Supramolecular Liquid-Crystalline Complexes Exhibiting Room-Temperature Mesophases and Electrooptic Effects. Hydrogen-Bonded Mesogens Derived from Alkylpyridines and Benzoic Acids

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Hydrogen-bonded liquid-crystalline complexes containing only two aromatic rings have been designed and obtained through 1:1 (molar ratio) complexation of 4-alkoxy- or 4-alkylbenzoic acid (*n*OBA or *n*BA; *n* is the carbon number of the alkyl group) and 4-octyl- or 4-undecylpyridine (8Py or 11Py). These supramolecular H-bonded complexes exhibit stable mesophases in the vicinity of room temperature. For a series of complexes obtained from *n*OBA and 8Py, only nematic phases are observed near room temperature. For example, the 1:1 complex obtained from an equimolar amount of 4-hexyloxybenzoic acid and 4-octylpyridine (6OBA–8Py) exhibits a nematic phase from 38 to 48 °C. In contrast, for a series of complexes from *n*BA and 8Py, only smectic phases are seen at room temperature. For example, 6BA–8Py shows a smectic A phase from 29 to 33 °C. On cooling, the smectic A phase appears at 33 °C and a subsequent smectic C phase is observed from 13 to 10 °C. The effects of lateral substituents on the liquid-crystalline behavior have been examined for 6OBA–8Py system using 3-chloro and 3-fluoro-4-hexyloxybenzoic acids as H-bond donors. The use of these substituents depresses the isotropization temperature and also induces smectic phases for the complexes. The mesophase range has been extended by the mixing of complexes because of the resulting depression of melting points. A mixture of nematogenic complexes can be aligned on a rubbed surface and shows electrooptic effects in a twisted nematic cell.

Introduction

The use of noncovalent interactions has great potential in the design of functional organic materials.[1–3] Hydrogen bonding is a powerful tool for assembling molecules and building supramolecular structures because of its stability and directionality.[1]

We have reported that supramolecular liquid-crystalline complexes can be obtained through the molecular self-assembly of carboxylic acid and pyridine fragments via intermolecular hydrogen bonding that operate as H-bond donor and acceptor, respectively.[4,5] Almost simultaneously, supramolecular liquid-crystalline materials using triplet hydrogen bonds were reported by Lehn and co-workers.[6] A few systems consisting of hydrogen bonds that function between identical molecules had been known.[7] However, prior to our work, no liquid-crystalline complexes prepared from different components had been reported.

A wide variety of supramolecular mesogenic structures can be obtained through the formation of a single hydrogen bond between carboxylic acids and pyridines.[8–19] For example, ferroelectric liquid-crystalline complexes have been obtained using chiral molecules

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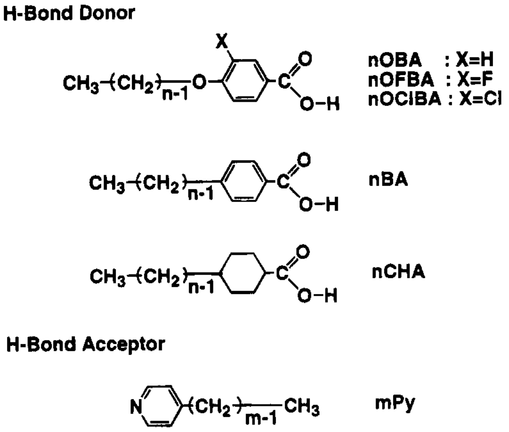
Chart 1



as H-bonding components.[9,10] These complexes exhibited chiral smectic phases and stable ferroelectric behavior in electric fields. To explore the potential use of the hydrogen-bonded liquid crystals, mesogens consisting of only two aromatic rings have been designed to induce room-temperature mesophases.[11] In a preliminary communication,[11] we have reported that the self-assembly of 4-alkoxybenzoic acid and 4-octylpyridine results in the formation of the simplest complex structure that shows nematic phases below 50 °C.

In this study, the liquid-crystalline properties have been examined for the hydrogen-bonded supramolecular complexes prepared from benzoic acid moieties and simple 4-alkylpyridines. The series of 4-alkoxybenzoic acid (nOBA: n is the carbon number of the alkyl group), 4-alkylbenzoic acid (nBA), and *trans*-4-alkylcyclohexanecarboxylic acid (nCHA) were used as H-bond donors (Chart 1). Simple 4-alkylpyridines (mPy, m is the carbon number of the alkyl group) were selected as H-bond acceptors (Chart 1). Complexes based on 3-substituted 4-alkoxybenzoic acids (nOXBA, X denotes the substituent) were also prepared with alkylpyridines to study the effects of substituents on thermal properties. The electrooptic effects of a mixture of nematogenic complexes have been studied in a twisted nematic cell.

