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Four types of 4,4′-bis(benzoyloxy)biphenyls were synthesized to investigate the effects of the lateral polar nitro group on appearance of mesophases as well as improvement of the mesomorphic property. In the case of 4,4′-bis(4-alkoxybenzoyloxy)biphenyls and 4,4′-bis(3,4- and 2,4-dialkoxybenzoyloxy)biphenyls, their transition temperatures were reduced by the introduction of the polar lateral nitro group because of the increasement of the molecular breadth. The nitro group in 4,4′-bis(3,4,5-trialkoxybenzoyloxy)biphenyls enhanced the transition temperatures and mesomorphic properties since the trialkoxy derivatives without a nitro group were not mesomorphic and those with a nitro group had a hexagonal columnar phase. The introduction of the nitro group did not increase the molecular breadth of the trialkoxy derivatives because they already have the wide molecular breadth.

Keywords: hexagonal columnar phase; lateral polar substituent; substituent effect; X-ray diffraction study

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INTRODUCTION

The mesomorphic property of rod-like liquid crystals is sensitive to modification of the structure [1]. It is known that the core structure provides the major anisotropy of the molecule, which is necessary for appearance of mesomorphic property and the flexible terminal groups control the transition temperatures as well as the kind of mesophases. The rigidity of the core structure is provided by at least two rings, which are connected directly or through a linking unit such as an ester or amide group. Lateral substituents also change thermal behaviors of rod-like molecules. They increase the molecular breadth to decrease the transition temperatures because of a reduction in the molecular length-to-breadth ratio [1]. From these points, introduction of the polar lateral substituents disfavored to form liquid crystalline states with higher thermal stability. The most important role of polar lateral substituents should be the formation of nematic phases with negative dielectric anisotropy, which are required in the vertically aligned (VA) mode display [2].

It is reported that there are quite close relationships between the shape of molecules and the types of mesophases. Rod-like molecules show lamellar phases whereas disk-like ones columnar phases. Other than these, rod-like molecules with a rigid core showed both lamellar and columnar phases when plural side chains are introduced at the terminal positions [3]. They are called polycatenars. According to the Malthête's definition, the term catenar is reserved for mesogens with a clear rod-like core and normal aliphatic chains only graphed on the two terminal benzene rings [3]. They pointed that with four side chains (tetracatenars), four rings are necessary to obtain mesomorphic properties. With five and six side chains (penta- and hexacatenars), at least five rings are convenient for the mesomorphism.

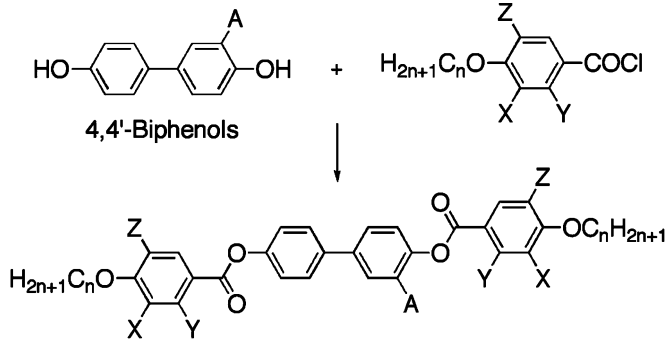
In this paper, we report the effects of a polar lateral nitro group on the appearance of mesophases of bis(alkoxybenzoyloxy)biphenyls. In fact, we modify the structure of bis(benzoyloxy)biphenyls by changing the number of alkoxy side chains at the terminal positions and by introducing a polar nitro group at a lateral position to investigate the mesomorphic property of bis(benzoyloxy)biphenyls.

RESULTS AND DISCUSSION

Synthesis

4,4′-Bis(benzoyloxy)biphenyls discussed here were synthesized in reactions of benzoylayion of 4,4′-biphenols. All new compounds satisfy the spectral data and the elemental analytic data.

