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Temperature Dependences of ^{13}C-NMR Spectra and Conductivities with Metal-Free Phthalocyanines Dispersed in Bisphenol-A-Polycarbonate

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Temperature dependences of conductivities of the thin films with α-, β-, τ- and X-forms metal-free phthalocyanines (H_2Pcs) dispersed in bisphenol-A-polycarbonate and solid-state cross-polarization magic-angle-spinning (CP/MAS) ^{13}C-NMR of H_2Pcs were measured. The activation energies at higher ($T>300$ K) and lower ($T<200$ K) temperature region could be calculated in the range of 140 and 373 K. ^{13}C-NMR spectra of the H_2Pcs indicated the apparent differences, furthermore, individual spectra were changed at the function of temperature due to the influences by the N-H tautomerism in the H_2Pc molecules.

KEYWORDS: H_2Pc, conductivity, activation energy, CP/MAS ^{13}C-NMR, temperature dependence

§1. Introduction

In the recent papers, we have shown a unique polymorph of metal-free phthalocyanine (H_2Pc) which was named τ-form.[1,2] This τ-H_2Pc is using as a charge generation material (CGM) of photoreceptors for laser beam printers equipped with diode laser having the wavelength usually at 780 nm in industrial point of view. Important characteristics of this material are as follows; 1) to exhibit high carrier generating ability, 2) to exhibit a large absorbance at near-infrared regions, thus this τ-H_2Pc is well suited for CGM. Therefore, it is necessary to measure the conductivities of the polymer films including H_2Pcs for understanding the behavior of holes and electrons.

Cross-polarization magic-angle spinning (CP/MAS) ^{13}C-NMR has been developed as an effective method to investigate the crystal state of molecular compounds. Meier *et al.*[3] and Toscano *et al.*[4] have been studying the relationship between inner protons and carbons in phthalocyanine molecules. In particular, an important theme, which suggests in Fig. 1, is whether the two inner protons in H_2Pc are directly bonded with a diagonally opposed pair nitrogens (bonded type) or are shared by four equivalent pyrrole nitrogens (bridged type). Therefore, it can be presumed that the conductivities of the polymer films including H_2Pcs are influenced by the behavior of inner protons.

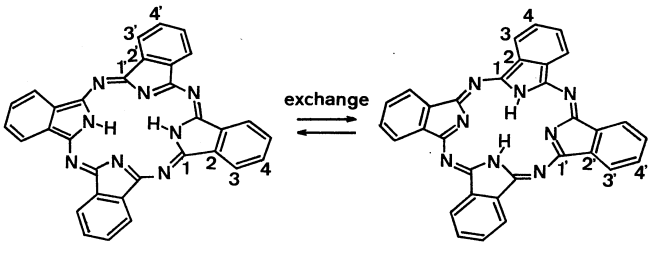

Fig. 1. Structure and N-H tautomerism of metal-free phthalocyanines.

In the series of our studies on H_2Pcs, we measured the conductivities as a function of temperatures, in the thin films of H_2Pcs dispersed in bisphenol-A-polycarbonate (PC) to investigate the influences of crystal forms. Furtheremore, solid-state CP/MAS ^{13}C-NMR spectra were measured to study the magnetic state of H_2Pcs. We found the relationship between the conductivities and ^{13}C-NMR spectra due to the N-H bond tautomerism in the range of $-100\sim120$°C.

§2. Experimental

The H_2Pcs used were prepared by the methods of previous papers,[1,5,6] and the particle sizes were controlled to almost the same diameters (≈0.05 μm) by the milling method. The differences of polymorphs were analyzed by X-ray powder diffraction patterns and IR spectra. The β-form is stable crystal, and α-form is meta-stable crystal. Both τ- and X-form are the crystals, which have middle energy stages.[1] However, the τ-form is more stable than X-form, and the crystal structure of X-form is assigned a dimer.[7] The strength of intermolecular forces will be $\alpha<X<\tau<\beta$ from C-H out-of-plane bending vibration in IR spectra, on the contrary the amounts of adsorbed oxygens will be $\alpha>X>\tau>\beta$ from XPS results.* H_2Pcs were dispersed with bisphenol-A-polycarbonate (Panlite K-1300; Teijin Co.) in tetrahydrofran. The cells for measurements were prepared by casting the solution on NESA glass to a thickness of approximately 10 μm, and dried slightly at 25°C for a day. An opposite gold electrode was deposited on the surface of film. The cell was attached in cryostat under the pressure of 10^{-2} Pa for an hour, and then measured. The conductivities of films can be calculated by the following equation.

