. Zwikker[‡]

Contribution from the Radiation Chemistry Department, IRI, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands, and Department of Physical Organic Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands. *Received April 13, 1992*

Abstract: Upon pulsed irradiation, long-lived, highly mobile charge carriers have been found in columnar stacks of thermotropic liquid-crystalline monomer octakis(dodecyloxy)phthalocyanine, Pc12, and polymeric octakis(octyloxy)phthalocyanine, $[Si(Pc8)O]_n$. The sum of the charge-carrier mobilities in the solid phase of Pc12 lies between 0.04×10^{-4} and 1.3×10^{-4} m^2/(V s) at room temperature. At the transition from the solid phase to the mesophase, a decrease in the mobilities by a factor of 8 is found. The activation energies associated with the mobilities are very small, on the order of 0 ± 0.05 eV, in both the solid phase and the mesophase. The conductive properties of the liquid-crystalline polymer change gradually over the temperature range studied, from −100 to +200 °C, and coincide with those of the monomer in its mesophase.

Introduction

The phthalocyanine ring system can be modified in several ways. Incorporation of a central metal atom, substitution around the periphery of the ring, and polymerization can bring about significant changes in the physical properties. In general, the phthalocyanine macrocycle, Pc, has a tendency to organize itself, forming stacks in which there is an interaction between the large π-systems of adjacent rings. As has been recognized, this results in a most interesting and varied group of organic materials which are capable of behaving as one-dimensional semiconductors.[1-4]

It has been established that phthalocyanines which are peripherally octasubstituted with long hydrocarbon chains form thermotropic liquid-crystalline materials in which the Pc macrocycles stack into hexagonally arranged columns.[5-11] The in-

---

[†] Delft University of Technology.

[‡] University of Utrecht.

(1) Simon, J.; André, J.-J. *Molecular Semiconductors*; Springer: Berlin, 1985.

(2) Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 857–879.

(3) Schultz, H.; Lehmann, H.; Rein, M.; Hanack, M. *Struct. Bonding* **1991**, *74*, 41–146.

(4) Eley, D. D. *Mol. Cryst. Liq. Cryst.* **1990**, *171*, 1–21.

(5) Piechocki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc.* **1982**, *104*, 5245–5247.

(6) Guillon, D.; Weber, P.; Skoulios, A.; Piechocki, C.; Simon, J. *Mol. Cryst. Liq. Cryst.* **1985**, *130*, 223–229.

0002-7863/92/1514-9028$03.00/0

tracolumnar arrangement in the mesophase is dependent on the sort of coupling used to bind the hydrocarbon chain to the macrocycle: tilted for *n*-alkyl and *n*-alkoxymethyl chains and horizontal for *n*-alkoxy chains, as was recently discussed.[12] This type of compound has been axially polymerized using polysiloxane as a backbone.[13-17] It has been shown by solid-state NMR spectroscopy and small-angle X-ray diffraction that the siloxane polymer containing Pc macrocycles substituted with *n*-alkoxy chains has a hexagonal columnar structure in which the Pc cores are horizontally stacked with respect to the columnar axis, even at ambient temperature.[17,18] In recent research, these compounds have been oriented using the Langmuir–Blodgett technique to obtain highly ordered films.[19-21]

The electronic properties of columnarly stacked π-systems are usually discussed in terms of a band model with a characteristic energy gap between extended valence and conduction bands.[1,2,4,22,23] In their pure form, phthalocyanines have an intrinsic band gap of approximately 2 eV,[24] making these materials insulators. In agreement with this, background conductivities lower than 10^{-10} S/m have been measured for unsubstituted[1] and peripherally substituted[25] Pc at room temperature in air-equilibrated samples. To convert the molecules to a (semi)conducting state, excess electrons or holes must be introduced into the conduction or valence bands, respectively.[26] In practice, this is achieved most often by chemical or electrochemical oxidation or reduction, commonly termed "doping". However, when high dopant concentrations are used, structural changes often accompany the doping process.[2] In an attempt to study the conductive properties of the structurally unperturbed materials, we have used the pulse-radiolysis time-resolved microwave conductivity (TRMC) technique.[27-30] Using nanosecond-duration pulses of ionizing radiation, a low concentration, less then 10 μM, of electron–hole pairs is produced throughout the bulk material. Microwaves are then used to monitor the change in conductivity of the medium resulting from the formation of mobile charge carriers.

Table I. Cell Parameters (Å) for Pc12 and $[Si(Pc8)O]_n$[a]

	Pc12		
	van der Pol et al.[10]	Ohta et al.[11]	$[Si(Pc8)O]_n$ van der Pol et al.[17]
solid phase	$Z = 4$	$Z = 2$	
orthorhombic	$a = 55.0$	$a = 27.8$	
	$b = 52.3$	$b = 25.8$	
	$c = 4.3$	$c = 4.3$	
mesophase	$Z = 1$	$Z = 1$	$Z = 1$
hexagonal	$D = 35.2$	$D = 35.0$	$D = 28.5$
	$h = 3.4$	$h = 3.4$	$h = 3.4$

[a] D = intercolumnar distance; h = stacking period; Z = molecules per unit cell.

The use of microwaves to monitor the radiation-induced conductivity in polycrystalline materials, such as those studied here, has distinct advantages over time-resolved, dc conductivity methods. Two advantages are of a practical nature: one is not having to apply ohmic electrode contacts to the sample, and the other is the built-in filtering out of broad-band EMI noise induced by the excitation pulse when waveguide transmission lines are used. In addition, problems connected with polarization of the material and field-induced drift of charge carriers to domain boundaries are absent. The latter effect, which results in a lower effective carrier mobility, is avoided if the frequency fulfills the following condition

$$f \gg [\mu(0)]E_0/2\pi d \tag{1}$$

In (1), $\mu(0)$ is the charge-carrier drift mobility within the bulk of the domain, E_0 is the field amplitude, and d is an average domain dimension. For the present materials, mobilities on the order of 10^{-4} m^2/(V s) might be expected to prevail.[31] For $d \sim 0.1$ μm and $E_0 \sim 10^4$ V/m, frequencies in the megahertz range or above must be used in order to be free of domain boundary effects. This condition is amply fulfilled for microwaves which have frequencies in the gigahertz range.