TABLE 1 Transition Temperatures of Compounds **1a** and **1b**



1a: A=H, X=Y=Z=H
1b: A=NO_2, X=Y=Z=H
2a: A=H, X=OC_nH_{2n+1}, Y=Z=H
2b: A=NO_2, X=OC_nH_{2n+1}, Y=Z=H
3a: A=H, X=Z=H, Y=OC_nH_{2n+1}
3b: A=NO_2, X=Z=H, Y=OC_nH_{2n+1}
4a: A=H, X=Z=OC_nH_{2n+1}, Y=H
4b: A=NO_2, X=Z=OC_nH_{2n+1}, Y=H

n	Transition temperature (°C)	n	Transition temperature (°C)
1a-1	4 Cr · 157.3 · SmC · 183.5 · SmA. 358.6 · N · 393.4 · Iso	**1b**-1	4 Cr · 119.8 · N · 299.7 · Iso
1a-2	8 Cr · 134.2 · SmC · 203.6 · N · 292.5 · Iso	**1b**-2	8 Cr · 101.7 · SmC · 159.3 · N · 249.0 · Iso
1a-3	12 Cr · 130.7 · SmC · 231.1 · N · 256.8 · Iso	**1b**-3	12 Cr · 83.4 · SmC · 199.6 · N · 216.5 · Iso
1a-4	16 Cr · 118.1 · SmC · 224.4 · Iso	**1b**-4	16 Cr · 91.1 · SmC · 200.2 · Iso

Determined by DSC on the second heating.

4,4′-Bis(4-alkoxybenzoyloxy)biphenyls (1a and 1b)

The thermal behaviors and microscopic textures were observed using a polarizing microscope equipped with a hot stage. The optical microscopic observation of compound **1** showed two kinds of mesophases, one of which is a nematic (N) phase because it has schlieren textures with two and four brushes. The other one is a smectic C (SmC) phase because of the observation of schlieren textures. The transition temperatures of 4,4′-bis(4-alkoxybenzoyloxy)biphenyls (**1a** and **1b**) are summarized in Table 1. Both showed N phases when the alkoxy side chains are short. When the alkoxy side chains are long, SmC phases appeared.

X-ray Diffraction Study and Packing Model of Compound 1a-3

The X-ray diffraction (XRD) study of compound **1a**-3 indicated that the layer spacing of the SmC phase is 33.4 Å at 180°C. The calculated molecular length of **1a**-3 is 51.4 Å by MM2 method. Figure 1 shows

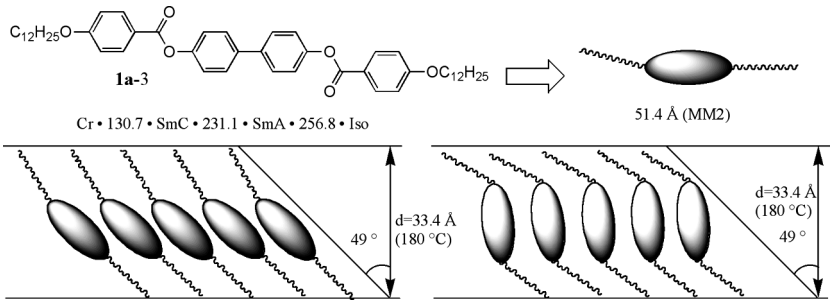


FIGURE 1 Packing model of the SmC phase of **1a**-3.

two types of packing models of the SmC phase of **1a**-3. When compound **1a**-3 forms a monolayer structure, the molecule should tilt as much as by 49° to the layer plane.

Similarly, the layer spacing of the SmC phase of compound **1b**-3 with a nitro substituent at a lateral position was 34.4 Å. The tilt angle is determined to be 48°.

Comparison of the thermal stability between compounds **1a** and **1b** demonstrated that compound **1a** had higher transition temperatures. The lateral nitro group decreased the transition temperatures because it enlarged the molecular breadth to reduce the length-to-breadth ratio.

4,4′-Bis(3,4-dialkoxybenzoyloxy)biphenyls (2a and 2b) and 4,4′-bis(2,4-dialkoxybenzoyloxy)biphenyls (3a and 3b)

The transition temperatures of compounds **2a** and **2b**, tetracatenars, are shown in Table 2. They were not mesomorphic. The lateral nitro group decreased the melting points of the tetracatenars.

When the alkoxy group at the C-3 position of compounds **2** was moved to the C-2 position, compounds **3a** and **3b** showed N phases with lowering transition temperatures as shown in Table 3. The N

TABLE 2 Transition Temperatures of Compounds **2a** and **2b**

	n	Transition temperature (°C)		n	Transition temperature (°C)
2a-1	4	Cr · 185.9 · Iso	**2b**-1	4	Cr · 136.2 · Iso
2a-2	8	Cr · 148.4 · Iso	**2b**-2	8	Cr · 123.9 · Iso
2a-3	12	Cr · 140.8 · Iso	**2b**-3	12	Cr · 122.7 · Iso
2a-4	16	Cr · 134.4 · Iso	**2b**-4	16	Cr · 121.5 · Iso

Determined by DSC on the second heating.