Experimental Section

Synthesis of 4-Alkylpyridine. 4-Alkylpyridines were prepared using the method of Comins and Abudullar[20] (Scheme 1). Grignard reaction of pyridine in the presence of ethyl chloroformate and cuprous iodide followed by aromatization through heating with sulfur gave 4-alkylpyridines. A typical synthetic procedure given for 4-octylpyridine is as follows. Pyridine (5.93 g, 75 mmol), CuI (0.48 g, 2.5 mmol), and 125 mL of THF were placed in a 500 mL flask under a nitrogen atmosphere. The solution was cooled to −15 °C. Ethyl chloroformate (5.43 g, 44 mmol) was added to the solution over 5 min with stirring. After 10 min, octylmagnesium bromide (50 mmol) in 35 mL of diethyl ether was added dropwise over 20 min. The mixture was stirred for 15 min at −15 °C and for 2 h at room temperature. Then, aqueous 20% NH_4Cl solution (40 mL) was added. The crude dihydropyridine was extracted by ether. After drying, the ether solution was filtered and evaporated to yield a yellow crude oil. The oil was treated with sulfur (1.60 g, 49.9 mmol) at 200 °C for 50 min under a nitrogen atmosphere. The reaction mixture was cooled and dissolved in 200 mL of ether. The product was extracted with three 100 mL portions of 10% HCl. The solution was treated with 50 mL of saturated aqueous K_2CO_3. The crude 4-octylpyridine was extracted with ether. The solution was dried over anhydrous K_2CO_3, then filtered, and evaporated to dryness. The crude product was vacuum distilled to give 2.28 g (27%) of 4-octylpyridine as a colorless liquid; bp 112−116 °C (2 mmHg). ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H), 1.26 (m, 10H), 1.62 (m, 2H), 2.59 (t, 2H), 7.10 (d, 2H), 8.47 (d, 2H).

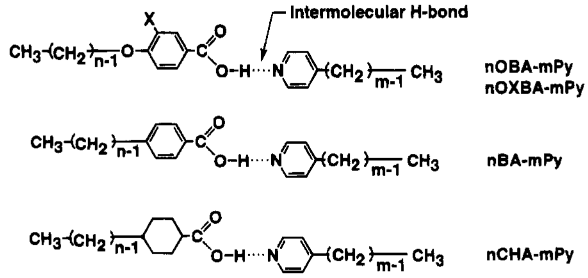
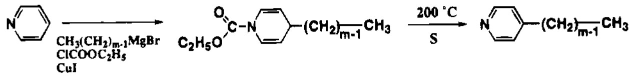


Figure 1. Structures of hydrogen-bonded liquid-crystalline complexes based on a simple pyridine ring.

Scheme 1



Preparation of Hydrogen-Bonded Complexes. The requisite equimolar amounts of hydrogen bond donor and acceptor molecules were directly mixed and heated to the isotropic states. The mixture formed was cooled to about 0 °C to form solid complexes.

Preparation of Phenyl Benzoates. Phenyl benzoates and 4-octylphenyl 3-fluoro- and -chloro-4-hexyloxybenzoates (OPHOClB and OPHOFB) were prepared by esterification of the corresponding benzoic acids and 4-octylphenol using dicyclohexylcarbodiimide (DCC) in the presence of 4-(dimethylamino)pyridine (DMAP). The structure of the products was confirmed by ^{1}H NMR and IR.

Characterization. A polarizing microscope equipped with a Mettler FP82HT hot stage was used for visual observations. DSC measurements were performed on a Mettler DSC 30 at a heating rate of 2 °C min^{-1}.

Measurement of Electrooptic Effects for H-Bonded Liquid Crystals. Two kinds of liquid crystal cells, cell I and cell II, in which the directions of rubbing of two surfaces were parallel and perpendicular, respectively, were used for the evaluation of the aligning capability of a hydrogen-bonded complex on the rubbed surface. All of them were purchased from EHC Co. The layer thickness of the cells was 12 μm. The active area of indium−tin oxide electrodes was 0.25 cm^2, which had been previously buffed in polyimide alignment layers. A 6:4 mixture of 6OBA−8Py and 8OBA−8Py was used for this measurement. The cells were filled with the H-bonded material by capillary action while it was in the isotropic state.