At high frequencies, the drift mobility will eventually decrease with increasing frequency according to (2). In (2), τ_m is the

$$\mu(\omega) = \mu(0)/[1 + (\omega\tau_m)^2] \tag{2}$$

momentum relaxation time associated with charge-carrier motion. Its magnitude can be estimated from the drift mobility via relationship 3.[32] For an electronic charge carrier (i.e. $m \approx m_e$), with

$$\tau_m \approx m\mu(0)/e \tag{3}$$

a mobility of ca. 10^{-4} m^2/(V s), τ_m is calculated to be on the order of 10^{-15} s. The denominator in (2) will therefore only exceed unity significantly for frequencies on the order of 10^{15} Hz and higher. The charge-carrier mobilities measured using the TRMC technique should therefore provide a measure of the drift mobility, $\mu(0)$, within the ordered, liquid-crystalline regions of the samples.

An increase in the dark conductivity with increasing frequency of the form

$$\sigma(\omega) = \sigma(0) + A\omega^s \tag{4}$$

with $0.5 < s < 1$, has been predicted and found for certain amorphous semiconductor materials.[32] This effect is a property of amorphous materials which have a very wide distribution of charge-carrier localization sites and relaxation times. It is not expected to play a role in the present experiments, where the conductivity results from the charge carriers within liquid-crys-

---

(7) Hanack, M.; Beek, A.; Lehmann, H. *Synthesis* **1987**, 703–705.

(8) Cook, M. J.; Daniel, M. F.; Harrison, K. J.; McKeown, N. B.; Thomson, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1086–1088.

(9) van der Pol, J. F.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 615–620.

(10) van der Pol, J. F.; Neeleman, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W.; Aerts, J.; Visser, R.; Picken, S. J. *Liq. Cryst.* **1989**, *6*, 577–592.

(11) Ohta, K.; Jacquemin, L.; Bosio, L.; Simon, J. *New J. Chem.* **1988**, *12*, 751–754.

(12) Weber, P.; Guillon, P.; Skoulios, A. *Liq. Cryst.* **1991**, *9*, 369–382.

(13) Sirlin, C.; Bosio, L.; Simon, J. *J. Chem. Soc., Chem. Commun.* **1987**, 379–380; **1988**, 236–237.

(14) Sauer, T.; Wegner, G. *Mol. Cryst. Liq. Cryst.* **1988**, *162B*, 97–118.

(15) Sauer, T.; Wegner, G. *Makromol. Chem., Makromol. Symp.* **1989**, *24*, 303–309.

(16) Caseri, W.; Sauer, T.; Wegner, G. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 651–657.

(17) van der Pol, J. F.; Zwikker, J. W.; Warman, J. M.; de Haas, M. P. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 208–215.

(18) Kentgens, A. P. M.; Markies, B. A.; van der Pol, J. F.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1990**, *112*, 8800–8806.

(19) Orthmann, E.; Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1105–1107.

(20) Sauer, T.; Arndt, T.; Batchelder, D. N.; Kalachev, A. A.; Wegner, G. *Thin Solid Films* **1990**, *187*, 357–374.

(21) Ali-Adib, Z.; Davidson, K.; Nooshin, H.; Tredgold, R. H. *Thin Solid Films* **1991**, *201*, 187–195.

(22) Orti, E.; Brêdas J. L. *Synth. Met.* **1989**, *29*, F115–F122.

(23) Gutmann, F.; Lyons, L. E. *Organic Semiconductors*; Wiley: New York, 1967.

(24) Usov, N. N.; Benderskii, V. A. *Phys. Status Solidi* **1967**, *20*, 481.

(25) Belarbi, Z.; Sirlin, C.; Simon, J.; Andre, J.-J. *J. Phys. Chem.* **1989**, *93*, 8105–8110.

(26) Marks, T. J. *Science* **1985**, *227*, 881–889.

(27) Warman, J. M.; de Haas, M. P. *Pulse radiolysis of irradiated systems*; CRC: Boca Raton, FL, 1991; pp 101–133.

(28) Warman, J. M. *The study of fast processes and transient species by electron pulse radiolysis*; Reidel: Dordrecht, The Netherlands, 1982; pp 129–161.

(29) Infelta, P. P.; de Haas, M. P.; Warman, J. M. *Radiat. Phys. Chem.* **1977**, *10*, 353–365.

(30) Warman, J. M.; de Haas, M. P.; Wentinck, H. M. *Radiat. Phys. Chem.* **1989**, *34*, 581–586.

(31) Cox, G. A.; Knight, P. C. *J. Phys. C: Solid State Phys.* **1974**, *7*, 146–156.

(32) Mott, N. F.; Davis. *Electronic Processes in Non-Crystalline Materials*; Clarendon Press: Oxford, U.K., 1979; p 224, 230.

