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Mesomorphic Phase Transitions of 5,10,15,20-Tetrakis(4-n-dodecylphenyl)porphyrin

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The title compound was found to exhibit two phases between the isotropic liquid and crystalline ones. The phase transition enthalpies and entropies were typical for those of discotic mesogens, though the two phases are highly viscous but not brittle. The X-ray diffraction study indicated the two phases have discotic lamellar structures with slight difference each other.

Porphyrin metal complexes are interested in various functions, represented by photo-electronic conversion, biomimetic properties, catalytic effects and so on.[1] On the other hand, the functions of materials are just owing to the molecular alignments as well as the molecular structures. From such viewpoints, mesomorphic states are fascinated to effectively realize molecular functions as a property of materials.

Discotic mesomorphic states are also interested as a candidate for studying relations between material functions and the mesomorphic structures. Nowadays, however, few knowledge are revealed for mesomorphic functions of discotic mesogens,[2] though discotic mesomorphic states have been extensively studied since 1977 when they were discovered.[3]

In this work, metal-free 5,10,15,20-Tetrakis(4-n-dodecylphenyl)porphyrin(C_{12}TPP) was investigated on the mesomorphic phase sequence and the structures.

The material was prepared by the usual synthetic method of tetraphenylporphyrin[4] and purified by column chromatography(activated alumina, benzene) after oxidation of the by-product, a chlorin derivative.[5] Further purifications were carried out by the Soxhlet extraction of impurities with

Table 1. Phase transition sequence of C_{12}TPP

	Crystal	m_1	m_2	Isotropic
Transition temperatures/°C	31.0 [10.5]a)	52.0 [50.0]	155.0 [149.0]	
$\Delta H/kJ \cdot mol^{-1}$	46.0	14.0	23.3	
$\Delta S/J \cdot K^{-1} \cdot mol^{-1}$ b)	152	43	54	

a) [ ]:phase transition temperatures on cooling at 5 °C/min.
b) Calculated values from the relation:$\Delta H = T \cdot \Delta S$.

methanol-acetone. Finally, the product was recrystalized from benzene-acetone solution.

The phase transitions were measured using a DSC(Daini Seikosha SSC-560 S) and a Nikon polarizing microscope equipped with a Mettler FP52 heating stage and FP5 control unit. The structural analysis was made by Rigaku Geigerflex(Cu-Kα radiation) with a temperature controlled hot plate

The phase transition sequence of C_{12}TPP is listed in Table 1. All phase transitions are enantiotropic. C_{12}TPP exhibits two phases between the isotropic liquid and crystalline ones. The two phases(m_1 and m_2 phases) are highly viscous, while the crystalline one is brittle. The DSC thermogram of C_{12}TPP is shown in Fig.1. The behavior of the phase transition enthalpies(ΔH) and entropies(ΔS) is similar to that of discotic mesogens,[6] in which the ΔH and ΔS for the crystal to mesophase transition are larger than those for the mesophase to isotropic liquid one. A comparison with 5,10,15,20-tetrakis(4-n-alkyloxyphenyl)porphyrins, which exhibit the direct phase

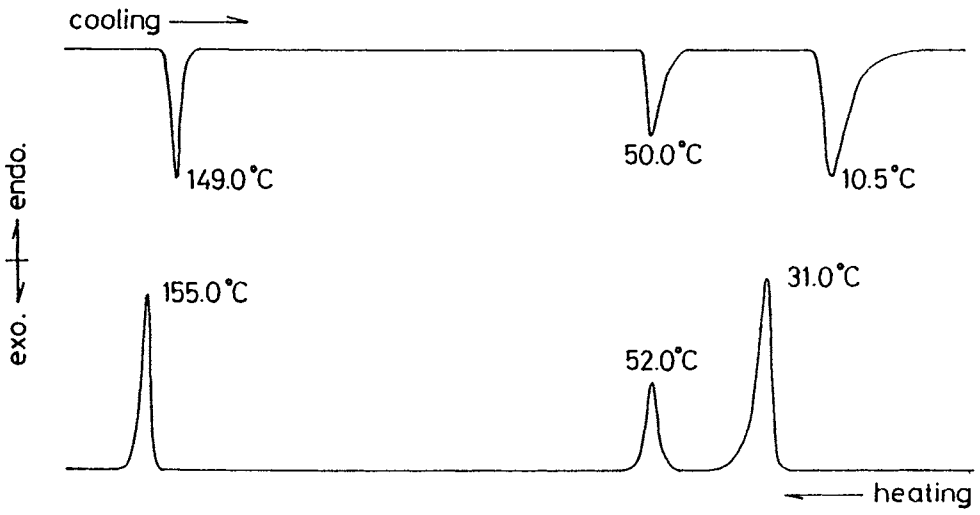

Fig.1. DSC thermogram of C_{12}TPP for heating and cooling rates at 5 °C/min.

transition from the crystalline phase to the isotropic liquid, also supports these two phases are mesomorphic.[7)]