$$\sigma=1/\rho=d\cdot I/S\cdot V \qquad (1)$$

where σ is the conductivity (S/cm), ρ the resistivity, d the thickness of film (cm), I the current (A), S the area of electrode (cm^2), and V the applied voltage (V). Activation

*Author's private data.

energies (E_a) can be calculated from the Arrhenius equation.

$$\sigma=\sigma_0\cdot\exp(-E_a/kT) \quad (2)$$

where σ_0 is the constant, k the Boltzmann constant and T the temperature. The current was measured by an electrometer (617; Keithley Instruments).

High-resolution CP/MAS ^{13}C-NMR spectra of H_2Pcs powder were obtained on a spectrometer (JOEL GSX-270W) at a frequency of 67.5 MHz. The techniques of magic-angle spinning, cross-polarization were employed in order to enhance the signal-to-noise ratio as well as the spectral resolution. The resolution was within 5 Hz at a spinning speed of 4.5 kHz. We could not measure the chemical shifts under -100°C because of the freezing of the equipments. The ^{13}C chemical shifts were determined by using liquid tetramethyl silane as an external reference.

§3. Results and Discussion

Figure 2 shows the temperature dependence of dark conductivities of the thin films with H_2Pcs dispersed in PC. These E_as were determined from the straight line part in the low temperature region. The temperature at which the conductivity start to increase off the straight line is designated a knick temperature (TC) in Fig. 2. E_a and TC are summarised in Table I. Though the dark conductivities of H_2Pc films were low as a whole, an apparent difference can be seen in the four crystal forms.

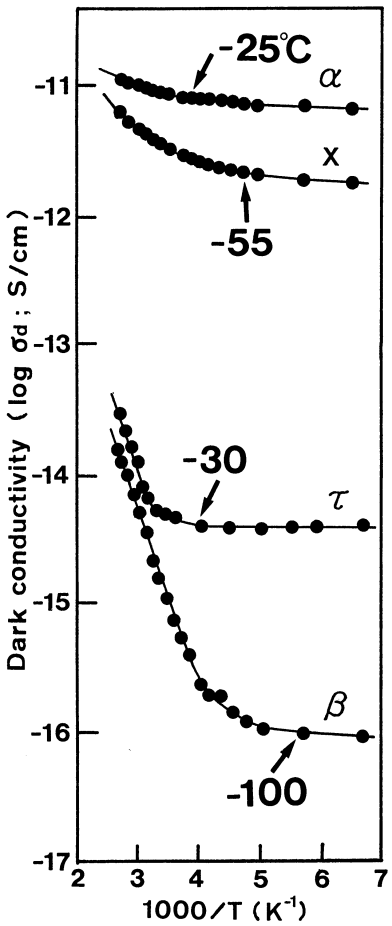

Fig. 2. Conductivities of metal-free phthalocyanines dispersed in the bisphenol-A-polycarbonate films. Numerals in this figure suggest the temperature (°C).

Table I. Activation energies, TC and TD of H_2Pcs dispersed in the bisphenol-A-polycarbonate films.

H_2Pc	Activation energy[a]		TC[b] (°C)	TD[c] (°C)
	$E_a(T>300$ K) (eV)	$E_a(T<200$ K) (eV)		
α	7.8×10^{-2}	1.6×10^{-3}	−25	−30
β	0.24	2.0×10^{-3}	−100	< −100
τ	0.19	$\fallingdotseq 0$	−30	−40
X	0.15	2.1×10^{-3}	−55	−40

a) E_a suggests the activation energies of higher ($T>300$ K) and lower ($T<200$ K) temperature regions, respectively (ref. Fig. 2).
b) TC is the point of the knick temperature, at which the conductivity start to increase off the straight line is designated a TC (ref. Fig. 2).
c) TD is the disappearing temperature of the chemical shifts from 140 to 160 ppm, which are attributed to inner carbons in H_2Pc molecule (ref. Fig. 3).