Results and Discussion

Liquid-Crystalline Properties. The mesogenic structure designed in the present study is shown in Figure 1. The H-bonded core structure consists of two rings. The thermal properties of a series of the 1:1 (molar ratio) complexes of 4-alkoxybenzoic acids (nOBA and nOXBA) and 4-alkylpyridines (mPys) are shown in Table 1. Complexes consisting of 4-alkoxybenzoic acids with n = 6−8, 10, and 8Py, which will be denoted as nOBA−8Py, exhibit enantiotropic nematic (N) phases near room temperature. For example, 6OBA−8Py shows a nematic phase from 38 to 48 °C on heating. The nematic phase is seen to 29 °C on cooling. A droplet

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Table 1. Transition Temperatures of Liquid-Crystalline Complexes Based on 4-Alkoxybenzoic Acids (*n*OBA and *n*OXBA) and 4-Alkylpyridines (mPy)

	transition temp[a]/°C				
complexes	K	S_C	S_A	N	I
6OBA–8Py	● 38			● 48	●
7OBA–8Py	● 43			● 49	●
8OBA–8Py	● 45			● 49	●
10OBA–8Py	● 43			● 46	●
6OFBA–8Py	● 28	● 31	● 33	● 39	●
7OFBA–8Py	● 40	(● 35)	(● 36)	● 42	●
8OFBA–8Py	● 38		(● 35)	● 45	●
6OClBA–8Py	● 32	(● 22)		(● 32)	●
8OClBA–8Py	● 35	(● 22)		(● 35)	●
6OBA–11Py	● 35	● 51	● 56	● 59	●
8OBA–11Py	● 47	● 52		● 60	●
6OFBA–11Py	● 39	● 49	● 52		●
8OFBA–11Py	● 21		● 55		●

[a] Transition temperatures of monotropic phases are in parentheses.

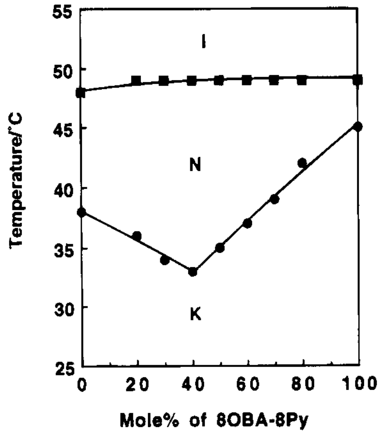

Figure 2. Binary-phase diagram for mixtures of hydrogen-bonded complexes 6OBA–8Py and 8OBA–8Py.

Chart 2

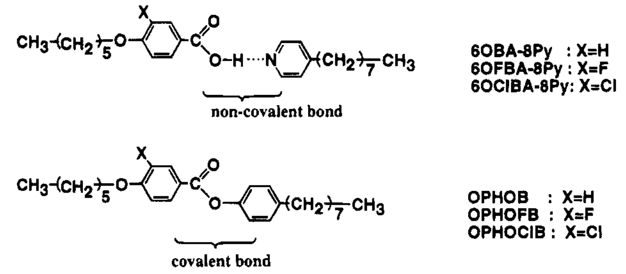

Table 2. Transition Temperatures of Liquid-Crystalline Complexes Based on 4-(Hexyloxy)benzoic Acids (6OBA and 6OXBA), 4-Octylpyridine (8Py), and 4-Octylphenyl 4-Hexyloxybenzoates (OPHOB and OPHOXB)

	transition temp[a]/°C				
	K	S_C	S_A	N	I
6OBA–8Py	● 38			● 48	●
OPHOB	● 43			● 61	●
6OFBA–8Py	● 28	● 31	● 33	● 39	●
OPHOFB	● 57			(● 45)	
6OClBA–8Py	● 32	(● 22)		(● 32)	●
OPHOClB	● 59				●

[a] Transition temperatures of monotropic phases are in parentheses.

texture is seen at the nematic–isotropic (N–I) transition as is the case for conventional nematic materials.

