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Induction of mesophases through the complexation between benzoic acids with lateral groups and polyamides containing a 2,6-diaminopyridine moiety

OSAMU IHATA, HIDEYUKI YOKOTA, KIYOSHI KANIE, SEIJI UJIIE†, and TAKASHI KATO*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
†Department of Material Science, Shimane University, Matsue, Shimane 690-8504, Japan

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Supramolecular liquid crystalline polymeric complexes have been prepared by the complexation of 4-alkyloxybenzoic acid derivatives and polyamides containing a 2,6-diaminopyridine moiety. 4-Alkyloxybenzoic acids substituted by methoxy, methyl, and nitro groups at the 3-position are used for the complexation. These polymeric complexes behave as single component liquid crystalline polymers and exhibit stable and enantiotropic mesophases. In contrast, simple 4-alkyloxybenzoic acids having no substituent at the 3-position, do not form stable complexes with the polymers. For low molecular mass complexes derived from 2,6-bis(acylamino)pyridine and 4-alkyloxybenzoic acid derivatives, substituent effects are different from those for the polymeric system. In these cases, mesomorphic behaviour is observed only for the complexes based on the simple 4-alkyloxybenzoic acid and 4-alkyloxy-3-methylbenzoic acid.

1. Introduction

Molecular association that leads to supramolecular mesogenic structures consisting of different and independent molecular species through the formation of intermolecular H bonds has been reported since 1989 [1, 2], while liquid crystals involving hydrogen bonds between identical molecules have been known for benzoic acids [3], amides [4] and polyols [5].

Supramolecular liquid crystalline polymeric structures such as side chain [6], main chain [7], and networks [8] have also been built through non-covalent interactions. Moreover, a variety of non-mesomorphic supramolecular polymers have been prepared via hydrogen bonds [9]. Recently, we have shown that complexation through double hydrogen bonds between 2,6-bis(acylamino)-pyridines and benzoic acid derivatives results in the formation of a new mesogenic polymer structure and the induction of mesomorphic behaviour [10, 11]. These complex structures are unique because they are not classified simply as either side chain or main chain polymers.

The supramolecular complexes of 4-alkyloxy-3-chloro-benzoic acids and polyamides containing a 2,6-diamino-pyridine moiety [11] show enantiotropic liquid crystalline phases, while only monotropic mesomorphic behaviour is observed for the supramolecular side chain polymers containing the same mesogen [12]. It is of interest that such polymeric structures based on polyamides exhibit stable mesomorphic behaviour [11]. Furthermore, a number of doubly hydrogen-bonded complexes consisting of identical or different molecules have been shown to be mesomorphic [13].

In the present study, we have examined the substituent effects for the doubly hydrogen-bonded mesogenic complexes consisting of 4-alkyloxybenzoic acid derivatives and these heterocyclic polyamides.

*Author for correspondence; e-mail: kato@chiral.t.u-tokyo.ac.jp

2. Experimental

2.1. *Preparation of materials*

2.1.1. *General*

Unless otherwise noted, the reagents and solvents were purchased as highest commercial quality and used without further purification. Tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone prior to use. Yields refer to materials purified by recrystallization and/or flash-column chromatography on silica gel (E. Merck, Kieselgel 60, 230–400 mesh). Unless otherwise noted, ^{1}H NMR spectra were recorded

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on a JEOL Lambda spectrometer at 400 MHz using $CDCl_3$ solutions. The following abbreviations are used to explain the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad.

2.1.2. *General procedure for the preparation of 3-substituted 4-alkyloxybenzoic acids (X-mOBAs) except for 4-alkyloxy-3-methylbenzoic acids (Me-mOBAs)*

A suspension of a 4-hydroxy-3-substituted benzoic acid (1.85×10^{-1} mol), an alkyl bromide (2.22×10^{-1} mol), and K_2CO_3 (3.70×10^{-1} mol) in DMF (200 ml) was stirred at 80°C until all of the benzoic acid was consumed. The resulting mixture was poured into an aqueous solution of NH_4Cl and organic matter extracted twice with CH_2Cl_2. The combined organic phase was washed with aqueous NH_4Cl (200 ml) and brine, dried and the solvent removed *in vacuo*. The residue was purified by recrystallization and/or flash-column chromatography to give the desired *X-m*OBAs. Isolated yields of selected products are: 3-chloro-4-decyloxybenzoic acid (Cl-10OBA), 90.5%; 4-decyloxy-3-methoxybenzoic acid (MeO-10OBA), 68.5%; 4-decyloxy-3-nitrobenzoic acid (NO_2-10OBA), 70.1%.

