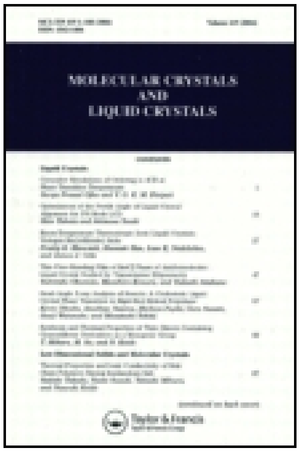

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Novel Phthalocyanine Polymers for Applications in Optical Devices

Thomas Sauer [a], Walter Caseri [a] & Gerhard Wegner [a]
[a] Max-Planck-Institut für Polymerforschung, Ackermannweg 10, Postfach 3148, D-6500, Mainz, FRG

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NOVEL PHTHALOCYANINE POLYMERS FOR APPLICATIONS IN OPTICAL DEVICES

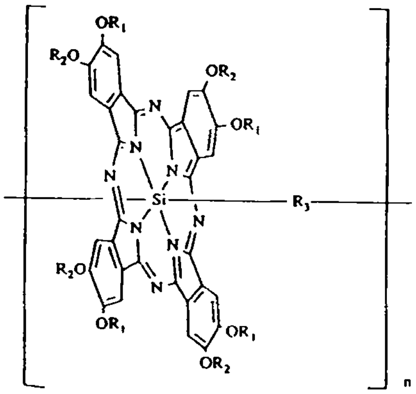
THOMAS SAUER, WALTER CASERI, GERHARD WEGNER
Max-Planck-Institut für Polymerforschung, Ackermannweg 10, Postfach 3148, D-6500 Mainz, FRG

Abstract: The optical properties of substituted phthalocyaninato-polysiloxanes and their copolymers having the chromophores separated by spacers are discussed in terms of the molecular exciton model. The shift of the Q band maximum of the siloxane polymer compared to the monomeric phthalocyanine as well as the absorption profile is well in accordance with the predictions of the model based on structural data of the materials. The electronic structure assumed by this model is further supported by emission spectroscopy. Separation of the chromophores by introduction of spacers within the main chain leads to materials with the optical properties of the monomeric phthalocyanine, even in the bulk. The band width of the polysiloxane polymer derived from the relative location of oxidation and reduction peaks as measured by cyclovoltammetry agrees well with the optical data.

INTRODUCTION

Recent interest in the optical properties of phthalocyanines results from the fact that their extended aromatic π-electron systems give rise to remarkable non-linear optical effects[1]. The application of these molecules in optical devices is further enhanced by their excellent chemical stability under ambient conditions. An interesting class of phthalocyanine derivatives became recently available in terms of highly soluble phthalocyaninato-polysiloxanes (PCPS) of high molecular weight as well as a new class of similar polymers where the phthalocyanine moieties are separated by a spacer[2] (see Fig. 1). These materials show appreciable third order non-linear effects[3]. The solubility of these polymers as well as their interfacial properties also allow for well defined deposition procedures such as the Langmuir-Blodgett technique[4]. Furthermore the structural characterization of these and similar materials which have been under investigation for many years[5] can be carried out by dilute solution methods where the neglect of intermolecular interactions allows for a much more umambiguous interpretation of data.

In this paper we discuss the optical properties of the phthalocyaninato-polysiloxanes shown in Fig. 1 in terms of the molecular exciton model by Kasha[12-14]. Furthermore it will be shown that the structural variation of the polymer by introduction of spacers between the phthalocyanine chromophores influences the optical properties in a well-defined way. Finally the spectroscopic investigations will be compared to results from electrochemical measurements.



Symbol	**R_1 , R_2 , R_3**
substituted phthalocyaninato-polysiloxanes: R_3 = -O-	
CnPCPS	$R_1 = R_2 = C_nH_{2n+1}$; n = 2,4,6 ,...,18
C1C8PCPS	$R_1 = CH_3$; $R_2 = C_8H_{17}$
spacer polymers *): $R_1 = CH_3$; $R_2 = C_8H_{17}$	
S1	$R_3 = -O-(CH_2)_4-Si(C_6H_5)_2-(CH_2)_4-O-$
S2	$R_3 = -O-(CH_2)_4-Si(CH_3)_2-C_6H_4-Si(CH_3)_2-(CH_2)_4-O-$
S3	$R_3 = -O-(CH_2)_4-Si(CH_3)_2-[O-Si(CH_3)_2]_4-(CH_2)_4-O-$
S4	$R_3 = -[Si(CH_3)(C_6H_5)]_n$; n $\simeq$ 6.6

*): for the synthesis and structure of these and further polymers having different spacers see ref. 2

FIGURE 1 Molecular structure of the substituted phthalocyaninato-polysiloxanes and the corresponding polymers having flexible spacers in the main chain (in the case of $R_1 \neq R_2$ the substituted phthalocyanine moiety is a mixture of four positional isomers)

EXPERIMANTAL PART

The detailed synthesis and structural characterization of the substituted phthalocyanine monomers, hereby abbreviated as CnPCSiCl$_2$ (dichloro form) and CnPCSi(OH)$_2$ (dihydroxy form of the silicon phthalocyanine; n denotes the number of carbon atoms per side chain), and the polymers according to Fig. 1 has been reported elsewhere[2, 6, 7]. Absorption spectra were taken with Perkin Elmer Lambda 3 and Lambda 9 spectrometers. Emission spectra were obtained with a Spex Fluorolog 1680 B spectrometer equipped with a double monochromator and a 450 W Xenon lamp. Solvents were of spectroscopical grade. Cyclovoltammetric measurements were performed under strictly oxygen-free conditions using the equipment described by Heinze[8] and a computer-assisted potentiostat M276 from EG&E. All measurements were done in anhydrous methylenechloride with 0.1 mol/l tetrabutylammoniumperchlorate as the supporting electrolyte versus a Ag/AgCl reference electrode. The sweep rate was 100 mV/s and the concentration of the solute approximately 10^{-3} mol/l.