Both a depression in the melting point and an extension of the liquid-crystalline temperature range are seen for the mixture of 6OBA–8Py and 8OBA–8Py, as shown in Figure 2. All data points were obtained by visual observation on heating. This type of phase diagram is common in liquid crystals obtained through only covalent bonding, which suggests that the supramolecular mesogenic complex behaves as one single component. In particular, the 6:4 mixture exhibits a broader nematic phase from 33 to 49 °C. The enthalpy change of the nematic–isotropic transition is 1.3 kJ/mol. A further depression of the melting point is observed for a quaternary mixture of complexes. A mixture of the four complexes, 5OBA–8Py, 6OBA–8Py, 7OBA–8Py, and 8OBA–8Py in the ratio of 3.5:3.0:1.5:2.0 exhibits a nematic phase between 25 and 48 °C on heating.

It is important to examine the effect of substituents in liquid-crystalline materials.[21] The introduction of lateral fluoro and chloro substituents into the 3-position of the benzoic acid component of the H-bonded structures induces the appearance of smectic phases. In particular, 6OFBA–8Py exhibits enantiotropic smectic C and A (S_C and S_A) phases. The chlorine-substituted complexes 6OClBA–8Py and 8OClBA–8Py show smectic C and nematic phases, which are monotropic. In addition, lateral substitution results in a depression of the isotropization temperatures and a reduction in the stability of the nematic phases of the complexes.

The liquid-crystalline behavior of the series of complexes 6OBA–8Py and 6OXBA–8Py (X = Cl or F) has been compared with that of similar covalently bonded molecules such as 4-octylphenyl 4-hexyloxybenzoate (OPHOB) and the corresponding halogenated benzoates (OPHOXB, Chart 2). Table 2 summarizes the transition temperatures of both series. The thermal properties of OPHOB were described in previous papers.[22,23] OPHOFB and OPHOClB were prepared for use in this study. Enantiotropic nematic phases are observed for both 6OBA–8Py and OPHOB, which have no substituent at the 3-position. The isotropization temperature of OPHOB is 13 °C higher than 6OBA–8Py. For the fluorine- and chlorine-substituted materials, the difference of the mesomorphic properties between 6OXBA–8Py and OPHOXB becomes more noticeable. Hydrogen-bonded complex 6OFBA–8Py shows enantiotropic smectic C, smectic A, and nematic phases. In contrast, only a monotropic nematic phase is seen for OPHOFB. Although no mesomorphic behavior is observed for OPHOClB, complex 6OClBA–8Py is mesogenic. It is worth noting that the introduction of substituents for the phenyl benzoates leads to higher melting points and less-stabilized mesophases, while the decrease of melting temperatures and stabilized smectic phases are observed for the substituted hydrogen-bonded complex. The cause of such lateral polar substituent effects for the H-bonded liquid crystals is now under examination.

Enantiotropic smectic C phases are induced and the mesophases are stabilized to higher temperatures for the complexes of 6OBA–11Py and 8OBA–11Py that

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Table 3. Transition Temperatures of Liquid-Crystalline Complexes Based on 4-Alkylbenzoic Acids (nBA) and 4-Octylpyridine (8Py)

	transition temp[a]/°C			
complexes	K	S_C	S_A	I
2BA–8Py	● 45			●
3BA–8Py	● 39		(● 33)	●
4BA–8Py	● 27	(● 20)	● 33	●
5BA–8Py	● 32	(● 15)	● 36	●
6BA–8Py	● 29	(● 13)	● 35	●
7BA–8Py	● 29		● 36	●
8BA–8Py	● 35		● 38	●
9BA–8Py	● 35		● 40	●

[a] Transition temperatures of monotropic phases are in parentheses.

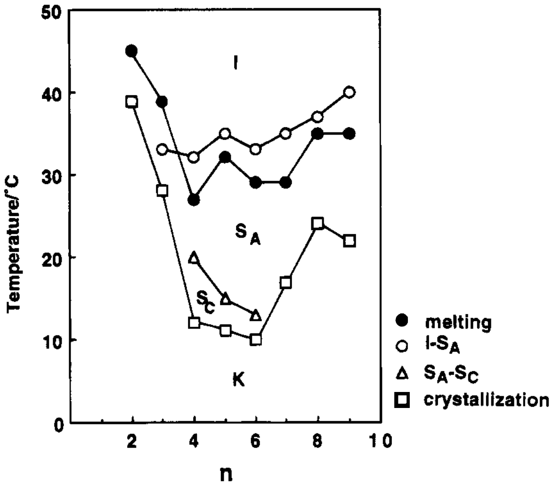

Figure 3. Plot of the transition temperatures against the carbon number (n) of the alkyl chain for the series of complex nBA–8Py.

have a longer alkyl chain than nOBA–8Py. For example, 8OBA–8Py exhibits the nematic–isotropic transition at 49 °C, while the smectic–isotropic transition occurs for 8OBA–11Py at 60 °C. The fluorine-substituted complexes, 6OFBA–11Py and 8OFBA–11Py, has become purely smectogenic.