In low temperature region ($T<200$ K), E_a of τ-H_2Pc exhibits apparently zero, whereas small activation energies approximately 2×10^{-3} (eV) can be seen for α-, β- and X-H_2Pcs. As the charge carrier mobility is limited by temperature, conductivities are dependent of potential barrier height. Temperature dependence may be explained by a transition from extrinsic to intrinsic conduction, that is, the drop of conductivity would be the increasing phonon scattering with increasing temperature until intrinsic conduction is acheieved. The barrier height of τ-H_2Pc was the lowest in H_2Pcs from E_a valures. At 200 K, the conductivities of α-, β-, τ- and X-H_2Pcs are 7.8×10^{-12}, 1.1×10^{-16}, 3.1×10^{-15} and 2.0×10^{-12} (S/cm), respectively. Conductivity of α-H_2Pc are greater than that of β-H_2Pc approximately five orders of magnitude. As the particles of H_2Pcs are almost the same size, the influences of particle size and space charge are negligible. Thus the conductivities may be influenced by the molecular stacking in the crystalline state, that is, the extent of overlapping of π-orbital and the amounts of absorbed oxygens. The electric field dependences of dark current for H_2Pcs also support these orders of conductivities.*

On the other hand, in high temperature region ($T>300$ K), the free carriers are presumed to be transferred by the hopping conduction followed by Poole-Frenkel effect of $\log\sigma_d\propto 1/T$. Therefore, E_a can be estimated as large values. In practice, the E_as except for α-form exhibit 0.15 ~ 0.24 (eV). Though satisfactory models of hopping mechanism for each H_2Pcs cannot be drawn as a simple concept, E_a may connect with the probability in hopping of carriers and the vertical distances of H_2Pcs. The planar molecular stacking of β-form has the shortest distance (3.4 Å) in comparison with other H_2Pcs, and the literature value of E_a suggests 0.91 (eV).[8] This difference of E_a may be attributable to the extent of carrier transport barrier. The curves in the wide range of temperatures were analyzed by Kelly and

*Author's private data.

Lubitz,[9] and explained by both monomolecular and bimolecular recombination kinetics. The *TC* of α-, β-, τ- and *X*-H_2Pcs are -25, -100, -30 and -55°C, respectively. As the increase of conductivity of β-H_2Pc began from -100°C, it can be presumed the carrier hopping occurs from the lowest temperature compared with other polymorphs. That is, *TC* would be influenced by morphology of H_2Pcs.