2.1.3. *Synthesis of 4-alkyloxy-3-methylbenzoic acid (Me-mOBA): general procedure*

2.1.3.1. *Synthesis of alkyl 2-methylphenyl ethers.* The title compounds were prepared by a similar alkylation procedure to that used for the preparation of the *X-m*OBAs; the following results are typical. Decyl 2-methylphenyl ether, yield 93.2%. ^{1}H NMR: $\delta = 0.88$ (t, $J = 6.7$ Hz, 3H), 1.27–1.34 (m, 12H), 1.43–1.50 (m, 2H), 1.75–1.82 (m, 2H), 2.22 (s, 3H), 3.94 (t, $J = 6.7$ Hz, 2H), 6.79–6.85 (m, 2H), 7.11–7.15 (m, 2H).

2.1.3.2. *Synthesis of alkyl 4-bromo-2-methylphenyl ethers.* These title compounds were synthesized by bromination of alkyl 2-methylphenyl ethers by use of 1,3-dibromo-5,5-dimethylhydantoin (DBMH) in the presence of strong acid [14]. To a solution of an alkyl 2-methylphenyl ether (1.56×10^{-2} mol) and H_2SO_4 (0.160 g, 1.56×10^{-3} mol) in CH_2Cl_2 (40 ml), DBMH (2.23 g, 7.80×10^{-3} mol) was added in one portion. The mixture, which rapidly changed to orange, was stirred at room temperature for 2 h. A saturated aqueous solution of $NaHSO_3$ was added to the reaction mixture until the orange organic layer was decolourized. The mixture was neutralized by the addition of a 2M aqueous Na_2CO_3 solution. The organic layer was separated and dried over anhydrous $MgSO_4$. The work-up and purification procedures described in § 2.1.2 gave the desired ethers. A typical result is given below. 4-Bromo-2-methylphenyl decyl ether, yield 90.0%. ^{1}H NMR: $\delta = 0.88$ (t, $J = 6.7$ Hz, 3H), 1.27–1.34 (m, 12H), 1.42–1.49 (m, 2H), 1.75–1.82 (m, 2H), 2.18 (s, 3H), 3.91 (t, $J = 6.7$ Hz, 2H), 6.66 (d, $J = 8.5$ Hz, 1H), 7.21 (d, $J = 8.5$ Hz, 1H), 7.23 (s, 1H).

2.1.3.3. *Synthesis of 4-alkyloxy-3-methylbenzoic acids (Me-mOBAs).* Part of a solution (about 1/10) of an alkyl 4-bromo-2-methylphenyl ether (1.48×10^{-2} mol) in THF (10 ml) was slowly added dropwise to a stirred mixture of magnesium (1.65×10^{-2} mol) in THF (3 ml) at room temperature. After the gentle exothermic reaction, a drop of 1,2-dibromoethane was added and the remaining solution of the alkyl 4-bromo-2-methylphenyl ether was added dropwise to the reaction mixture over 10 min, maintaining gentle boiling of the solvent. The mixture was then heated under reflux for 2 h with stirring. The resulting mixture was cooled to 0°C and slowly warmed to room temperature for over 30 min with passage of CO_2 gas. Work-up was completed by the addition of H_2SO_4 to remove remaining magnesium. Then the mixture was poured into aqueous NH_4Cl (100 ml) and the organic product extracted with CH_2Cl_2 (twice). The purification described in § 2.1.2 gave the desired Me-*m*OBA of which an example is follows. 4-Decyloxy-3-methylbenzoic acid (Me-10OBA), yield 75.3%. ^{1}H NMR: $\delta = 0.89$ (t, $J = 6.7$ Hz, 3H), 1.27–1.34 (m, 12H), 1.42–1.51 (m, 2H), 1.75–1.86 (m, 2H), 2.25 (s, 3H), 4.03 (t, $J = 6.7$ Hz, 2H), 6.84 (d, $J = 8.5$ Hz, 1H), 7.88 (s, 1H), 7.93 (d, $J = 8.5$ Hz, 1H).