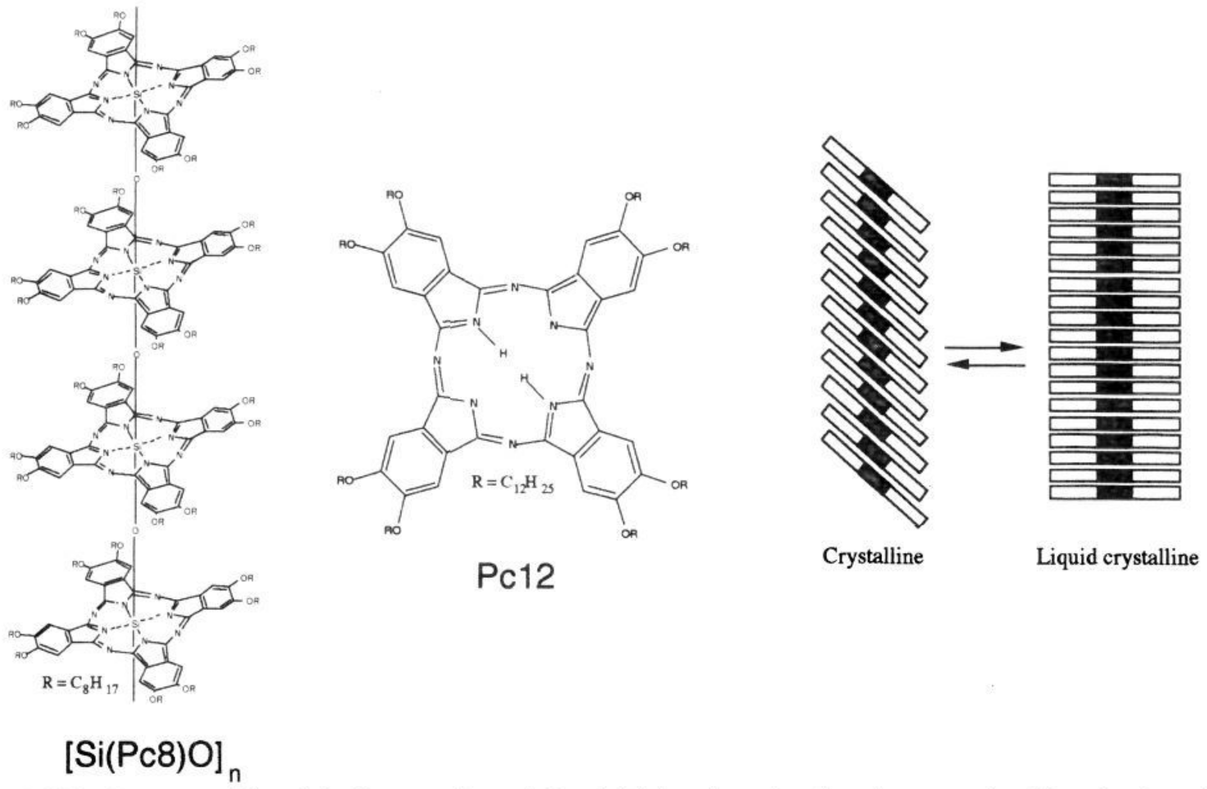

Figure 1. Molecular structure of the peripherally octa-*n*-alkoxy-substituted phthalocyanines and a schematic representation of the molecular stacking in the solid and liquid-crystalline phases of Pc12.

talline domains produced by pulsed ionization.

Recently, the pulse-radiolysis TRMC method has been applied to closely related mesogenic porphyrins to confirm that electrons and/or holes can move rapidly along the axis of columnar-stacked π-systems.[33] Also, it has been shown previously using this technique that the mobile charge carriers within the Pc cores recombine via intercolumnar electron tunneling through the intervening hydrocarbon mantle.[34] In this paper, we present a comparative study of intracolumnar conductivity in polymerized and nonpolymerized phthalocyanine stacks. Furthermore, a quantitative discussion of the charge-carrier mobilities associated with the observed radiation-induced conductivity is given.

Experimental Section

The structures of the compounds studied in the present paper are displayed in Figure 1. The methods of synthesis and characterization have been published previously.[9,17] The polysiloxane compound was obtained by thermal polymerization of the silanediol monomer at 200 °C in the liquid-crystalline phase. Small-angle X-ray scattering (SAXS) measurements have revealed the average degree of polymerization to be 98 ± 16 for the analogous $[Si(Pc12)O]_n$ compound. The polydispersity was found to be approximately 2.2.

It has been reported that, using differential scanning calorimetry (DSC), the metal-free phthalocyanine peripherally substituted with eight dodecyloxy chains, Pc12, undergoes a phase transition at ca. 90 °C from the solid to a liquid-crystalline phase.[9,11] Upon cooling, solidification occurs at 65 °C, showing a hysteresis of 25 °C. SAXS measurements performed by van der Pol et al.[10] and Ohta et al.[11] on this independently synthesized compound show in the solid phase an orthorhombic lattice of columnarly stacked Pc macrocycles, tilted with respect to the columnar axis with a center-to-center distance along the columnar axis of 4.3 Å. The crystallographic data are summarized in Table I. When the unit cell used by van der Pol et al. is converted to a unit cell with $Z = 2$, one obtains $a = 27.5$ Å and $b = 26.2$ Å, which agree very well with the parameters determined by Ohta et al. on the basis of $Z = 2$. At the transition to the mesophase, the columnar packing changes to a hexagonal form with an intercolumnar distance of 35.1 ± 0.1 Å.[10,11] At the same time, the macrocycles become horizontally stacked with respect to the columnar axis with a center-to-center distance of 3.4 Å.

The polymer formed by Pc macrocycles peripherally substituted with eight octyloxy chains linked by a siloxane backbone, $[Si(Pc8)O]_n$, does not undergo a phase transition between room temperature and 300 °C, as monitored by differential-scanning calorimetry.[17] The structure is the same as that found in the mesophase of Pc12, i.e. horizontally stacked columns of Pc units with hexagonal columnar packing, as revealed by SAXS.[17] The intracolumnar center-to-center Pc distance is also found to be the same at 3.4 Å. The intercolumnar distance was found to be 28.5 Å. Solid-state NMR measurements on similar Pc monomer and polymer compounds give further evidence for the structural assignment obtained with SAXS.[18]

The materials were stored in a vacuum oven at 60 °C prior to the experiment. During the course of the experiment, the samples were exposed to normal atmospheric conditions. No change in signal height or decay kinetics were observed under the given conditions. The compounds were compressed, using a close-fitting Teflon rod, into a piece of rectangular, 3.55×7.1 mm^2 microwave waveguide (the cell) which was closed at one end with a metal short-circuiting plate. The sample length, of approximately 10 mm, and weight, approximately 200 mg, were accurately measured. The temperature of the cell could be varied over the range from −100 to +200 °C. The top wall of the cell was reduced to a 0.5-mm thickness to minimize attenuation of the electron beam.

