A New Homologous Series of Phenol Derivatives Exhibiting Liquid Crystalline Phase

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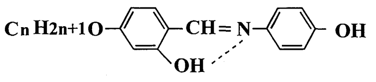
A new homologous series of 4-(4-*n*-alkoxy-2-hydroxybenzylideneamino)phenol was synthesized, and the phase transitions were determined using a differential scanning calorimeter and an ordinary polarizing microscope. It is shown that the homologues having a terminal alkoxyl chain longer than C10-member exhibit a smectic phase through an intermolecular hydrogen bonding.

Since Gray's first suggestion,[1] it has been generally accepted that *para*-substituted phenol derivatives are not favorable for the formation of calamitic liquid crystalline phases. Actually, only a few kinds of the phenolic compounds exhibiting liquid crystalline phases have been reported in the literature,[2-5] and all of them contain three benzene rings. Taking account of a recent advance of developing liquid crystals due to intermolecular hydrogen bondings,[6-8] we consider that it is possible to synthesize without difficulty the structually much simpler phenolic compounds which consist of two benzene rings and exhibit the mesomorphic properties.

In this paper we wish to describe that such a new homologous series of the *para*-substituted phenol having the following structure exhibits the liquid crystalline phase through the intermolecular hydrogen bonding as the end alkoxyl chain is lengthened.



POH(n) (n = 1~18)

Alkylation of 2,4-dihydroxybenzaldehyde was carried out according to a known method,[9] and then the aldehyde obtained was condensed with 4-aminophenol by refluxing in ethanol for a few hours. The crude product was purified by repeated recrystallizations, and column chromatography when necessary, giving a constant phase-transition temperature.

The phase-transition temperatures of these homologues are summarized in Table 1. It is apparent that the homologues with an alkoxyl chain longer than C10 exhibit a smectic phase whereas the first nine members show no liquid crystalline phases. On cooling the isotropic liquid, so-called smectic bâttonets appear at the phase transition to the smectic state. These bâttonets soon disappear, and change to a pseudo-isotropic texture(homeotropic alignment). This characteristic behavior of the microscopic textures indicates that the smectic phase observed for this homologous series can be identified as a smectic A.[10,11] Furthermore, it should be stressed that phase-transition temperatures described above on the basis of the texture change are in good accord with those measured from a

Table 1. Phase transition temperatures / °C

n	Smectic	Isotropic
1		195
2		165
3		138
4		129
5		152
6		130
7		127
8		128
9		130
10	(117)	130
12	(127)	131
14	(128)	129
16	127	128
18	126	127

The parentheses show the monotropic transitions.

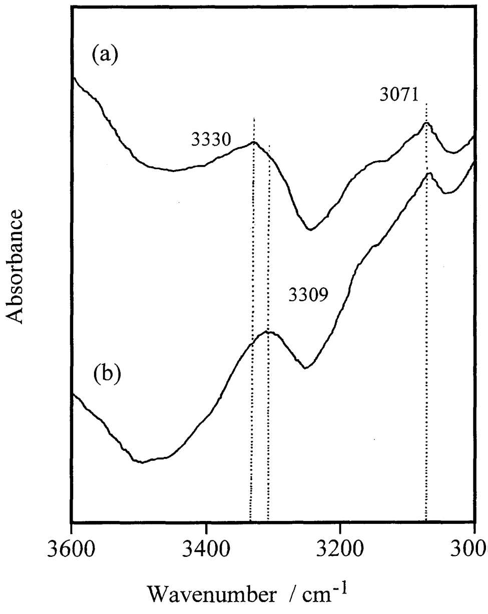


Figure 1. IR spectra observed at 132 °C in the isotropic (a) and at 125 °C in the smectic (b) of **POH** (14).

differential scanning calorimeter(DSC).

In addition, it should be emphasized that the intermolecular hydrogen bonding plays an important role for the appearance of the liquid crystalline phase. This is confirmed by FT-IR measurements. A broad peak observed at about 3070 cm^{-1} for **POH**(14) which is likely to be ascribed to an intramolecular O-H stretching band is independent of the phase transition from the isotropic to the smectic phase.[12] However, another broad O-H band centered around 3300 cm^{-1} which is associated with the intermolecular hydrogen bonding is shifted 21cm^{-1} to lower wave number when the phase transition to the smectic state takes place, as shown in Fig.l. It has been established that N-salicylideneaniline and related compounds are structually stabilized due to the intramolecular hydrogen bonding, and the H-bonding greatly contributes to the formation of the liquid crystalline phases.[13-15] Therefore, it is easily understood that **POH**(n = 10 to 18) described above exhibit the smectic phase, while no liquid crystalline phases are observed in the case of the the homologous series similar to **POH** (n = 1 to 16) in which *o*-hydroxy group does not exsist, *i.e.*, no intramolecular hydrogen bondings occur.[8]

Finally, it is worthwhile to point out that all the members(n=1 to 18) studied here show a thermochromic property in the crystalline state. With regard to this feature, a detailed study is in progress.

References and Notes

1 G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, London, Chap. 8 (1962).

2 D. C. Schroeder and J. P. Schroeder, *J. Am. Chem. Soc.*, **96**, 4347(1974).

3 H. Takeda, Y. Sakurai, S. Takenaka, H. Miyake, T. Doi, and S. Kusabayashi, *Chem. Lett.*, **1989,** 1335.

4 H. Kresse, C. Dorscheid, I. Szulzewski, R. Frank, and R. Paschke, *Ber. Bunsenges. Phys. Chem.*, **97**, 1345 (1993).

5 Y. Sakurai, A. Tamatani, K. Teshima, S. Kusabayashi, and S. Takenaka, *Mol. Cryst. Liq. Cryst.*, **213**, 163 (1992). In this paper, it has been described that 4-(4-*n*-decyloxybenzoyloxy)phenol exhibits a monotropic nematic phase. However, we confirmed by means of both DSC measurementsand texture observations that this homologue exhibits no liquid crystalline phase if the sample is carefully purified.

6 M. J. Brienne, J. Gabard, J. M. Lehn, and I. Stibor, *J. Chem. Soc., Chem. Commun.*, **1989,** 1868.

7 T. Kato, H. Adachi, A. Fujishima, and J. M. J. Fréchet, *Chem. Lett.*, **1992**, 265.

8 T. Koga, H. Ohba, A. Takase, and S. Sakagami, *Chem. Lett.*, **1994**, 2071.

9 T. Sakurai, K. Sakamoto, M. Honma, K. Yoshino, and M. Ozaki, *Ferroelectrics*, **58**, 21(1984).

10 G. W. Gray and J. W. G. Goodby, "Smectic Liquid Crystals," Leonard Hill, Glasgow (1984).

11 D. Demus and L. Richter, "Textures of Liquid Crystals," Verlag Chemie, Weinheim (1978).

12 M. D. Joesten and L. J. Schaad, "Hydrogen Bonding," Marcel Dekker, New York (1974).

13 G. O. Dudek and E. P. Dudek, *J. Am. Chem. Soc.*, **88**, 2407 (1966).

14 I. Teucher, C. M. Paleos, and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **11**, 187 (1970).

15 B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, E. L. Sorkin, B. A. Strukov, and S. A. Taraskin, *Ferroelectrics*, **24,** 309 (1980).