OPTICAL PROPERTIES OF SOLUBLE PHTHALOCYANINATO-POLYSILOXANES

The absorption spectrum of a substituted PCPS as well as that of the corresponding monomer is shown in Fig. 2. The monomer exhibits two regions of considerable absorption: the B or Soret band at 340 and 358 nm as well as the Q band located at 680 nm with vibronic side bands at 651 and 612 nm. The spectral assignment follows the nomenclature given by Gouterman[9] for porphyrinic systems. Both bands arise from allowed $\pi^* \leftarrow \pi$ transitions with the transition dipole moments lying in the ring plane[10]. Because of the nearly D_{4h} symmetry, the lowest unoccupied molecular orbital (LUMO) is doubly degenerate. This degeneracy is not

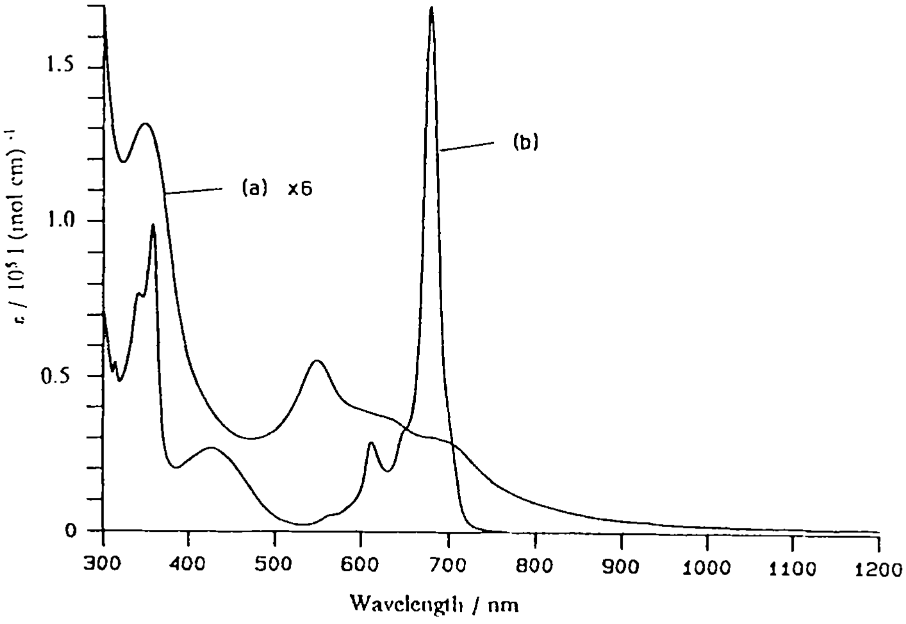


FIGURE 2 Absorption spectra of ClC8PCPS (a, scaled with a factor of 6) and the corresponding monomer ClC8PCSiCl$_2$ (b) measured in chloroform

influenced by the nature of the lateral substituents[11], but only a decrease in symmetry leads to a splitting of the Q band which is well-known from metal-free phthalocyanine[10].

The cofacial arrangement of the phthalocyanine units in the corresponding polymer leads to a strong mutual influence of the chromophores which results in a considerable blue shift of the maximum and a broadening of the Q band (see Fig.2). These spectral changes can be described fairly well with the theory of molecular excitons mainly explored by Kasha[12].

We consider the following dimer model (Fig. 3): two planar, cofacial chromophores are seperated by a distance r_{12}. The transition dipole moments are lying in the molecular planes defining a torsion angle α when viewed along r_{12}. The quantum mechanical treatment of this system in the limit of strong coupling[13] leads to the energy level diagram shown in Fig. 4.

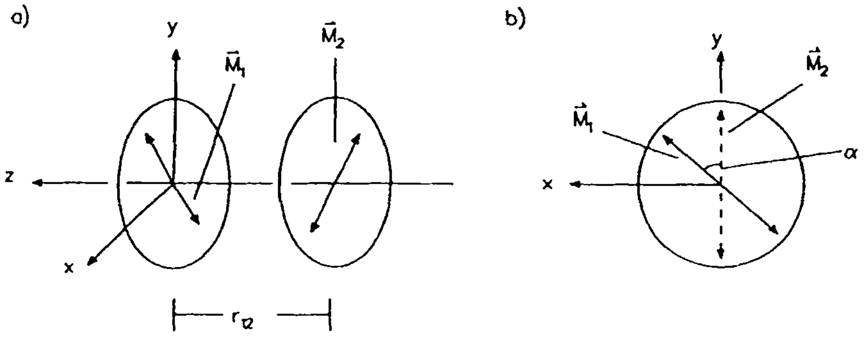


FIGURE 3 Model of a molecular dimer (a) and projection along the direction of r_{12} (b)