As expected, all of these results are compatible with the formation of the supramolecular mesogenic structure shown in Figure 1.

The transition temperatures of the series of 1:1 complexes of nBA-8Py are presented in Table 3. The values are plotted in Figure 3. Enantiotropic smectic A phases are observed for nBA–8Py with $n = 4–9$ at room temperature. Monotropic smectic C phases are also seen for the complexes with $n = 4–6$. For example, 4BA–8Py melts at 27 °C and a smectic A phase is observed up to 33 °C. Upon cooling, the complex shows a smectic A phase from 32 to 20 °C and a monotropic smectic C phase below 20 °C. It is of interest to note that the two individual components of the complexes would be considered as unlikely candidates for the formation of room-temperature mesogens. This is because 4BA shows a nematic phase due to dimer formation above 100 °C, while 8Py is an isotropic liquid at room temperature. The DSC thermogram of 4BA–8Py on heating is shown in Figure 4. Complex 4BA–8Py shows crystalline-smectic A (K–S_A) and isotropization (S_A–I) transitions. The S_A–I transition enthalpy is 8.1 kJ mol^{-1}, a value similar to those observed for conventional liquid crystals. A monotropic liquid-crystalline behavior is seen for 3BA–8Py. Complex 2BA–8Py is nonmesogenic.

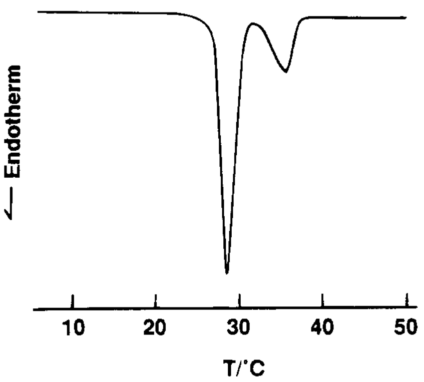

Figure 4. DSC thermogram of hydrogen-bonded complex 4BA–8Py on heating.

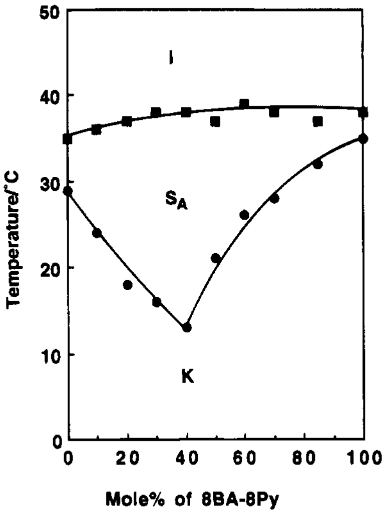

Figure 5. Binary phase diagram of hydrogen-bonded complexes of 6BA–8Py and 8BA–8Py.

Table 4. Transition Temperatures of Complexes Based on *trans*-4-Alkylcyclohexanecarboxylic Acids (nCHA) and 4-Octylpyridine (8Py)

	transition temp/°C	
complexes	K	I
3CHA–8Py	● 31	●
4CHA–8Py	● 33	●
5CHA–8Py	● 37	●
6CHA–8Py	● 40	●

The isotropization temperatures of the series of nBA–8Py are lower than those of the series of nOBA–8Py. This trend is generally observed for mesogenic compounds. It is noteworthy that only smectic phases are observed for the series of nBA–8Py, while the series of nOBA–8Py show only nematic phases.

A binary phase diagram for H-bonded complexes of 6BA–8Py and 8BA–8Py is shown in Figure 5. The largest mesomorphic temperature range is observed for the 6:4 mixture that shows a smectic A phase from 13 to 38 °C.

The transition temperatures of the H-bonded complexes obtained from *trans*-4-alkylcyclohexanecarboxylic acid (nCHA; n is the carbon number of the alkyl group) and 4-octylpyridine (8Py) are given in Table 4. No mesomorphic behavior is observed for the complexes of nCHA–8Py with $n = 3–6$. The crystal–isotropic transition temperatures are all between 31 and 40 °C.

