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Liquid Crystalline Phases through Intermolecular Hydrogen Bonding Formed in a Mixture of Phenol Derivatives and 4,4'-Bipyridine

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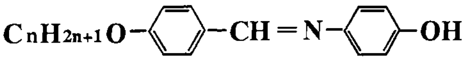
Smectic liquid crystalline phases are formed due to the intermolecular hydrogen bonding in a binary mixture of phenol derivatives and 4,4'-bipyridine as the length of the terminal alkyl or alkoxyl chains are increased.

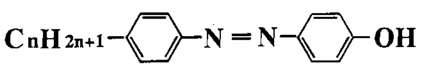
Almost all of conventional liquid crystals are made up of only covalent bonds 1,2) except for a few systems existing as dimers formed through intermolecular hydrogen bond such as carboxylic acids 3) or monosaccharides.4) Therefore, the hydrogen bondings between different molecules have been seldom employed as a direct method of designing new mesogens although Brienne et al. have reported recognition-dependent liquid crystals bearing triple hydrogen bonding.5)

Recently, Kato and co-workers have, however, reported several studies in which mesomorphic temperature range was increased or new mesophases were induced due to the formation of the intermolecular hydrogen bondings.6-11) In addition, Yu has reported hydrogen bonded-induced ferroelectric liquid crystals.12) In their studies only carboxylic acids are used as a H-bond donor whereas several derivatives of pyridine are utilized as a proton acceptor.

In this paper we wish to describe that some derivatives of phenol which show no mesomorphic phases exhibit the liquid crystalline phases through the intermolecular hydrogen bonding under suitable conditions. Phenolic compounds studied here were two homologous series having the following structures, and 4, 4'-bipyridine (**BP**) was used as a proton acceptor.



CHN(n)



AZO(n)

Table 1. The phase transition temperatures of the binary mixtures(°C)

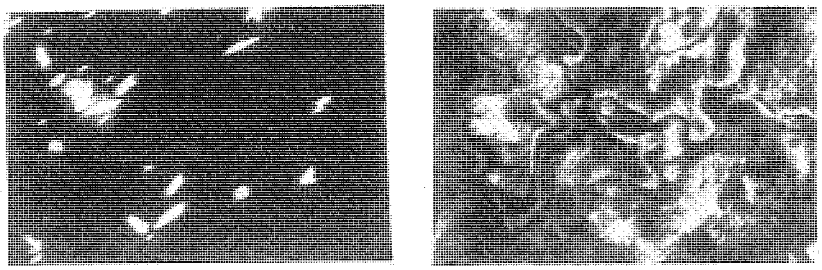
Mixture	n	Crystal	Smectic(II)	Smectic(I)	Isotropic
	10	· 102	–	(· 95)	·
CHN(n)	12	· 107	(· 87)	(· 103)	·
	14	· 98	(· 97)	· 103	·
	16	· 98	· 102	· 108	·
AZO(n)	7	·105	–	(· 102)	·
	8	·106	–	· 107	·

The parentheses show the monotropic transitions.

It should be first of all stressed that neither of these compounds shows liquid crystalline behavior. A stoichiometric (2:1) mixture of the phenolic compound and **BP** was obtained by weighing and melting to form the homogeneous isotropic phase under a nitrogen atomosphere.

Some of these mixtures exhibit liquid crystalline phases as shown in Table 1. In these binary mixtures the most striking is that a relatively long alkyl or alkoxyl chains are necessary for occurrence of the mesomorphic phases, and that a nematic phase is not found at all. In the case of **AZO**(n) the lower homologues than C_7 exhibit no liquid crystalline phases. For **CHN**(n) the smectic phase can be found only for the members having an alkoxyl chain longer than C_9. This finding that only the smectic phases are observed for both the homologous series is not surprising, for the disappearance of the nematic phase is not unusual, and has been frequently observed as the length of the alkoxyl or alkyl chain increases in other homologous series of liquid crystalline materials.[2)]