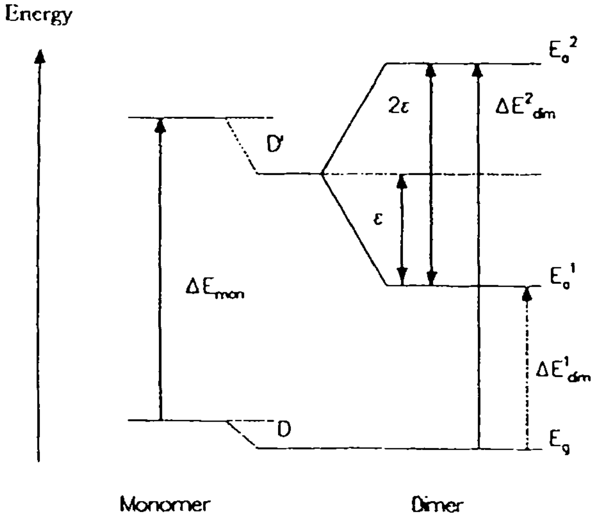


FIGURE 4 Exciton band scheme of a molecular dimer with parallel transition dipole moments (for explanation of symbols see text)

The main result of the interaction is the splitting of the excited state. Using the point dipole approximation this exciton splitting energy is given by[14]

$$2\varepsilon = -(E_a^2 - E_a^1) = -2\frac{|\vec{M}^2|}{r_{12}^3}\cos\alpha \tag{1}$$

$\vec{M}$ is the transition dipole moment which is related to the experimental value of the oscillator strength f.

$$f = 4.32\times 10^{-9}\int_{\nu_1}^{\nu_2}\varepsilon'(\nu)d\nu \tag{2}$$

$$|\vec{M}^2| = \frac{3he^2 f}{8\pi^2 m_e c\, g_n \Delta E_{mon}} \tag{3}$$

h is the Planck's constant, e the charge and m_e the mass of the electron, c the velocity of light, g_n the degree of degeneracy of the excited state, ΔE_{mon} the transition energy of the monomer Q band and $\varepsilon'(\nu)$ the molar decadic extinction coefficient which is integrated in the range $[\nu_1, \nu_2]$. Although eq. (1) suggests that the exciton splitting 2ε can be determined experimentally, only the higher energy transition ΔE^2_{mon} of the dimer is allowed by selection rules[14] when $\alpha = 0$. In the case of $\alpha > 0$ also the lower energy transition is weakly allowed, but in general only one level of the splitted exciton band can be observed experimentally as a peak in the spectrum.

Another possibility to determine 2ε and also α according to eq.(1) not discussed in literature so far arises from the magnitude of the band shift. The dimer transition energy $\Delta E^2_{\rm dim}$ is given by[12] (see Fig. 4)

$$\Delta E^2_{\rm dim} = (E_a^2 - E_g)_{\rm dim} = \Delta E_{mon} + \Delta D - \varepsilon \tag{4}$$

ΔE_{mon} is the transition energy of the monomer and $\Delta D = D' - D$ is the difference between the van der Waals interaction terms which cause a lowering both of the ground and excited state of the molecular dimer (Fig. 3). From this relation the exciton splitting follows

$$2\varepsilon = 2[-(\Delta E^2_{\rm dim} - \Delta E_{mon}) + \Delta D] \tag{5}$$

The transformation of this model to the case of a polymer with the degree of polymerization N results in a exciton splitting energy of

$$2\varepsilon = -4\left[\frac{N-1}{N}\frac{|\vec{M}^2|}{r^3}\cos\alpha\right] \tag{6}$$

where r is the repeat distance in chain direction. A comparison of eqs. (1) and (6) shows that for a high molecular weight polymer where $(N\text{-}1)/N \simeq 1$ the value of 2ε is twice as high as for the dimer, when only nearest neighbour interactions are considered and end groups neglected. Allowing also for longer range interactions, the numerical factor in eq. (6) results to be 4.8[12], and combination of eqs. (5) and (6) leads to

$$2[-(\Delta E_{pol} - \Delta E_{mon}) + \Delta D] = -4.8\left[\frac{N-1}{N}\frac{|\vec{M}^2|}{r^3}\cos\alpha\right] \tag{7}$$

where ΔE_{pol} is the energy corresponding to the polymer Q band maximum.

Besides ΔE_{pol}, ΔE_{mon}, N, r and $|\vec{M}^2|$ which can be determined experimentally, also the value of ΔD is required to determine the torsion angle α according to eq. (7). Molecular orbital calculations by Woolsey and Hush[15] based on a model dimer of PCPS give the following band shifts compared to the monomer absorption

$$\Delta E^2_{dim} - \Delta E_{mon} = \Delta D - \varepsilon = 820\,cm^{-1}$$

$$\Delta E^1_{dim} - \Delta E_{mon} = \Delta D + \varepsilon = -2110\,cm^{-1}$$

from which a value of

$$\Delta D = -615\,cm^{-1}$$

follows. Optical measurements on this dimer by Kenney et al.[16] prove these results. In which way ΔD is changed when going from a dimer to a polymer is presently not known, so that the value for the dimer has to be used in a first approximation.