2.1.4. *2,6-Diaminopyridine derivatives*

A series of these derivatives, denoted P*n*APy, was synthesized as reported previously [11].

2.2. *Preparation of hydrogen-bonded complexes*

Hydrogen-bonded complexes were prepared by mixing the components in the molten state under a nitrogen atmosphere. The mixtures once heated to their isotropic homogeneous states were used for the experiments. The values of the association constants (K) were calculated from NMR data obtained using $CDCl_3$ solutions as previously described [15].

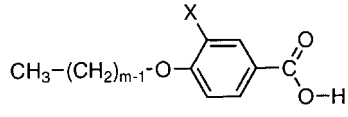
2.3. *Characterization*

Thermal properties were examined using a polarizing microscope equipped with a Mettler FP82HT hot stage and a differential scanning calorimeter (Mettler DSC30). A heating rate of 10°C min^{-1} was used for the DSC measurements. X-ray diffraction measurements on the complexes in their liquid crystalline states were carried out using a Rigaku X-ray Rad 2B system and Ni-filtered Cu K_α radiation. Samples were placed on a Mettler FP52 hot stage for the X-ray measurements.

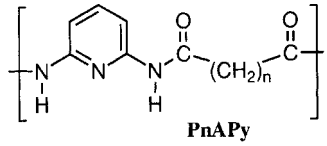
3. Results and discussion

The molecular structures of the single components used in this study are shown in figure 1 below, and the thermal properties of the benzoic acids are given in table 1. No mesomorphism is observed for the dimers of 3-methoxy- and 3-nitro-4-alkyloxybenzoi c acids, while 3-chloro- and 3-methyl-4-alkyloxybenzoi c acids exhibit monotropic mesophases. In contrast, simple 4-alkyloxybenzoic acids show enantiotropic nematic and smectic phases. In these cases, the lateral substitution on the rod-like mesogens reduces the anisotropy of the molecular structures, which leads to suppression of liquid crystallinity. Table 2 presents thermal properties of three polyamides P*n*APy. These polymers are non-mesogenic and semicrystalline.

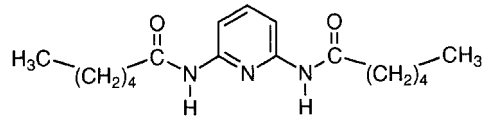
Figure 2 shows the DSC curve of the 1 : 1 complex P10APy/MeO-10OBA. After a very weak glass transition at 73°C, a small exotherm is observed at 100°C. These transitions are due to minor amorphous regions in the complexes. The complex is however mainly crystalline in the solid state. The sharp endothermal melting peak is observed at 110°C, followed by the mesophase–isotropic transition at 172°. The transitions typical of each of the non-mesomorphic single components do



X-mOBA
m=6, 8, 10
X=MeO, Me, H, Cl, NO_2



PnAPy
n=6, 8, 10



5APy

Figure 1. Molecular structures of the components used in this study.

Table 1. Thermal properties of 4-alkyloxybenzoic acid derivatives. Monotropic transitions are in parentheses. Cr = crystalline, SmC = smectic C, N = nematic, I = isotropic.

	Transition temperatures/°C							
Component	Cr		SmC		N		I	
MeO-6OBA	•	118					•	
Me-6OBA	•	135			(•	110)	•	
H-6OBA	•	107			•	154	•	
Cl-6OBA	•	121			(•	97)	•	
NO_2-6OBA	•	135					•	
MeO-8OBA	•	109					•	
Me-8OBA	•	114			(•	98)	•	
H-8OBA	•	100	•	107	•	148	•	
Cl-8OBA	•	98			(•	95)	•	
NO_2-8OBA	•	114					•	
MeO-10OBA	•	108					•	
Me-10OBA	•	104			(•	95)	•	
H-10OBA	•	98	•	125	•	143	•	
Cl-10OBA	•	101			(•	88)	•	
NO_2-10OBA	•	97					•	

Table 2. Thermal properties of polymeric components P*n*APy used for supramolecular complexes. T_g = glass transition, T_c = cold crystallization, T_m = melting.