Figure 1 shows liquid crystalline textures formed from the mixture(**CHN**(16) and **BP**) which were observed with an ordinary polarizing microscope under crossed polarizers. When the isotropic liquid is cooled, so-called smectic bâttonets[13)] appear at the phase transition to the smectic(I) state(Fig.1(A)). As the temperature falls, these bâttonets disappear and a pseudo-isotropic texture(homeotropic alignment) is observed. On further



(A) (B)

Fig. 1. Photomicrograph of the mixture (**CHN**(16) and **BP**) between crossed polarizers, (A)smectic(I), (B) smectic(II).

cooling, at the phase transition to the smectic (II) phase a smectic schlieren texture appears on the homeotropic alignment as shown in Fig. 1(B). In addition, it is worthwhile to state that the liquid crystalline phase transitions described above are in good accord with those measured by means of differential scanning calorimetry.

From the investigations of these characteristic textures and the thermal analysis,it is quite likely to be concluded that the smectic (I)phase is a smectic A, and the smectic(II) state is a smectic C. Furthermore, it should be pointed out that the binary mixtures of another homologous series(**AZO**(n)) as well as the other members of **CHN**(16) yield quite similar textures to those observed for **CHN**(16). Since none of the indivisual components of the mixtures are liquid crystalline, the occurrence of the smectic phases described previously is likely to indicate the formation of the intermolecular hydrogen bonding. This is confirmed by FT-IR measurements as shown in Fig. 2. The fact that a broad OH band centered around 3300 cm^{-1} is definitely observed in the smectic phases and almost completely disappears in the isotropic liquid is ascribed to the existence of the hydrogen bonding between phenolic OH

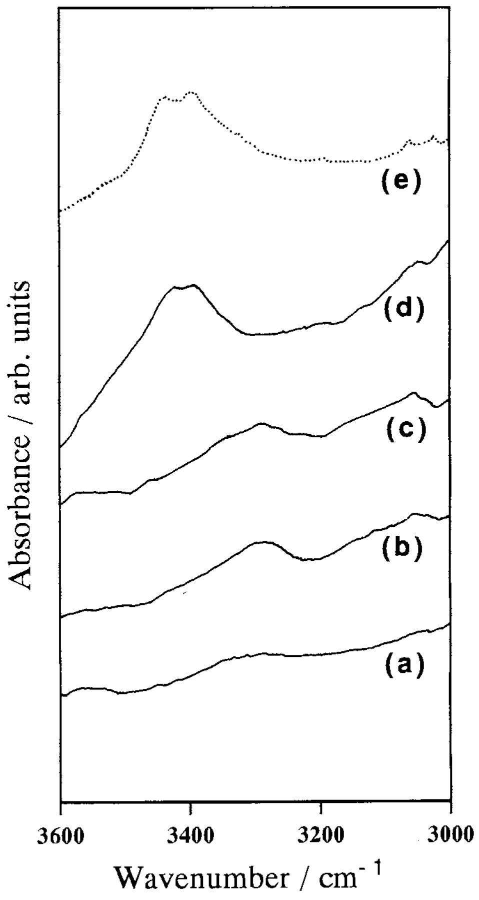


Fig. 2. Observed IR spectra, (a) isotropic (b) smectic (I), (c) smectic (II), (d) solid at 25 °C, (e) solid of **CHN**(16) at 25 °C.

and **BP** in the smectic phases. It is also evident from Fig. 2 that the O-H stretching band observed for the binary mixture is shifted about 15 cm^{-1} to lower wavenumber compared with that for the phenolic compound itself. This finding reveals that the hydrogen-bond energy in the complex is grater than that for the phenol derivative.14)

In summary, we wish to emphasize that the phenol derivatives which have been considered to exhibit no liquid crystalline phases15) can be utilized as a new mesogen through the intermolecular hydrogen bondings. It is also expected that the other different phenolic compounds than those studied here may give the liquid crystals. A detailed study is in progress.

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