The experimentally determined band shift (Fig. 2) is

$$\Delta E^2_{pol} - \Delta E_{mon} = 3609 \pm 56\,cm^{-1}$$

according to Q band maxima of 546 and 680 nm (± 1 nm). From this value the exciton splitting 2ε follows according to eq. (5)

$$2\varepsilon = -8448 \pm 112\,cm^{-1}$$

The approximation $(N-1)/N \simeq 1$ holds in this case with an error smaller than 2% since $N > 50$ for the polymer used here[17]. r is 3.33 Å as determined by powder X-ray diffraction. The integration of the monomer band in the range from 13500 to 18500 cm^{-1} leads to

$$f = 0.6 \pm 0.01$$

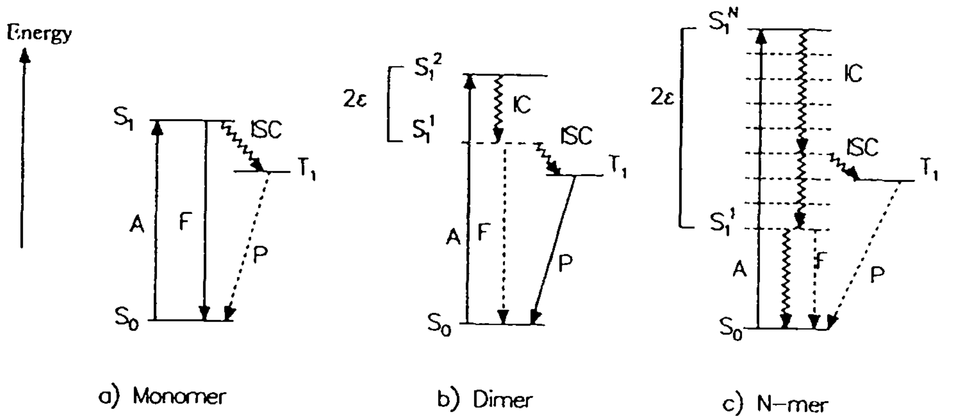
$$|\vec{M}^2| = (4.4 \pm 0.06)\, 10^{-35}\, (erg\, cm)^2$$

Similar values were reported by Fujiki et al.[18] for monomeric phthalocyanines showing strong aggregation in solution. From the value of f we see that we deal with an allowed electric dipole transition which is a major criterion for the applicability of the molecular exciton model. Evaluation of eq. (7) now results in a value of the torsion angle α of

$$\alpha = 72.9° \pm 3.5°$$

The error in α has been estimated from the relative errors of all experimental quantities. Since there is no estimate of the accuracy of the value of ΔD in this calculation as discussed above, an additional error of ± 3.2° in α may arise when ΔD is thought to be wrong by a factor of 2.

Because of the fourfold symmetry of the phthalocyanine this value is equivalent to a mutual



a) Monomer b) Dimer c) N–mer

FIGURE 5 Schematic representation of absorption and emission processes in a monomer, a dimer and a n-mer having parallel transition dipole moments. S_0, S_1: Ground and first excited singulett state; T_1: triplett state; A: absorption; F: fluorescence; P: phosphorescence; 2ε: exciton splitting; IC: internal conversion; ISC: intersystem crossing; $\sim>$: radiationless processes. Electronic levels are drawn without vibrational structure for the sake of simplicity.

geometrical torsion of adjacent monomer units of about 17°. This angle is surprisingly close to the value of 15.9° found by crystal structure analysis of a model trimer[19] although lot of approximations have been used in the spectral analysis.

As mentioned earlier, a non-vanishing value of α leads to a weakly allowed lower energy transition in the dimer[12, 15]. In the case of a polymer this leads to a situation where the highest energy transition shows the highest intensity while the transitions to the (N-1) lower energy levels of the exciton band are weak in intensity. The whole situation is complicated by the polydispersity of the polymer which leads to a smearing of a possible fine structure of the absorption band. Therefore theory predicts a slowly decaying Q band which has non-vanishing intensity at least up to 1000 nm as estimated by the experimental value of 2ϵ. As can be clearly seen from Fig. 2, this intensity distribution of the polymer Q band is nicely

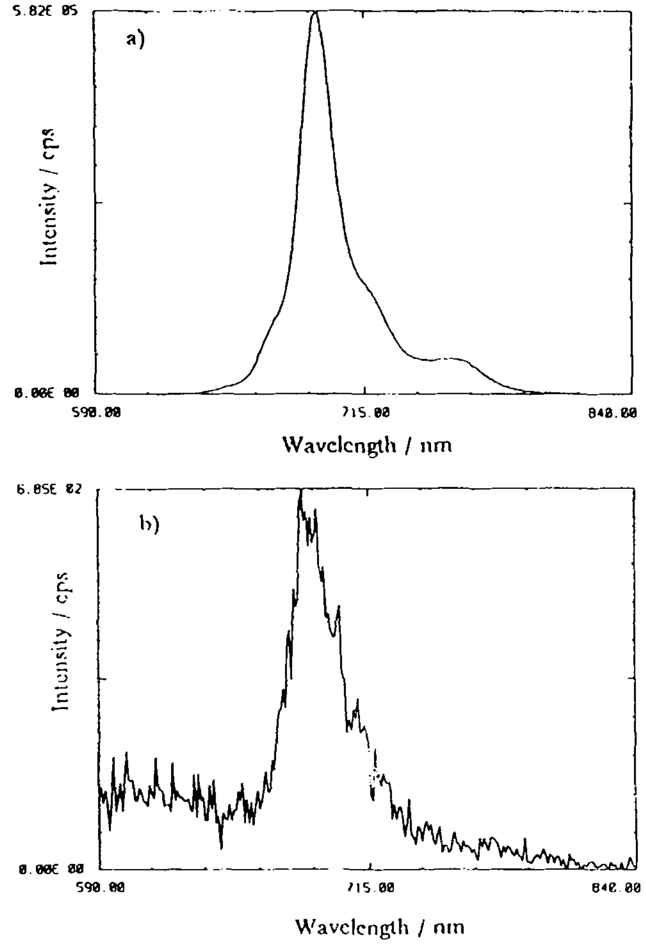


FIGURE 6 Emission spectra of the phthalocyanine monomer ClC8PCSiCl$_2$ (a) and ClC8PCPS (b) in chloroform (excitation wavelength: 560 nm)

reproduced by experiment.