The samples were irradiated with 2–20-ns pulses of 3-MeV electrons from a Van de Graaff accelerator. The total beam charge in the pulse, Q nC, was monitored routinely by deflection onto a 50-Ω coaxial target. The energy deposited per unit volume within the sample was determined to be $D = 0.58 \times 10^3$ J/m^3 per 1 nC of beam charge, using Far West Technology-92 radiochromic thin-film dosimeters.

The penetration depth of the primary 3-MeV electrons is 10 mm in 1 g/cm^3 material. This is much greater than the 3.5-mm thickness of the sample, thus ensuring close to uniform energy deposition within the materials studied. Energy is dissipated along the track of a primary high-energy electron by way of individual excitation and ionization events. The latter occur, on the average, a distance of greater than 1000 Å apart in 1 g/cm^3 material. High-energy electrons transfer energy to a medium in proportion to the local electron density. In the present samples therefore ionization events leading to the formation of electrons and holes will occur initially with close to equal probability per unit volume in the phthalocyanine and saturated hydrocarbon regions of the material.

---

(33) Schouten, P. G.; Warman, J. M.; de Haas, M. P.; Fox, M. A.; Pan, H.-L. *Nature* **1991**, *353*, 736–737.

(34) Warman, J. M.; de Haas, M. P.; van der Pol, J. F.; Drenth, W. *Chem. Phys. Lett.* **1989**, *164*, 581–586.

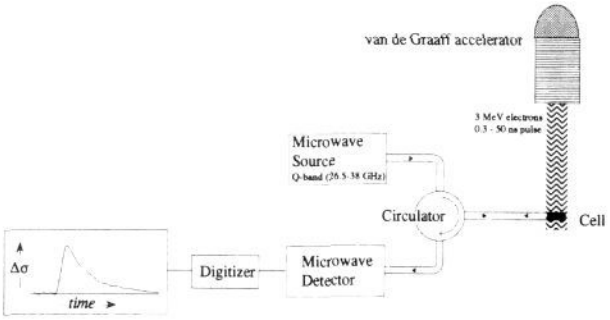

Figure 2. Schematic representation of the experimental setup.

Chemical changes resulting from irradiation are expected to be minimal because of the low total dose used per pulse and the known insensitivity of phthalocyanine moieties to radiation damage.[35] No effects were observed during the course of the measurements which could be ascribed to degradation of the sample due to the accumulated irradiation dose. Furthermore, SAXS measurements on Pc12 carried out after an extensive series of experiments showed no change to have occurred in the cell parameters in either the solid or the liquid-crystalline phase.

Any change occurring in the conductivity of the medium on irradiation is monitored as a change in the microwave power reflected by the sample, ΔP_r, as is schematically illustrated in Figure 2. Measurements were made in the 26.5–38-GHz region. For small changes, ΔP_r is directly proportional to the conductivity change $\Delta\sigma$

$$\Delta P_r / P_r = -A\Delta\sigma \quad (5)$$

The quantitative relation between the microwave loss and the conductivity change, i.e. parameter A, was determined using computational and data-fitting procedures described previously.[27-30] The radiation-induced conductivity changes measured in the present study lie between 10^{-4} and 10^{-3} S/m. This is at least 6 orders of magnitude higher than the background conductivity values found.[25]

Changes in the output of the microwave detector diode were monitored using either a Tektronix 7912 digital oscilloscope or a tandem combination of a Tektronix 2205 oscilloscope (7A13 plug-in) and a Sony/Tektronix RTD 710 digitizer. Using the former, the response time was approximately 1 ns. The latter combination had a rise time of only 5–10 ns but was capable of registering data using a pseudologarithmic time base. This allowed the recording of transient data from 10 ns to milliseconds using a single accelerator pulse. The conductivity transients determined are presented in the subsequent text and figures in a dose-normalized form, $\Delta\sigma/D$. The value of $\Delta\sigma/D$ at the end of the radiation pulse is denoted $\Delta\sigma_{\mathrm{eop}}/D$. The significance of this parameter is discussed in the next section.

Results and Discussion

On pulsed irradiation, readily measurable microwave conductivity transients were observed for both the monomeric, Pc12, and the polymeric, $[\mathrm{Si(Pc8)O}]_m$, compounds with lifetimes much longer than the pulse duration. The kinetics of the conductivity decay after the pulse are highly disperse, as shown in Figure 3. This aspect of the results will be discussed in a subsequent publication. In the present paper, we will concentrate on the absolute magnitude of the conductivity just after the pulse, i.e. the "end-of-pulse" conductivity.

As discussed in the Introduction, the change in the microwave conductivity resulting on pulsed ionization of the medium is related to the drift mobilities of the positive and negative charge carriers formed, $\mu(+)$ and $\mu(-)$, and their concentration at a time t, $N_p(t)$, by

$$\Delta\sigma(t) = e[\mu(+) + \mu(-)]N_p(t) \quad (6)$$

where e is the elementary charge, 1.60×10^{-19} C. As a result of the large penetration depth of 3-MeV electrons, energy deposition within the samples is close to uniform. For an infinitely short pulse, a dose D J/m^3 will result in an initial concentration of electron–hole pairs, e^-–h^+, given by

$$N_p(0) = D/eE_p \quad (7)$$

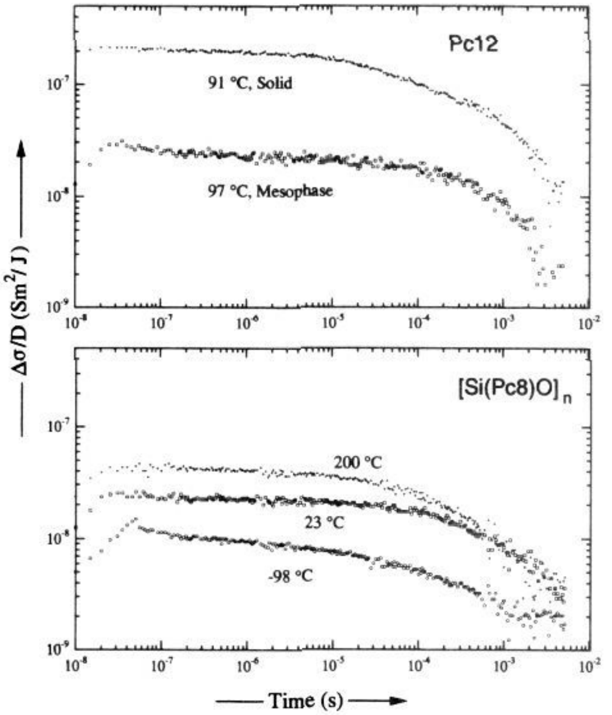

Figure 3. Conductivity transients at different temperatures for Pc12 and $[\mathrm{Si(Pc8)O}]_n$. Use was made of 5–20-ns pulses with beam charges of 12–40 nC.