Molecular Alignment and Electrooptic Effects in Cell Devices. It is of interest to examine molecular

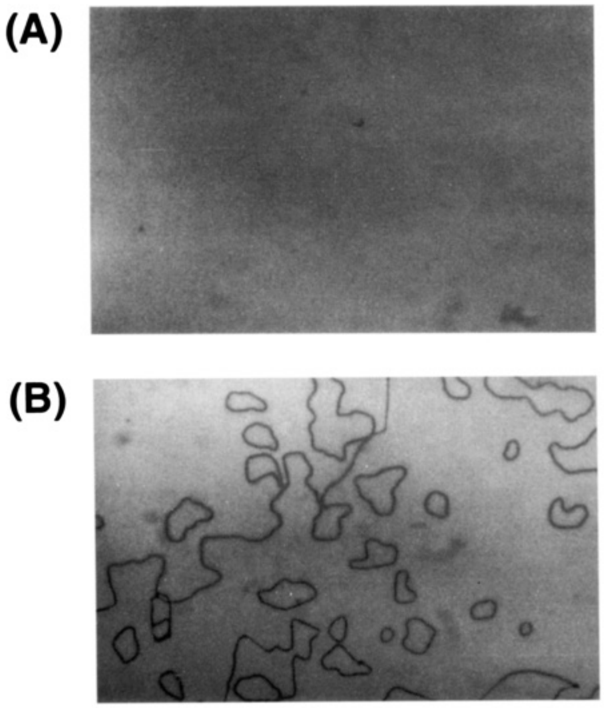

Figure 6. Photomicrographs of textures displayed by 6:4 mixture of 6OBA−8Py:8OBA−8Py in glass cells at 38 °C: (A) in a homogeneous cell (cell I); (B) in a twisted nematic cell (cell II).

alignment and dynamics in electric fields and interactions with surfaces for the hydrogen-bonded liquid crystals because the structure of the complex consists of noncovalent bonds between interacting molecular species. As an initial approach, twisted nematic cells have been used to examine such behavior. Twisted nematic cells are widely used as commercial electrooptic devices.[24] In the twisted nematic cell, the planar alignment of conventional molecules can be achieved by the use of a rubbed polyimide surface.

The molecular alignment of our liquid-crystalline H-bonded complexes has been tested in cell I (parallel rubbing direction) and cell II (perpendicular rubbing direction). The 6:4 mixture of 6OBA−8Py and 8OBA−8Py was selected for this experiment because it shows an adequately wide nematic temperature range. Figure 6A shows the homogeneous texture resulting from a homogeneous alignment in cell I. Two domains are observed for cell II as shown in Figure 6B. These observations show that a twisted nematic state appears. The existence of two kinds of domains corresponds to right- and left-handed directions of the helical sense. The alignment of the H-bonded liquid crystal can be controlled by the substrate surfaces.

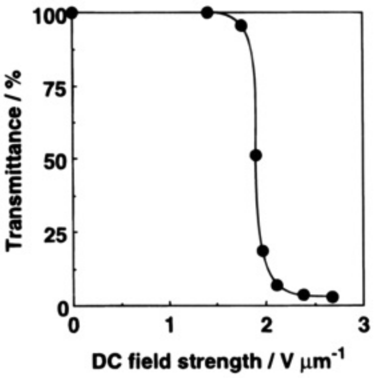

Figure 7. Transmittance as a function of the applied dc field strength for a 6:4 mixture of 6OBA−8Py:8OBA−8Py at 38 °C in a twisted nematic cell.

To examine the electrooptic effects of the H-bonded liquid crystal, dc fields were applied to the liquid-crystalline layer in cell II at 38 °C and transmittance of light was recorded by a photodiode detector. The transmittance plotted against the dc field strength is shown in Figure 7. A sharp decrease of the transmittance is observed when a dc field of 1.92 V μm^{-1} is applied. The transmittance becomes 4% when a dc field of 2.1 V μm^{-1} is applied. By removal of the dc field, the transmittance is recovered reversibly without hysteresis. Theses results show that the orientation of the director can be realigned from the rubbing direction to the direction of the dc electric field. Further studies on the electrooptic effects of the H-bonded liquid crystals are now in progress.

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