Further evidence for this model is derived from emission spectroscopy. As shown in eqs. (1) and (6), the exciton splitting energy 2ε is proportional to the square of the transition dipole moment. According to this approximation, the energy level of the triplet state T_1 is not influenced by the interaction between chromophores since the oscillator strength of the $T_1 \leftarrow S_0$ transition vanishes according to Laporte's rule. A very simple model of the emission characteristics for the molecules discussed here is shown in Fig. 5. In the case of the monomer strong fluorescence is assumed and also found in experiment (see Fig. 6a), showing a maximum at 694 nm. In the case of a dimer, a radiationless decay from the allowed exciton level to the symmetry forbidden lower exciton level should lead to a strong enhancement of triplet state population which gives rise to phosphorescence. Indeed, strongly enhanced triplet emission with high quantum yield is observed in a variety of aggregating dye molecules[12]. Transfering this model formally to a polymer with a large exciton splitting 2ε, the energy level diagram shown in Fig. 5c results. Since the radiationless decay from the allowed exciton state does not favour any level from which the triplet state T_1 can be populated, only a very weak fluorescence is expected in the near infrared which cannot be measured with the spectrometer we used. The luminescence spectrum of the polymer (Fig. 6b) shows the same profile as the

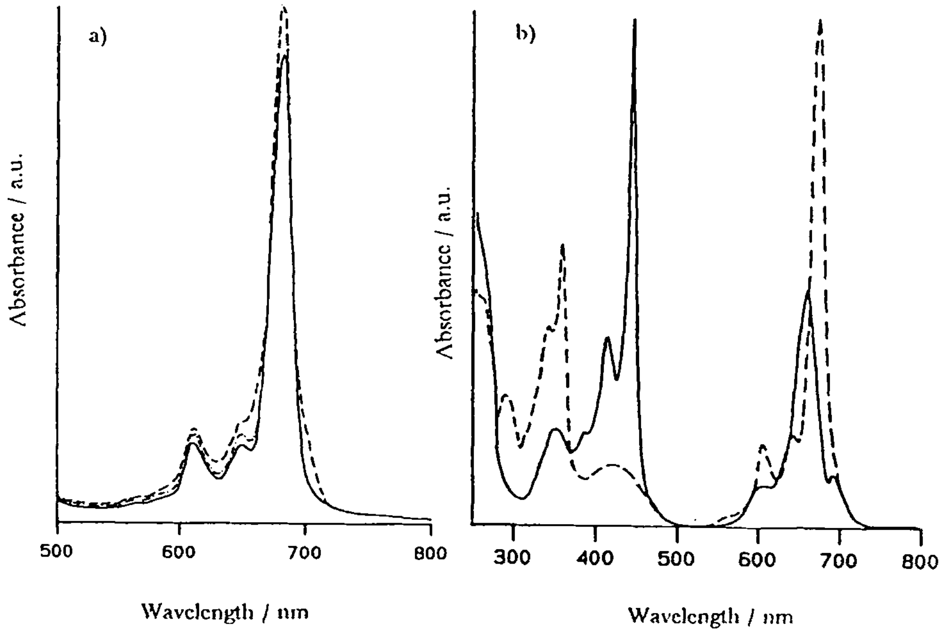


FIGURE 7 Absorption spectra of spacer polymers S1 (-.-.-), S2 (-----) and S3 (———) in chloroform (a) and S4 (———) in comparison with the phthalocyanine monomer ClC8PCSiCl$_2$ (-----) in THF (b)

monomer spectrum. But normalized to the same concentration of chromophores, the intensity has decreased by a factor of 2×10^4. This signal is likely due to traces of monomer left in the sample, but a weak phosphorescence cannot be ruled out umambigiously. Time resolved emission spectroscopy is required for a final answer to this question. But nevertheless, an enhanced triplet emission as in the case of molecular dimers is not observed.

These results give valuable guidelines on what has to be done if a reduction of 2ε is wanted in order to tailor macromolecules with their optical properties ranging between the two extreme cases of monomer and polymer. The torsion angle α is very difficult to control since it is determined by packing forces between phthalocyanine units along the polymer chain. A systematic variation of substituents and a method for the determination of α independent from optical spectroscopy would be required to gain a structure-property relationship. Also it seems not possible to predict if large variations in α with the nature of the substituents are likely to occur in this type of polymer. A decrease in N again leads to the monomer which shows a very sharp Q band in solution, but the polymer properties are lost. Also the monomers tend to crystallize in stacks which again leads to a broadening of the absorption band. The most obvious possibility is to increase the distance r between adjacent phthalocyanine units. Increasing the side chain volume fraction in the polymer from short (C1C8PCPS: r = 3.33 Å, $\lambda_{max} = 546\,nm$) up to very long side chains (C18PCPS: r = 3.46 Å, $\lambda_{max} = 570\,nm$) is one possibility to separate the chromophores on a small scale. The difference in the absorption maxima correlates well with the r^{-3}-dependence given by eq. (7) although some care has to be taken since the polymers having different side chain length also differ in their degree of polycondensation N[17]. The introduction of spacers between the phthalocyanine units changes this separation on a large scale so that we are provided with a possibility to achieve monomer-like spectra as shown in Fig. 7. The nature and the length of these spacers can be varied to a great extent[2]. Besides the fact that the molecular exciton model, e. g. eq. (7) is not applicable any longer in this case of very weak coupling, the mere fact that the exciton bandwidth 2ε depends on the inverse cube of the inter-chromophore separation explains why the spacer polymers S1 to S3 where r is of the order of magnitude of 10 Å reproduce the optical spectrum of the isolated phthalocyanine. Interesting to note is the optical spectrum of polymer S4 bearing a polysilane spacer. The sharp absorption band centered at 448 nm with vibronic side bands at 414 and 386 nm has to be attributed to the polysilane chain. The strong red shift of this band compared to other polysilanes[20] is a clear indication of interaction with the π-electron system of the phthalocyanine which is also demonstrated by the slight alteration of the phthalocyanine Q band profile in this compound.