In (7), E_p is the average energy required to form one e^-–h^+ pair in electronvolts. For organic materials it has a value of approximately 25 eV.[36,37] However, immediately after e^-–h^+ pairs have been formed, their number will be reduced as a consequence of recombination events. The fraction of e^-–h^+ pairs which survive recombination during the course of the pulse duration, Δt, is denoted by W_{eop}. The concentration of e^-–h^+ pairs at the end of the pulse is then given by

$$N_p(\Delta t) = W_{\mathrm{eop}}D/eE_p \quad (8)$$

The corresponding end-of-pulse conductivity per unit dose, $\Delta\sigma_{\mathrm{eop}}/D$, is obtained by combining (6) and (8)

$$\Delta\sigma_{\mathrm{eop}}/D = [\mu(+) + \mu(-)]W_{\mathrm{eop}}/E_p \quad (9)$$

Since for a given material E_p is expected to be constant, changes in $\Delta\sigma_{\mathrm{eop}}/D$ will reflect changes in the product of the charge-carrier mobilities and the survival probability. Possible upper and lower limits to W_{eop} and corresponding limiting values which can be derived for the charge-carrier mobilities will be discussed below after first presenting the experimental data.

The upper graph in Figure 4 displays the temperature dependence of the end-of-pulse conductivity per unit dose for Pc12. Starting at 7.7×10^{-8} S m^2/J at −100 °C in the solid phase, $\Delta\sigma_{\mathrm{eop}}/D$ increases with increasing temperature, reaching a value of 23.2×10^{-8} S m^2/J just before the transition to the mesophase at 93 °C. At the phase transition, the end-of-pulse conductivity decreases abruptly by a factor of 8 to a value of 2.9×10^{-8} S m^2/J. In the mesophase, $\Delta\sigma_{\mathrm{eop}}/D$ increases with further increase in temperature. Upon cooling, the temperature dependence is found to be reversible, apart from a hysteresis of approximately 25 °C, as is also found using DSC.[9]

The lower plot of Figure 4 gives the temperature dependence for the Pc polymer $[\mathrm{Si(Pc8)O}]_n$. A gradual increase in conductivity with increasing temperature is observed over the whole temperature range from 1.1×10^{-8} S m^2/J at −97 °C to 4.4 ×

---

(35) Zuppiroli, L. *Radiat. Eff.* **1982**, *62*, 53–68.

(36) Schmidt, W. F.; Allen, A. O. *J. Phys. Chem.* **1968**, *72*, 3730–3736.

(37) Warman, J. M. In *The study of fast processes and transient species by electron pulse radiolysis*; Baxendale, J. H., Busi, F., Eds.; Reidel: Dordrecht, The Netherlands, 1982; pp 433–533.

Table II. End-of-Pulse Conductivity per Unit Dose, $\Delta\sigma_{eop}/D$, and Lower and Upper Limits for the Sum of Charge-Carrier Mobilities

		Pc12		$[Si(Pc8)O]_n$	
T (°C)	W_{esc}[a]	$\Delta\sigma_{eop}/D$[b] (10^{-8} S m^2/J)	$\sum\mu_{min}$,[c] $\sum\mu_{max}$[d] (10^{-6} m^2/(V s))	$\Delta\sigma_{eop}/D$[b] (10^{-8} S m^2/J)	$\sum\mu_{min}$,[c] $\sum\mu_{max}$[d] (10^{-6} m^2/(V s))
-100	0.0042	7.73	1.93, 460	1.14	0.29, 67.9
-50	0.012	10.7	2.68, 224	1.36	0.34, 28.3
23	0.029	15.0	3.75, 129	2.52	0.63, 21.7
93	0.051	23.2	5.79, 114	3.37	0.84, 16.5
97	0.053	2.91	0.73, 13.7	3.44	0.86, 16.2
195	0.089	3.74	0.94, 10.5	4.42	1.11, 12.4

[a] Onsager escape probability determined using the Gaussian range distribution function from ref 36. [b] Values are interpolated from the heating trajectory data in Figure 4. [c] Calculated from (9) with $W_{eop} = 1$ and $E_p = 25$ eV. [d] Calculated from (9) with $W_{eop} = W_{esc}$ and $E_p = 25$ eV.

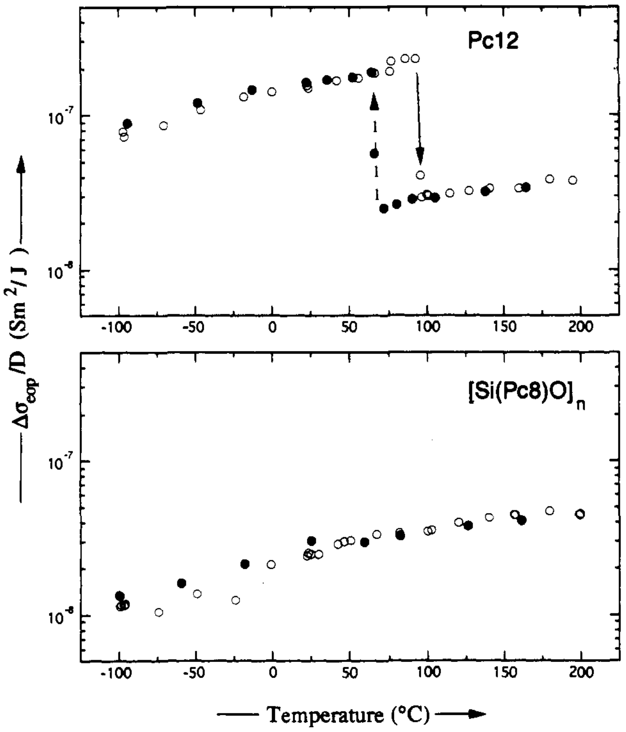

Figure 4. Temperature dependence of the end-of-pulse conductivity per unit energy absorbed on heating (open circles) and cooling (filled circles) for Pc12 and $[Si(Pc8)O]_n$.