	Transition temperatures/°C		
Polyamide	T_g	T_c	T_m
P6APy	60	137	222
P8APy	74	—	220
P10APy	70	133	201

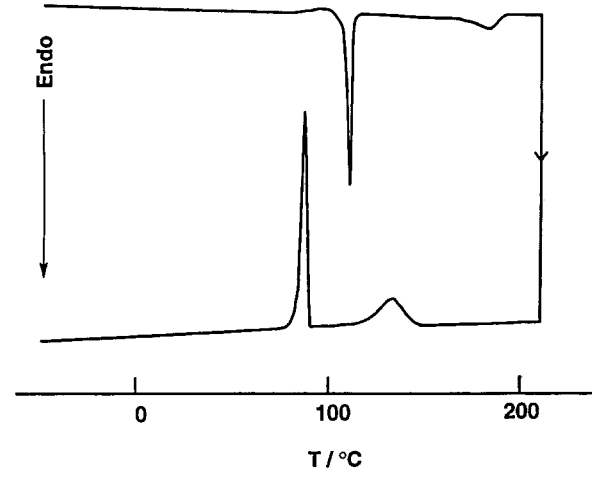


Figure 2. DSC thermograms (upper curve is for heating) for the 1 : 1 complex P10APy/MeO-10OBA.

not appear on the DSC thermographs of the complex. Microscopic observation also confirms that the complex displays a mesophase after melting. These results confirm the formation of supramolecular polymeric complexes of the bend observed for acids containing the chloro substituent (figure 3) [11].

The X-ray diffraction pattern of P10APy/MeO-10OBA in the mesophase at 140°C on heating consists of one sharp peak at 26.6 Å and one diffuse halo at 4.6 Å. These peaks are consistent with the molecular arrangement of the complex illustrated in figure 4, in which the sharp peak corresponds to the layer spacing.

The thermal properties of the 1:1 complexes of the polyamides and 3-substituted 4-alkyloxybenzoic acid derivatives are given in tables 3 and 4. The polymeric complexes with the 4-alkyloxybenzoic acid derivatives substituted by methoxy, methyl, chloro, and nitro groups at the 3-position behave as single polymeric systems and exhibit enantiotropic mesomorphic behaviour. The series of polymeric complexes containing the methyl substituent exhibits the highest melting points (table 3).

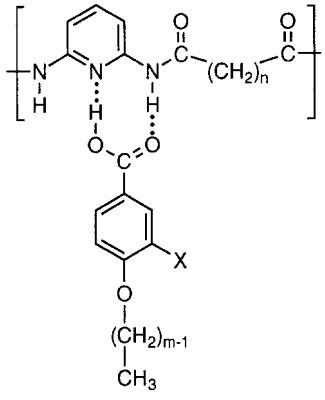


Figure 3. Structure of the polymeric complex P*n*APy/X-*m*OBA.

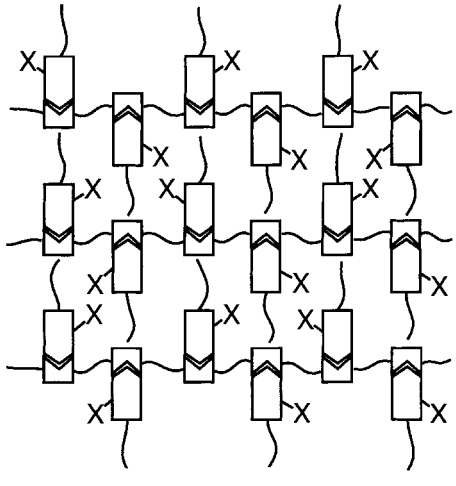


Figure 4. Schematic illustration of the molecular arrangement in the polymeric complex P*n*APy/X-*m*OBA.