Furthermore, the same arguments which were discussed to influence the optical properties of the isolated polymer hold for their spectral properties in the bulk. The polarized absorption spectra of a C1C8PCPS film prepared by the Langmuir-Blodgett technique[4] are shown in Fig. 8a. Again, the strong interaction between adjacent chromophores results in a very broad Q band which shows a dichroism because of the macroscopic ordering of the macromolecules. In contrast, the absorption profile of the spacer polymer S3 in a Langmuir-Blodgett film is rather narrow and monomer-like (Fig. 8b) although a residual broadening results from intermolecular interactions in the bulk.

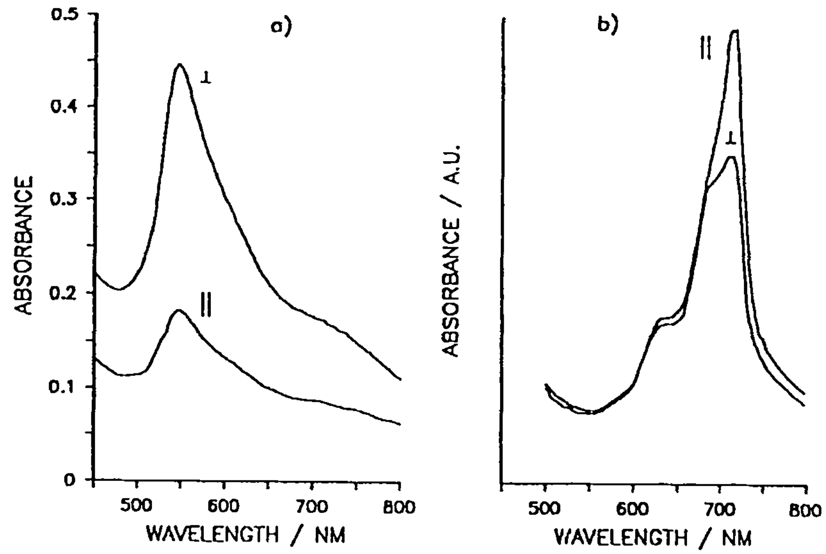


FIGURE 8 Polarized absorption spectra of Langmuir-Blodgett films from ClC8PCPS (a, 100 layers) and S3 (b, 50 layers) on quartz. Spectra were taken with the electric field vector parallel (||) and perpendicular (⊥) to the dipping direction of the substrate.

ELECTROCHEMISTRY

Additional information concerning the electronic structure of the polymers investigated here can be derived from electrochemistry. For this purpose, cyclovoltammetric studies[8] were carried out to verify the results from optical spectroscopy.

Systematic studies on defined oligomers of PCPS by Armstrong, Kenney and coworkes[21, 22] show that the mutual influence of adjacent phthalocyanine units leads to an overlap and consequently to a delocalization of π-electron density along the chain[23, 24, 25]. At the same time the first oxidation state is stabilized by a significant decrease of the first oxidation potential. The influence on the first reduced state is much smaller[22], and Armstrong et al.[21] even find a weak destabilization which is expressed by a slow decrease of the first reduction potential when going from a monomer to a trimer. Although obvious contradictions exist in detail, the decrease of the potential difference between the first reduction and the first oxidation potential with increasing chain length can be derived as a general feature from experimental results. The same finding was reported for planar aromatic systems with increasing extension of the π-electron system[26].

The substituted PCPS shows a number of reversible redox peaks in the cyclovoltammogram. As an example, Fig. 9 compares monomer and polymer bearing hexyloxy side chains. The variation of the side chain length does not result in systematic variations of the locations of the electrochemical potentials. All data are collected in Tab. 1. Compared to the monomer, the potential difference

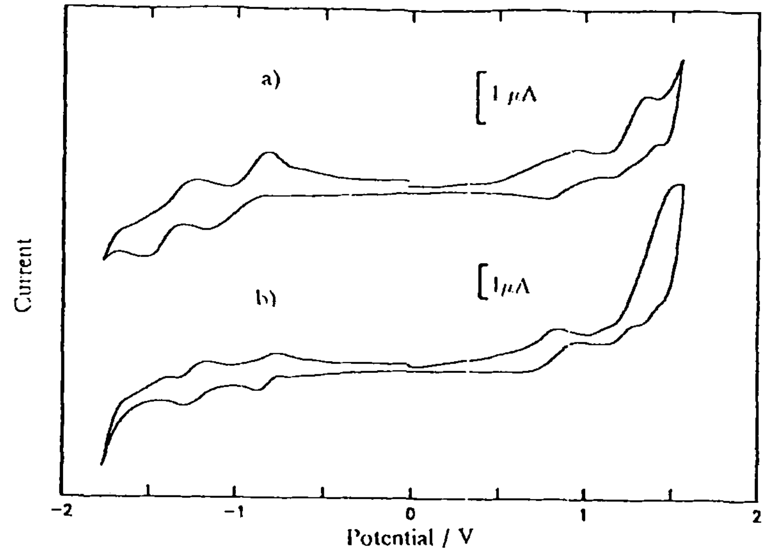


FIGURE 9 Cyclovoltammograms of the monomer $C6PCSi(OH)_2$ (a) and the corresponding polymer C6PCPS (b)