10^{-8} S m^2/J at 200 °C. The absolute values are seen to be close to those found for Pc12 in the region of the mesophase. No abrupt changes in conductivity are found, as was expected, since DSC measurements gave no indication of first-order phase transitions.[17] An indication of a possible structural change was however found in the TRMC data in the form of a slight change in slope and a reduction in scatter of the results above a temperature of 25 °C.

Values of $\Delta\sigma_{eop}/D$, at several temperatures, obtained for the two compounds are listed in Table II.

In a previous paper on analogous porphyrin derivatives, we have shown that the organized columnar stacking of the macrocycles is a prerequisite for observing mobile charge carriers on pulsed irradiation.[33] In addition, we have found, for mesomorphic phthalocyanine systems similar to those studied here, that the lifetime of the charge carriers in the rigid phases increases exponentially with the chain length of the alkoxy substituents.[34] To explain these observations, we have proposed that the mobile charge carriers observed are derived from those e^-–h^+ pairs for which the electron and hole have escaped very rapid (picosecond time scale) "geminate" recombination and have become localized on the macrocyclic cores of different neighboring columns. While localized within the columnar core, the charge carriers are free to undergo rapid, one-dimensional motion along the core axis. Charge recombination is retarded by the intervening hydrocarbon mantle and can only occur via long-distance tunneling of electrons from core to core.

As mentioned, not all initially formed e^-–h^+ pairs will lead to long-lived mobile charge carriers. Some will undergo rapid, geminate recombination on a picosecond time scale in competition with core localization. In addition, the electron and hole may become localized on the same column and undergo rapid intracolumnar recombination. A very low quantum efficiency of charge-carrier generation of only 10^{-8} is found on irradiation of metal-free phthalocyanine single crystals with light.[31] This suggests that recombination is extremely efficient in the absence of an insulating barrier between the charge carriers. In agreement with this, we have also found very low radiation-induced conductivity transients for the octamethoxy analogue (Pc1) of Pc12.[34]

While an accurate estimate of the fraction of initially formed pairs which contribute to the end-of-pulse conductivity, i.e. W_{eop} in (8) and (9), cannot be made at present, it is possible to provide reasonable upper and lower limits. The indisputable upper limit to the survival probability is 1, corresponding to the situation where all e^-–h^+ pairs are scavenged by Pc macrocycles with e^- and h^+ on separated columns. Therefore, taking $W_{eop} = 1$ and $E_p = 25$ eV in (9) will result in the derivation of the minimum possible value of the sum of charge-carrier mobilities, $\sum\mu_{min} = [\mu(+) + \mu(-)]_{min}$, corresponding to a given value of $\Delta\sigma_{eop}/D$, i.e.

$$\sum\mu \geq E_p\Delta\sigma_{eop}/D = \sum\mu_{min} \tag{10}$$

$\sum\mu_{min}$ values are listed at several temperatures in Table II.

A consequence of the assumption that W_{eop} has the maximum constant value of 1 is that any temperature dependence found for $\Delta\sigma_{eop}/D$ must reflect directly the temperature dependence of the mobility alone. One would then conclude from the $\Delta\sigma_{eop}/D$ data shown in Figure 4, and the values of $\sum\mu_{min}$ in Table II, that the mobility is thermally activated in the Pc polymer and in both the solid and the liquid-crystalline phases of Pc12, apart from the sudden drop in mobility at the transition to the mesophase. When the temperature dependence of $\sum\mu_{min}$ is plotted in an Arrhenius fashion, activation energies for Pc12 of 0.029 eV in the solid phase and 0.038 eV in the mesophase are found. For the $[Si(Pc8)O]_n$ polymer, a value of 0.033 eV is found over the complete temperature range of −100 to +200 °C. The conclusion that the mobility is weakly thermally activated based on $W_{eop} = 1$ should however be treated with caution, as shown by the following considerations.

Studies of the ionization of hydrocarbon media by high-energy radiation have shown that a small fraction of electron–hole pairs, W_{esc}, undergo complete escape from their mutual Coulombic attraction and become "free". These free charge carriers will become trapped by even very low concentrations of trapping sites. W_{esc} therefore represents a reasonable *lower* limit to the yield of charge carriers trapped on Pc moieties in the present systems. Since the reason for the escape of the free charge carriers is mainly their initial large separation distance, it is also reasonable to assume that the electron and hole of such pairs will react with Pc molecules in different columns. In what follows, we consider the magnitude of the escape probability and the consequences of taking this as a lower limit for W_{eop}.

The probability that a pair of ions in a homogeneous medium separated initially by a distance r undergoes complete diffusional separation from the mutual Coulombic attraction and becomes "free" is given by the Onsager escape probability[38]

$$W_{esc}(r) = \exp(-r_c/r) \qquad (11)$$

The Onsager escape distance, r_c, is the distance at which the Coulomb energy is equal to the characteristic thermal energy k_BT, i.e.

$$r_c = e^2/4\pi\epsilon_0\epsilon_r k_BT \qquad (12)$$

For nonpolar materials (i.e. $\epsilon \approx 2$) at room temperature, r_c is 200–300 Å.