Table 3. Thermal properties of polymeric complexes of P*n*APy/*X*-10OBA. M = mesophase.

Complex	Transition temperatures/°C				
	Cr		M		I
P6APy/MeO-10OBA	•	105	•	210	•
P6APy/Me-10OBA	•	110	•	202	•
P6APy/H-10OBA	phase separation				
P6APy/Cl-10OBA[a]	•	93	•	211	•
P6APy/NO_2-10OBA	•	105	•	196	•
P8APy/MeO-10OBA	•	106	•	189	•
P8APy/Me-10OBA	•	105	•	191	•
P8APy/H-10OBA	phase separation				
P8APy/Cl-10OBA[a]	•	98	•	186	•
P8APy/NO_2-10OBA	•	95	•	182	•
P10APy/MeO-10OBA	•	110	•	172	•
P10APy/Me-10OBA	•	118	•	180	•
P10APy/H-10OBA	phase separation				
P10APy/Cl-10OBA[a]	•	101	•	177	•
P10APy/NO_2-10OBA	•	110	•	173	•

[a] Compounds previously reported in [11].

Table 4. Thermal properties of polymeric complexes of P10APy/*X*-*m*OBA.

Complex	Transition temperatures/°C				
	Cr		M		I
P10APy/MeO-6OBA	•	118	•	173	•
P10APy/MeO-8OBA	•	77	•	182	•
P10APy/MeO-10OBA	•	110	•	172	•
P10APy/Me-6OBA	•	131	•	175	•
P10APy/Me-8OBA	•	120	•	178	•
P10APy/Me-10OBA	•	118	•	180	•
P10APy/NO_2-6OBA	•	120	•	169	•
P10APy/NO_2-8OBA	•	101	•	171	•
P10APy/NO_2-10OBA	•	110	•	173	•

In contrast, it is noteworthy that no stable complex formation has been observed when attempts are made to complex simple benzoic acids (H-*m*OBA) with P*n*APy. Table 4 shows that in the series of complexes based on P10APy, the highest melting temperatures are seen for the complexes formed by 4-hexyloxybenzoic acid derivatives which have the shortest alkyl chain used, while no appreciable difference is observed for the isotropization temperatures. The highest isotropization temperature is 211°C for P6APy/Cl-10OBA, and it is of interest that the mesophases displayed by these polymeric complexes exhibit such high thermal stabilities. The formation of hydrogen bonds between the amide groups of the polymer backbone may also contribute to the induction and stabilization of the mesophases [10, 11].

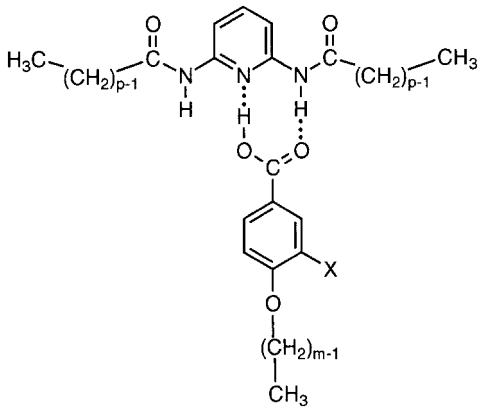


Figure 5. Structure of the low molecular mass complex *p*APy/*X*-*m*OBA.

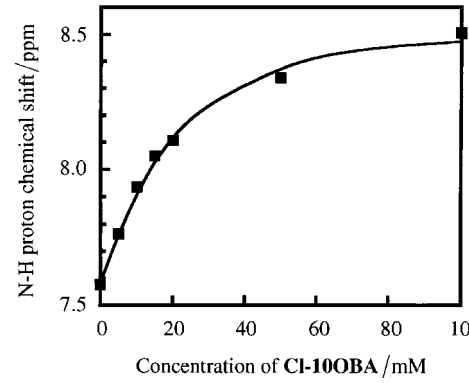


Figure 6. NMR data for the determination of the association constants K of the complexes of 5APy/Cl-10OBA in chloroform-d.