$$\Delta E_{\pm ½} = E_{p,½}(+1) - E_{p,½}(-1) \tag{8}$$

between the first oxidation and the first reduction potential (determined as the mean value from all experiments, see Tab. 1) is significantly smaller in the polymer

$$\Delta E_{\pm ½}\,(monomer) = 1.86 \pm 0.12\ V$$

$$\Delta E_{\pm ½}\,(polymer) = 1.60 \pm 0.10\ V$$

But this effect is smaller than assumed from extrapolating the results from short chain oligomers^{21}. The potential difference $\Delta E_{\pm ½}$ can be correlated with optical data since this difference equals the energy required to produce a bound electron-hole pair which is an exciton by definition. Recalculating potential differences into energies (1 eV equals 8065.4 cm^{-1}) the following absorption energies and wavelengths are obtained:

Monomer: ν = 15002 ± 968 cm^{-1}; λ = 670 ± 40 nm

Polymer: ν = 12905 ± 807 cm^{-1}; λ = 775 ± 45 nm

The experimental errors are quite large because of the broadness of the redox peaks. But nevertheless, the calculated absorption maximum of the monomer is nicely reproduced (λ_{max} = 680 *nm* from UV/VIS spectroscopy). The calculated transition wavelength of the polymer would suggest a red shift of the Q band while in optical spectroscopy a blue shift is

TABLE I Electrochemical data of substituted phthalocyanine monomers and polymers (for experimental details see Experimental Part)

Sample	charge per ring	$E_{p,c}$ [*V*]	$E_{p,a}$ [*V*]	ΔE_p [*mV*]	$E_{p,½}$ [*V*]	*)
C6PCSi(OH)$_2$	-2	-1.51	-1.24	270	-1.38	
(monomer)	-1	-1.17	-0.93	240	-1.05	
	+1	0.79	0.95	160	0.87	
	+2	1.20	1.37	170	1.29	
C10PCSi(OH)$_2$	-2	-1.30	-1.27	30	-1.29	
(monomer)	-1	-0.86	-0.84	20	-0.85	
	+1	0.83	0.97	140	0.90	
	+2	1.24	1.37	130	1.31	
C18PCSi(OH)$_2$	-2	-1.71	-1.46	250	-1.59	
(monomer)	-1	-1.20	-0.92	280	-1.06	
	+1	0.79	0.91	120	0.85	
C1C8PCPS	-1	-1.22	-1.10	120	-1.16	
(polymer)	+1	0.56	0.66	100	0.61	
	+2	1.18	1.32	140	1.25	
C6PCPS	-2	-1.28	-1.19	90	-1.24	
(polymer)	-1	-0.86	-0.79	70	-0.83	
	+1	0.72	0.83	110	0.77	
	+2	1.28	1.38	100	1.33	
C10PCPS	-1	-0.93	-0.79	140	-0.86	
(polymer)	+1	0.75	0.87	120	0.81	
	+2	1.20	1.30	100	1.25	
S1	-2	-1.52	-1.33	190	-1.43	
(polymer)	-1	-1.12	-0.83	290	-0.98	
	+1	0.76	0.93	170	0.85	
	+2	1.26	1.38	120	1.32	
S2	-2	-1.54	-1.33	210	-1.44	
(polymer)	-1	-1.13	-0.79	340	-0.96	
	+1	0.71	0.86	150	0.79	
	+2	1.31	1.39	80	1.35	

*): $E_{p,a}$ and $E_{p,c}$: anodic and cathodic peak potential; $\Delta E_p = |E_{p,a} - E_{p,c}|$; $E_{p,½}$: mean value from $E_{p,a}$ and $E_{p,c}$

observed. But electrochemistry is not restricted to the selection rules governing optical absorption. Assuming a symmetrical splitting of the exciton band about the excited monomer level which seems to be a good approximation if the experimental errors are taken into account, the above result from cyclovoltammetry leads to a maximum of the allowed polymer absorption band located at

$$\lambda_{pol} = 565 \pm 45\,nm$$

This is well in the range of the spectroscopically determined polymer absorption maxima which vary between approximately 545 and 570 nm for the different samples differing in side chain length (and also molecular weight) discussed here.

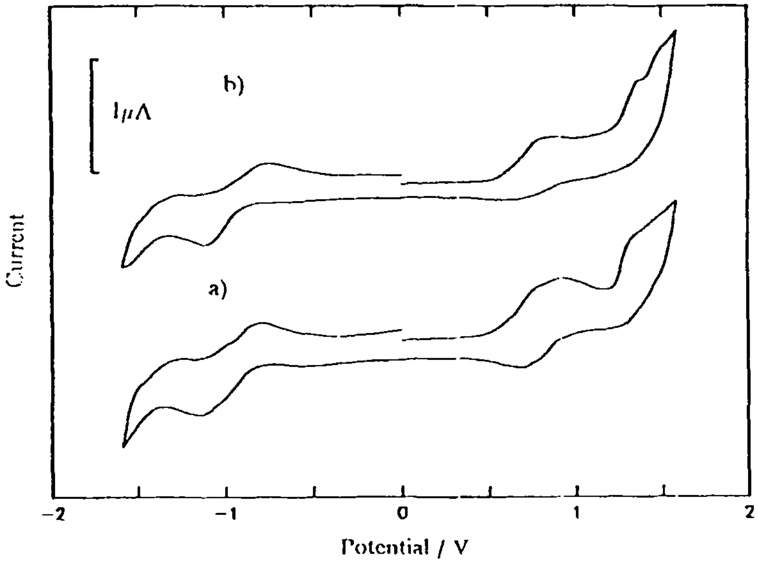


FIGURE 10 Cyclovoltammograms of the spacer polymers S1 (a) and S2 (b)

The electrochemistry of the spacer polymers, however, is the same as in the case of the substituted phthalocyanine monomers as can be seen for the case of polymers S1 and S2 from Fig. 10 and the data in Table 1. The missing interaction between the phthalocyanine units as indicated by optical spectroscopy is reflected by the fact that the positions of the redox peaks as well as the peak separation $\Delta E_{\pm 1/2}$ is almost the same as in the case of the monomer. Further work has to show what the situation is in polymers like S4 where the electrochemically active moiety is coupled to the electronic system of the spacer.