TABLE 3 Transition Temperatures of Compounds **3a** and **3b**

	n	Transition temperature (°C)		n	Transition temperature (°C)
3a-1	4	Cr · 163.1 · Iso	**3b**-1	4	Cr · 111.2 · (N · 44.7 ·) Iso
3a-2	8	Cr · 89.6 · (N · 75 ·) Iso	**3b**-2	8	Cr · 61.0 · (N · 31.9 ·) Iso
3a-3	12	Cr · 82.6 · (N · 58 ·) Iso	**3b**-3	12	Cr · 63.3 · (N · 29.7 ·) Iso
3a-4	16	Cr · 87.5 · (N · 56 ·) Iso	**3b**-4	16	Cr · 61.9 · (N · 32.8 ·) Iso

Determined by DSC on the second heating.

phase showed schlieren textures with two and four brushes. The transition temperatures were extremely decreased when compared with those of compounds **2a** and **2b**. The alkoxy side chains at the C-2 position of compounds **3** destroy the linearity of the molecules, which decreased the melting points to disclose the mesomorphic property of compounds **3a** and **3b**.

4,4′-Bis(3,4,5-trialkoxybenzoyloxy)biphenyls (4a and 4b)

When one more alkoxy side chain was introduced to the C-5 position of compounds **2**, the melting points of compounds **4a**, hexacatenars, decreased more than those of **2a**. Compounds **4a** without a lateral nitro group showed only melting points as shown in Table 4. However, compound **4b**-2 has the textures between crossed polarizers shown in Figure 2a, which suggested that **4b**-2 had a columnar (Col) phase since it has pseudo-focal conic fan-shaped textures.

The Col_h phase of compound **4b**-2 was relatively viscose. The photograph of Figure 2b shows recrystallization process of the phase after shearing of the Col_h phase.

X-ray Diffraction Study and Packing Model of Compound 4b-2

The X-ray diffraction study of compound **4b**-2 in Figure 3 showed four reflections at 30.1, 16.7, 15.1, and 10.0 Å and a broad halo peak. Since

TABLE 4 Transition Temperatures of Compounds **4a** and **4b**

	n	Transition temperatures (°C)		n	Transition temperature (°C)
4a-1	4	Cr · 73.0 · Iso	**4b**-1	4	Cr · 95.5 · Iso
4a-2	8	Cr · 77.5 · Iso	**4b**-2	8	Cr · 91.7 · (Col_h · 72.6 ·)Iso
4a-3	12	Cr · 80.4 · Iso	**4b**-3	12	Cr · 75.1 · Col_h · 77.1 · Iso
4a-4	16	Cr · 50.6 · Iso	**4b**-4	16	Cr · 61.3 · (Col_h · 32.7 ·) Iso

Determined by DSC on the first heating.

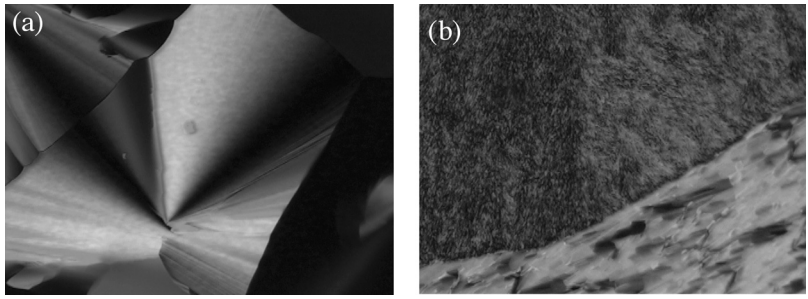


FIGURE 2 (a) Textures of compound **4b**-2 at 71.4°C on cooling process and (b) recrystallization of the state after shearing of the Col_h phase at 71.4°C. The recrystallization started from the upper left side.

the reflections in the small angle region are correlated to 1: $1/\sqrt{3}$: 1/2: 1/3, it could be proved that compound **4b**-2 has a hexagonal columnar (Col_h) phase although the intensity of the 2D reflection at 16.7 Å is low.