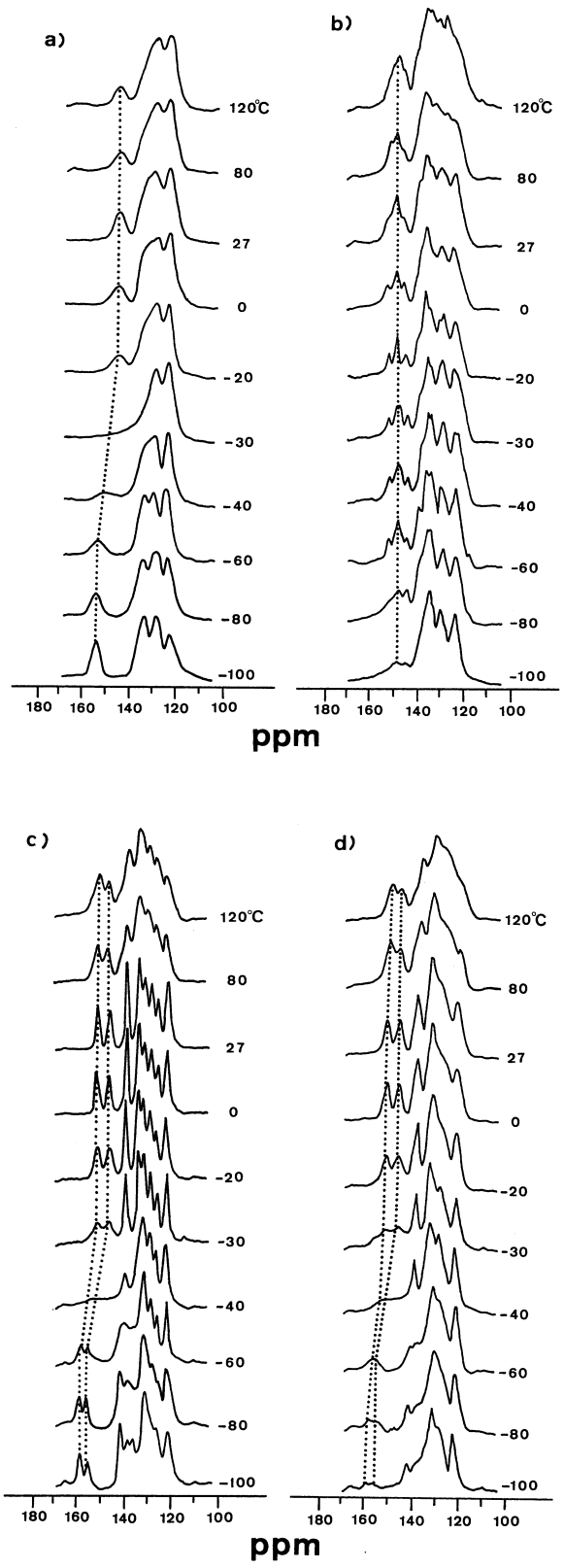

Fig. 3. Solid-state ^{13}C-NMR spectra of metal-free phthalocyanines using the CP/MAS technique from -100°C to 120°C. a) α-form, b) β-form, c) τ-form, d) *X*-form. Numerals in this figure suggest the temperature (°C). Dashed lines suggest the chemical shifts of inner carbons on the individual polymorphs.

In order to study the N-H tautomerism behavior of H_2Pcs, the temperature dependences of solid-state ^{13}C-NMR spectra were measured. The spectra of four representative H_2Pcs are shown in Fig. 3. In the case of α-H_2Pc, hydrogen exchanges between the inner nitrogens are fast, therefore, the resonance lines of carbons are separated four shifts. As the molecules of β-H_2Pc tend to be as close as their geometry allows, the spectra show a number of chemical shifts. τ-H_2Pc are assigned to the eight well-splited carbon atoms, which relate whether the bridge nitrogens are bonded with the inner hydrogens or not. Though *X*-H_2Pc has relatively similar shifts compared to τ-H_2Pc, broad shifts can be seen from 125 to 130 ppm. These broad shifts are believed to be the well-overlapped π-electrons of benzene rings in H_2Pc molecules.

As can be seen in Fig. 3, the spectra are very dependent on the temperature. The dashed lines show the behavior of individual inner carbons (1 and 1′). In the case of α-, τ- and *X*-H_2Pcs, these chemical shifts are attributable to a change in the exchange limit due to the decreasing intermolecular interaction, while the intramolecular interaction increases. The chemical shifts consequently show a limit of change at a temperature of approximately -30°C. Chemical shifts assigned to the inner carbons (dashed lines) disappear at $-30\sim-40$°C, the temperature is named *TD*, but clearly appear again toward lower magnetic fields below -60°C, resulting from the proton exchange velocity.[3] On the other hand, we cannot observe the disappearance of chemical shifts with β-H_2Pc. This result may be because the strong interaction of molecular packing prevents the formation of intramolecular N-H bonding, instead of the intermolecular N-H bonding with neighbor molecules. The temperature dependence of β-H_2Pc is rather low, and chemical shift at -100°C tend to disappear, therefore, the temperature of disappearance will be below -100°C.

*TD*s, which are shown in Table I, are almost the same temperature as *TC*s. *TD* would reflect the transitional temperature of transfer velocity of inner hydrogens in H_2Pc. Therefore, *TC* shows the transitional temperature between lower and higher velocities. These transfer velocities would influence the conductivities of films. Hydrogen exchanges between the inner nitrogens promotes intramolecular and intermolecular interaction, in practice, the broad resonance lines such as α-and *X*-H_2Pcs compared with β- and τ-H_2Pcs would mean the wide magnetic distribution, which promote the high conductivities. We think that the formation of intermolecular N-H bonding also promotes the carrier mobility, which reflects the conductivities.

§4. Conclusion

We showed the temperature dependences of conductivities of the thin film with the four kinds of H_2Pcs. The E_as at higher ($T>300$ K) and lower ($T<200$ K) tempera-

ture region, and individual *TC*s were also shown. The conductivities of H_2Pcs were differed in the range of five orders of magnitude. Furthermore, ^{13}C-NMR spectra of the H_2Pcs indicated the apparent differences, and individual spectra were changed as a function of temperature due to the influences by the N-H tautomerism in the H_2Pc molecules. Finally, we found the relationships between conductivities and ^{13}C-NMR spectra, and the steep and slight changes of the conductivities, and also relationship of *TC*s and *TD*s, can be presumed by these tautomerism.

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