CONCLUSION

This investigation shows that the molecular exciton model is appropriate to describe the optical properties of substituted phthalocyaninato-polysiloxanes. Recent criticism on this model by Fujiki et al.[18] who stated are large overestimation of the band shift by the molecular exciton model seems not to be justified since independent data from spectroscopy, structural investigations and electrochemistry lead to a unique result as shown here. This is mostly due to the fact that in this covalently bonded array of chromophores the geometrical relation between adjacent subunits is much more defined than in physical aggregates as were used in the investigations by Fujuki and coworkers[18].

The introduction of spacers between the phthalocyanine chromophores provides a new class of tractable polymeric materials with finely tunable optical properties. Their capability to form ultrathin film of controlled thickness deposited by the Langmuir-Blodgett technique as well as their non-linear optical properties make them interesting candidates for application in optical devices. Furthermore, the coupling of different chromophores as demonstrated in the polysilane copolymer S4 is one preliminary example for expanding this principle of modelling optical properties over the whole spectral range. Further work on these materials is in progress.

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REFERENCES

1. Z. Z. Ho, C. Y. Hu, W. M. Hetherington, *J. Appl. Phys.*, **62**, 716 (1987); Z. Z. Ho, N. Peyghambarian, *Chem. Phys. Lett.*, **148**, 197 (1988)
2. T. Sauer, W. Caseri, G. Wegner, *Macromolecules*, submitted
3. A. Kaltbeitzel, D. Neher, C. Bubeck, T. Sauer, G. Wegner, W. Caseri, In: H. Kuzmany, M. Mehring, S. Roth (eds.), *Electronic Properties of Conjugated Polymers*, Springer, 1989, in press
4. A. A. Kalachev, T. Sauer, V. Vogel, N. A. Plate, G. Wegner, *Thin Solid Films*, submitted; T. Sauer, T. Arndt, D. N. Batchelder, A. A. Kalachev, G. Wegner, *Thin Solid Films*, submitted
5. T. J. Marks, *Science*, **227**, 881 (1985)
6. T. Sauer, G. Wegner, *Mol. Cryst. Liq. Cryst.*, **162B**, 97 (1988)
7. W. Caseri, T. Sauer, G. Wegner, *Makromol. Chem., Rapid Commun.*, 9, 651 (1988)
8. J. Heinze, *Angew. Chem.*, **96**, 823 (1984)
9. M. Gouterman, *J. Chem. Phys.*, **30**, 1139 (1959)
10. A. B. P. Lever, *Adv. Inorg. Radiochem.*, 7, 27 (1965)
11. E. Ciliberto, K. A. Doris, W. J. Pietro, G. M. Reisner, D. E. Ellis, I. Fragala, F. H. Herbstein, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.*, **106**, 7748 (1984)
12. M. Kasha, In: B. DiBartolo (ed.), *Spectroscopy of the Excited State*, Plenum Press, New York, 1976
13. M. Kasha, H. R. Rawls, M. Ashraf El-Bayouni, *Pure Appl. Chem.*, **11**, 371 (1965)
14. E. G. Rae, M. Kasha, In: L. Augenstein, R. Mason, B. Rosenberg (eds.), *Physical Processes in Radiation Biology.*, Academic Press, New York, 1964
15. N. S. Hush, I. S. Woolsey, *Mol. Phys.*, **21**, 465 (1971)

16. A. R. Kane, J. F. Sullivan, D. H. Kenney, M. E. Kenney, *Inorg. Chem.*, **9**, 1445 (1970)
17. T. Sauer, G. Wegner, manuscript in preparation
18. M. Fujiki, H. Tabei, T. Kurihara, *J. Phys. Chem.*, **92**, 1281 (1988)
19. D. R. Swift, *Ph. D. Thesis*, Case Western University, Cleveland/Ohio, 1970
20. L. A. Harrah, J. M. Zeigler, *Macromolecules*, **20**, 601 (1987)
21. T. R. Mezza, N. R. Armstrong, G. W. Ritter, J. P. Iafalica, M. E. Kenney, *J. Electroanal. Chem.*, **137**, 227 (1982)
22. D. W. deWulf. J. K. Leland, B. L. Wheeler, A. J. Bard, D. A. Batzel, D. R. Dininny, M. E. Kenney, *Inorg. Chem.*, **26**, 266 (1987)
23. A. B. Anderson, T. L. Gordon, M. E. Kenney, *J. Am. Chem. Soc.*, **107**, 192 (1985)
24. K. A. Doris, D. E. Ellis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.*, **106**, 2491 (1984)
25. M. H. Whangbo, K. R. Stewart, *Isr. J. Chem.*, **23**, 133 (1983)
26. V. D. Parker, *J. Am. Chem. Soc.*, **96**, 5656 (1974)