Schmidt and Allen have determined the yield of free ions in pulse-irradiated hydrocarbon liquids using the clearing field method.[36] In the analysis of their data, they assumed that, at the end of electron thermalization, the e^-–h^+ separation distances are distributed according to a Gaussian function

$$G(r) = (4\pi r^2/\pi^{3/2}b^3)\exp(-r^2/b^2) \qquad (13)$$

The total probability of escape, W_{esc}, is then obtained by integrating the product of $G(r)$ and the Onsager escape probability over all distances. This yields a function that is only dependent on r_c/b

$$W_{esc} = (4/\pi^{1/2})\int_0^\infty x^2 \exp(-x^2 - (r_c/bx))\,dx \qquad (14)$$

with $x = r/b$. From the experimentally determined values of W_{esc}, values for the characteristic separation distance, b, were calculated.[36] The product bd, with d being the density, was found to be independent of temperature for n-alkanes and equal to 45 Å g/cm^3.

For a material with a relative dielectric constant of 2.5, which we find, for the present materials, r_c is 226 Å at 295 K. Using a density of 0.9 g/cm^3, as determined for Pc12,[10] and the value of bd given above, the total probability of escape is found to be 0.029 at 295 K. Values of W_{esc} at different temperatures are listed in Table II. These values have been used to calculate the "maximum" values for the sum of charge-carrier mobilities, $\sum\mu_{max}$

$$\sum\mu \le \frac{E_p\Delta\sigma_{eop}/D}{W_{esc}} = \sum\mu_{max} \qquad (15)$$

As can be seen, $\sum\mu_{max}$ *decreases* with increasing temperature in the polymer and in both phases of Pc12 rather than increasing as was found for $\sum\mu_{min}$. The activation energies associated with $\sum\mu_{max}$, defined as $E_a = d(\ln \sum\mu_{max})/d(1/T)$, are therefore negative and equal to −0.036 and −0.044 eV for Pc12 in the solid phase and the mesophase, respectively, and −0.035 eV for the polymer over the temperature range of −100 to +200 °C. While the sign of the activation energy changes depending on whether $\sum\mu_{min}$ or $\sum\mu_{max}$ is taken, it is worth pointing out that the two limiting cases both predict an activation energy which is quite small in absolute terms, i.e. close to k_BT over the temperature range studied. It is clear that charge motion along the stacks is not strongly thermally activated. An effective negative activation energy of the mobility can be envisaged as arising from an increase in the structural disorder within the columns with increasing temperature. It should be emphasized that we are concerned here with the activation energy of the charge-carrier mobility alone and not with that of the dark conductivity which contains, in addition, the activation energy associated with thermal charge-carrier generation. The dark conductivity, of course, would be expected to be strongly thermally activated in the present type of compounds, as is in fact found.[25]

Since the average distance between the Pc columns is similar to the initial pair separation distance, there are clearly many phthalocyanine trapping centers which can scavenge charge carriers prior to their rapid geminate recombination. Therefore, the value of W_{eop} relevant to the present systems would be expected to lie somewhere between the upper and lower limits of 1 and W_{esc}. We would also expect the activation energy associated with the mobility to lie between the positive and negative values determined on the basis of the two limiting cases.

Table III. Extreme Limits for Activation Energies of the Mobilities for Pc12 and $[Si(Pc8)O]_n$ and Activation Energies Determined for Electron and Hole Mobility in Pc Single Crystals by Drift Measurements[31,40]

compd	state	E_a (eV) min	E_a (eV) max
Pc12	solid	−0.036	0.029
	liquid crystalline	−0.044	0.038
$[Si(Pc8)O]_n$	liquid crystalline	−0.035	0.033
Pc	single crystal (electron)	−0.045	
	single crystal (hole)	−0.039	

We are presently in the process of attempting to obtain a more accurate quantitative insight into the problem by carrying out Monte Carlo type calculations on the statistics of charge-carrier scavenging similar to those recently carried out for the simpler homogeneous scavenging case.[39] Also, dc pulse-radiolysis conductivity experiments are planned which should allow us to determine separately the absolute mobilities of the individual carriers and the charge-carrier yield. We hope therefore to be able to present more definitive data in future publications. At this time we will discuss the results only in general terms in the light of the $\sum\mu_{min}$ and $\sum\mu_{max}$ limits found.

In the crystalline phase of Pc12, the Pc moieties are arranged in tilted stacks similar to the arrangement in unsubstituted phthalocyanine. It is of interest therefore to compare the mobility values determined in the present work for Pc12 in the crystalline phase with previously measured drift mobilities in phthalocyanine. Drift mobilities have been measured in single crystals of phthalocyanine using pulsed light sources to produce charge carriers. For single crystals at room temperature, Cox and Knight[31] have found the mobilities for electrons and holes along the stacking axis to be almost equal, with $\mu_e = 1.7 \times 10^{-4}$ m^2/(V s) and $\mu_h = 1.5 \times 10^{-4}$ m^2/(V s), which give for the mobility sum $\sum\mu = 3.2 \times 10^{-4}$ m^2/(V s). Somewhat lower values have been reported for single crystals by Usov and Benderskii,[40] who found $\mu_e \approx 0.5 \times 10^{-4}$ m^2/(V s) and $\mu_h \approx 0.4 \times 10^{-4}$ m^2/(V s), giving $\sum\mu \approx 0.9 \times 10^{-4}$ m^2/(V s). Both groups find a temperature dependence of electron and hole mobilities of the form $\mu \propto T^{-n}$ with on average $n = 1.6$ for electrons and $n = 1.4$ for holes. These temperature dependences correspond to activation energies of −0.045 and −0.039 eV for electrons and holes, respectively, with an average value of −0.042 eV.

The mobilities determined from the present conductivity measurements on randomly oriented polycrystalline materials would be expected to be a factor of 3 smaller than the one-dimensional mobilities in the direction of the columnar axis. The values of $3\sum\mu_{max} = 3.9 \times 10^{-4}$ m^2/(V s) and $3\sum\mu_{min} = 0.1 \times 10^{-4}$ m^2/(V s) found for Pc12 at room temperature correspond therefore to upper and lower limits for the mobility along the Pc-stack axis. These values encompass the literature values of 3.2×10^{-4} and 0.9×10^{-4} m^2/(V s) determined for single-crystal phthalocyanine in the drift measurements mentioned above. Furthermore, comparable low activation energies are found for both the single-crystal Pc and Pc12 in the solid state, as is summarized in Table III. We conclude that the mode and dynamics of charge transport do not differ substantially between single-crystal phthalocyanine and the crystalline columnar phase of Pc12. The peripheral hydrocarbon tails appear to have little influence on the charge-carrier dynamics within the Pc core. As pointed out above, the hydrocarbon tails do, of course, play a decisive role in determining the rate of *intercolumnar* electron tunneling and hence the time scale of charge recombination. The hydrocarbon mantle serves to increase

---

(38) Onsager, L. *Phys. Rev.* **1938**, *54*, 554.