Low molecular mass complexes derived from 2,6-bis(hexanoylamino)pyridine (5APy; m.p. 115°C) and *X*-*m*OBA as shown in figure 5 have been prepared to examine substituent effects on the mesomorphism of such a mesogenic complex structure. Table 5 shows the phase behaviour of the low molecular mass complexes. In contrast to the results for the polymeric complexes, no mesomorphic behaviour is observed for the complexes containing the polar substituents such as methoxy, chloro, and nitro at the 3-position of the benzoic acid moieties. Only complexes of 5APy with Me-*m*OBA and H-*m*OBA exhibit monotropic mesomorphic behaviour. Crystal B phases are also observed for these complexes.

To evaluate the substituent effects on the stability of the complexes of 2,6-bis(acylamino)pyridyl moieties and the benzoic acid derivatives, the association constants for the complexes have been estimated using NMR measurements made on the solution state. The acidities of 4-alkyloxybenzoic acid derivatives are dependent on the substitution in the benzoic acids and this may affect the association with the pyridyl moieties. The change of the N–H shift of 5APy with the concentration of Cl-10OBA is in good agreement with calculated values, as shown in figure 6. Table 6 shows the association constants of the complexes of 5APy/*X*-10OBA in chloroform. Although the association constants of the complexes show an increasing trend with increase in the acidities of the 4-alkyloxybenzoic acids, these differences do not seem to be large enough to determine the complexation behaviour. Moreover, there is no correlation between the association constants and the mesomorphic behaviour of the polymer and low molecular mass complexes as summarized in table 7.

In a previous paper [11], the different complexation behaviour of the polyamides for 4-alkyloxy-3-chlorobenzoic acid and the simple 4-alkyloxybenzoic acid with no substituent at the 3-position was explained on the basis of more stable complex formation due to the increased acidities of the chloro-containing acids and the existence of dipole–dipole intermolecular interactions between chloro groups in the complexes. In the present study, the stable liquid crystalline behaviour is also shown in the supramolecular structures of polyamides and benzoic acid derivatives with methoxy, nitro, and methyl groups, which are electron-donating, electron-withdrawing, and non-polar, respectively. In particular, the non-polar methyl group induces and stabilizes the mesophases (tables 3 and 4). These results suggest now

Table 5. Thermal properties of doubly hydrogen-bonded complexes of low molecular mass molecules on cooling.[a] B = crystal B.

	Transition temperatures/°C				
Complex	I		B		Cr
5APy/MeO-10OBA	•	63			•
5APy/Me-10OBA	•	88	•	64	•
5APy/H-10OBA[b]	•	86	•	67	•
5APy/Cl-10OBA[c]	•	64			•
5APy/NO_2-10OBA	•	15			•

[a] 5APy; m.p. 115°C.
[b] Homologous complexes were previously reported in [12]. These complexes also show crystal B phases.
[c] Complex previously reported in [11].

Table 6. Association contants K of the complexes of 5APy/*X*-10OBA in chloroform-d.

Complex	K/M^{-1}
5APy/MeO-10OBA	89
5APy/Me-10OBA	94
5APy/H-10OBA	95
5APy/Cl-10OBA	103
5APy/NO_2-10OBA	114

Table 7. Complexation behaviour and mesomorphism for 3-substituted 4-alkyloxybenzoic acids and 2,6-diaminopyridines. LC: liquid crystalline; complex: stable complex formation; non-LC: non-mesomorphic.

	Compounds for the complexation with benzoic acids	
Benzoic acids	5APy	P10APy
MeO-10OBA	complex non-LC	complex LC (enantiotropic)
Me-10OBA	complex LC (monotropic)	complex LC (enantiotropic)
H-10OBA	complex LC (monotropic)	phase separation
Cl-10OBA	complex non-LC	complex LC (enantiotropic)
NO_2-10OBA	complex non-LC	complex LC (enantiotropic)

that in the polymeric system these substituents simply fill the extra space in the supramolecular arrangement shown in figure 4 and stabilize the orientations in the mesogenic complexes.

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