The X-ray diffraction powder patterns indicate the m_1 and m_2 phases

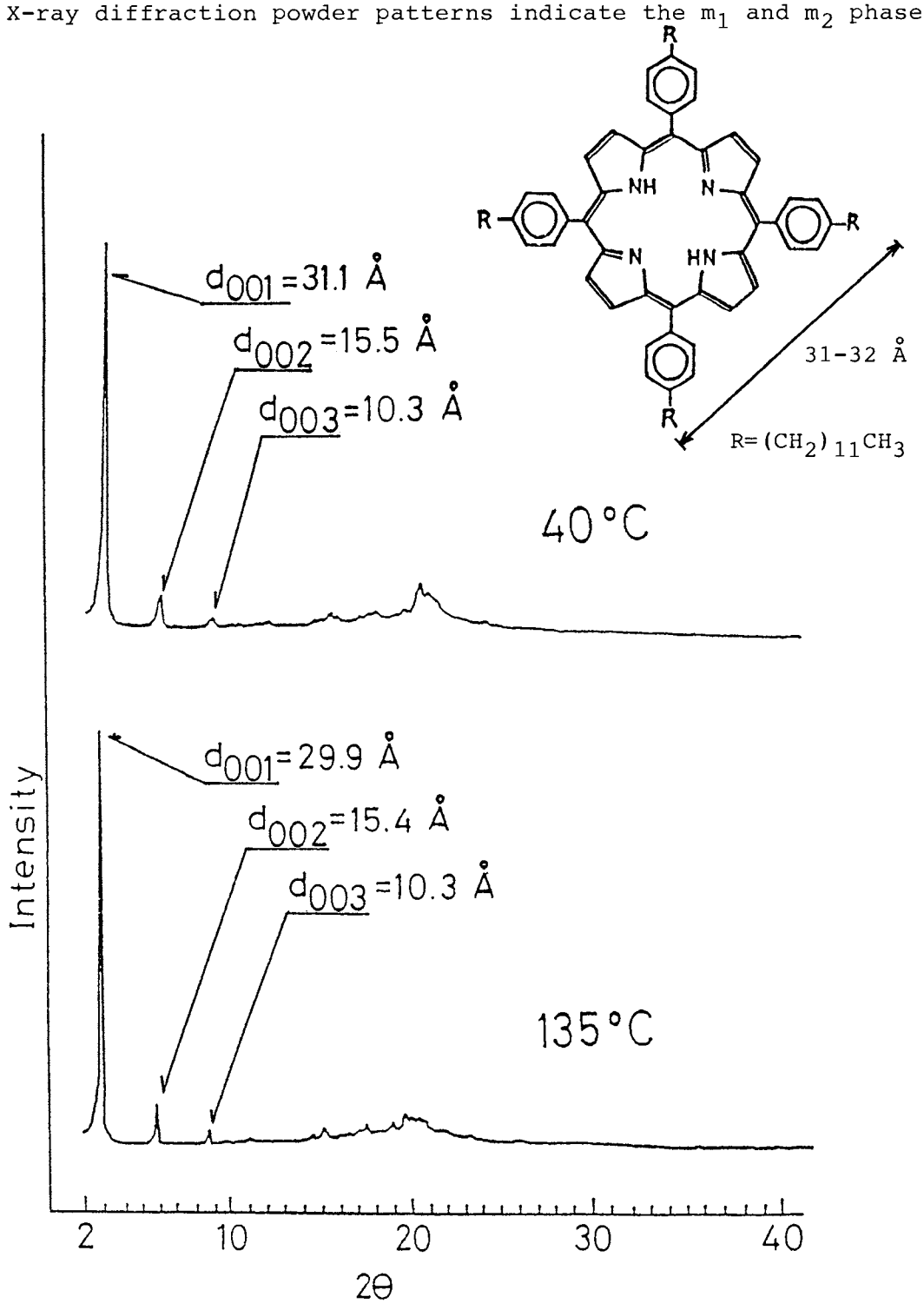

Fig.2. X-Ray diffraction patterns of C_{12}TPP(powder) for the m_1(the upper) and m_2(the lower) phases.

have discotic lamellar structures:three sharp peaks appear in the low angle regions as shown in Fig.2. These spacings are 31.1 Å, 15.5 Å, and 10.3 Å for the m_1 phase, and 29.9 Å, 15.4 Å, and 10.3 Å for the m_2 phase. The ratios of these spacings are 1:1/2:1/3, being characteristic of discotic lamellar structure[8] and the layer spacings for the m_1 and m_2 phases are about 31 Å and 30 Å, respectively. These values correspond to the molecular size of C_{12}TPP being estimated to be 31-32 Å.

The difference of the structures between the m_1 and m_2 phases is not clear at present, but the fine peaks around $2\theta=20°$ change slightly, indicating that the structural change on the m_1 to m_2 phase transition is rather small.

This is the first example that the mesomorphic phase transitions of tetraphenylporphyrin derivatives are classified. Further investigations including the metal complexes are in progress.

These tetraphenylporphyrins with long aliphatic chains are applicable to studies on various kinds of functions because of the high solubility to organic solvents like non-polar benzene, hexane, dichloromethane as well as weakly polar chloroform, though immiscible to methanol, ethanol, acetone, and N,N-dimethylformamide.

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