(39) Wojcik, M.; Bartczak, W. M.; Kroh, J. *Chem. Phys. Lett.* **1991**, *177*, 184–188.

(40) Usov, N. N.; Benderskii, V. A. *Phys. Status Solidi* **1970**, *B37*, 535–543.

the one-dimensional, "molecular wire" nature of charge migration in the present systems compared with unsubstituted Pc.

At the solid phase to mesophase transition of Pc12, no significant change is found to occur in either the density or the dielectric constant of the material. Therefore, there is no reason to expect a large increase or decrease in W_{eop}. We conclude that the much smaller conductivity found in the mesophase is a result of a much lower charge-carrier mobility. This result was not a priori expected. In fact, we had thought that the change from a tilted to a horizontal configuration of the Pc moieties would result in a greater degree of π–π overlap and hence more facile charge movement.[41] In support of this, results on exciton migration in similar columnar aggregates[42–44] have suggested that an increase in the rate of energy migration accompanies the change from a tilted to a horizontal configuration.

Theoretical calculations for both unsubstituted Pc monomers and Pc polymers have shown that the width of the band structures formed by the overlapping π-orbitals is influenced by factors such as molecular tilting, rotations of the macrocycle about the columnar axis, and longitudinal and lateral displacement within a column.[45–47] These perturbations from ideal columnar stacking all increase the resistivity toward charge migration, with longitudinal displacement and rotations having particularly pronounced effects. Since an increase in the occurrence and/or amplitude of all of these motions would be expected to accompany the melting of the hydrocarbon tails, it is perhaps not suprising with hindsight that the mobility does in fact decrease. It would appear that these perturbative effects more than counteract any increase in mobility which might have resulted from increased π–π overlap. Apparently, the flow of energy is less sensitive to columnar disorder.

Since the magnitude of the mobilities is lower than 10^{-3} m^2/(V s), it seems appropriate to discuss the charge-carrier transport in terms of polaronic motion corresponding to the hopping of more or less localized charge between neighboring Pc sites.[48] For an isotropic distribution of columnar axes, as in the present nonaligned samples, the average jump time between sites, τ_j, is related to the mobility by

$$\tau_j = ed_j^2/6k_BT\mu \tag{16}$$

The jump distance, d_j, in the present case is the distance between the centers of adjacent Pc macrocycles measured in the direction of the axis of the stack, i.e. 4.3 Å in the solid phase and 3.4 Å in the mesophase of Pc12 and 3.4 Å for [Si(Pc8)O]$_n$. Approximately half of the decrease, by a factor of 8, in the mobility in the mesophase of Pc12 can be attributed to the decrease in the center-to-center distance between macrocycles. The upper and lower limits ot the charge-carrier mobility in Pc12 at room temperature correspond to jump times between 0.01 and 0.3 ps, respectively. The limits of τ_j in the mesophase just above the transition temperature are determined to be 0.04–0.8 ps. The values are obtained using the sum of the mobilities as presented in Table II. When equal mobilities for positive and negative charge carriers are assumed, the hopping times will be twice as large.

The hopping times calculated by Markovitsi et al.[44] for exciton migration in a similar zinc octakis(alkoxymethyl)phthalocyanine were 45 and 0.4 ps in the solid and liquid-crystalline phases, respectively. Comparison with the times derived above for charge-carrier hopping would suggest that energy migration is considerably slower than charge transport in the solid phase but is of the same order of magnitude in the mesophase.

For [Si(Pc8)O]$_n$, the lower and upper limits of τ_j are 0.03 and 1.2 ps at room temperature. Interestingly, the siloxane backbone appears to have little influence on the dynamics of charge transport along the macrocyclic core except insofar as it preserves at all temperatures the horizontal stacking and the freedom of motion characteristic of the discotic liquid-crystalline phase of the monomeric compounds.

Conclusions

Upon pulsed irradiation, large conductivity transients have been measured in thermotropic liquid-crystalline phthalocyanines. Upper and lower limits for the sum of the electron and hole mobilities have been calculated over the temperature range from −100 to +200 °C. It has been found for the monomeric Pc that at the transition from the solid phase to the mesophase, the sum of the mobilities of charge carriers decreases abruptly by a factor of 8. This is attributed to an increase in perturbations from the ideal columnar stacking in the liquid-crystalline phase. The siloxane polymer with its fixed mesophase structure extends the conductive properties found for the mesophase of Pc12 to low temperatures. If the mobilities are considered to originate from hopping of localized charges between adjacent Pc macrocycles, the average jump time from site to site is found to be approximately 1 ps or less at room temperature.

---

(41) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

(42) Blanzat, B.; Barthou, C.; Trecier, N.; André, J.-J.; Simon, J. *J. Am. Chem. Soc.* **1987**, *109*, 6193–6194.

(43) Blasse, G.; Dirksen, G. J.; Meyerink, A.; van der Pol, J. F.; Neeleman, E.; Drenth, W. *Chem. Phys. Lett.* **1989**, *154*, 420–424.

(44) Markovitsi, D.; Lécuyer, I.; Simon, J. *J. Phys. Chem.* **1991**, *95*, 3620–3626.

(45) Whangbo, M.-H.; Stewart, K. R. *Isr. J. Chem.* **1983**, *23*, 133–138.

(46) Canadell, E.; Alvarez, S. *Inorg. Chem.* **1984**, *23*, 573–579.

(47) Pietro, W. J.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 5387–5391.

(48) Mott, N. F. *Conduction in Non-Crystalline Materials*; Clarendon: Oxford, U.K., 1987; pp 55–70.