The packing model of the Col_h is shown in Figure 3. The diameter of the Col_h is calculated to be 34.8 Å. The number (n) of the molecules

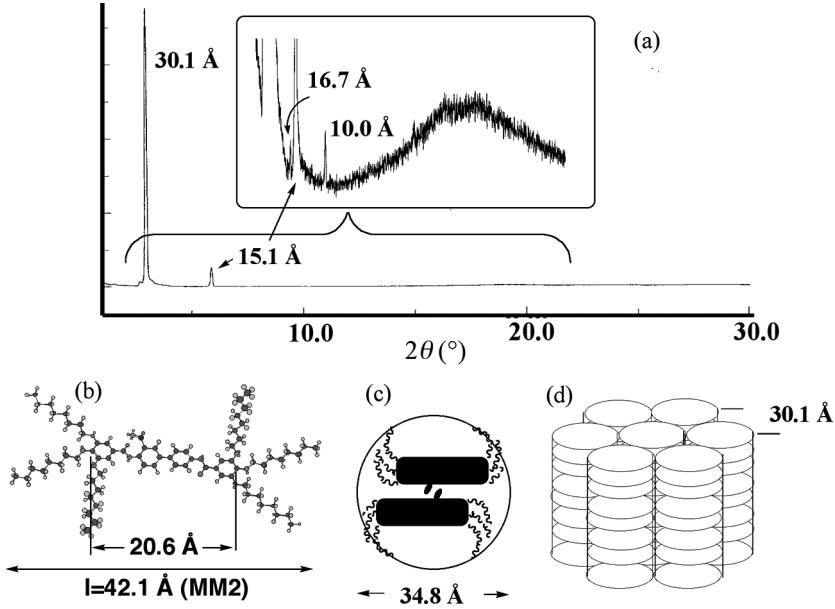


FIGURE 3 (a) XRD data of compound **4b**-2 at 46.9°C on cooling process. (b) Structure of **4b**-2 obtained from Chem3D calculation. (c) Two molecules in a disk. (d) Packing model of the Col_h phase.

in a disk is calculated to be 2 by using the equation [4] when the distance between is 4.3 Å and the density of **4b**-2 is estimated to be 1 g/cm^3. In a disk, the nitro groups interacted to form a head-to-tail dimer, which is the major factor to induce mesomorphic property because hexacatenars **4a** without a lateral nitro group were not mesomorphic.

Effects of the Polar Lateral Nitro Group

Compounds **1a** and **1b** had lamellar phases whereas compounds **2a** and **2b** had not. The positional isomeric tetracatenars **3a** and **3b**, however, showed N phases due to the depression of the melting points. Compounds **4a**, hexacatenars with a nitro group, did not show any mesophases while hexacatenars **4b** with a nitro group showed a Col_h phase.

The structural requirement when hexacatenars form a mesophase is that molecules should have at least five rings in the core structure [3]. It is common that when the number of the alkoxy side chains was increased, mesomorphic compounds with a lamellar phase sometimes destroy the mesomorphic property. Increase of the number of the side chains induces a mismatch of the volume between the chains and the core, which gives rise to expansion of the lateral distance between the cores. Since the expansion makes it weakened the lateral interaction of the cores to keep the lamellar phases, a curved interface resulted in a lamellar structure to a break-up of the lamellar structure to form columnar phase [5].

In the case of compounds **4a**, they have four rings in the core. However, the core structure could not provide sufficient strength to keep mesomorphic property. The introduction of the polar nitro group at the lateral position enhances the strength between the neighboring molecules, which induced a Col_h phase.

CONCLUSIONS

The polar lateral nitro group behaves differently depending on the types of molecules. In the case of bis(mono- and di-alkoxybenzoyloxy)-biphenyls, the nitro group decreases the transition temperatures because of increase of the molecular breadth to reduce the molecular length-to-breadth ratio. The hexacatenars **4a** without a nitro group were not mesomorphic whereas the hexacatenars **4b** with a nitro group had Col_h phases. The nitro group made it possible to form the Col_h phases and to enhance the transition temperatures.

Since the molecular breadth of hexacatenars **4b** is wide enough, the introduction of a nitro group did not affect the molecular breadth.

Therefore, the nitro group acted as a polar lateral substituent to strengthen the lateral molecular interaction, which kept making self-assembly since hexacatenars **4a** without a nitro group were not mesomorphic. Thus, the effects of the nitro group in appearance of mesophases were depending on the molecular structures.

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