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Misuzu Konishi^a, Katsuhiko Fujita^a & Tetsuo Tsutsui^a

^a Department of Applied Science for Electronics and Materials, Interdisciplinary Graduate School of Engineering Science, Kyushu University, Fukuoka, Japan

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GIANT DOMAIN FORMATION IN A THIN FILM OF BISSTYRYLANTHRACENE DERIVATIVES BY A SIMPLE MELT PROCESS

Misuzu Konishi, Katsuhiko Fujita, and Tetsuo Tsutsui
Department of Applied Science for Electronics and Materials,
Interdisciplinary Graduate School of Engineering Science,
Kyushu University, Kasuga, Fukuoka 816-8580, Japan

Bisstyrylanthracene derivatives with long alkyl side chains (BSA), which were prepared into the thin films composed of giant anisotropic domains by simple melt process, showed interesting property. The derivatives that changed the chains length and chains form were synthesized. We introduced the film preparation and investigated thermal properties of the films using differential scanning calorimetry (DSC), polarization micrograph, and fourier transform infrared spectroscopy (FT-IR). The phenomena of the giant domain formation and phase transition in BSA films are discussed.

Keywords: anisotropic domain; organic film preparation; phase transition

INTRODUCTION

The study on devices consisting of organic thin films is in the spotlight, recently. In those devices, organic materials are expected to play various important roles as not only insulators but also semiconductors. Especially in organic thin film field effect transistor (FET), wide variety of device structure has been demonstrated [1]. For example, it was fabricated on a flexible substrate [2,3], was embedded electrodes into polymer films [4], or was integrated with a light emitting diode [5]. One of the substantial advantages of using organic materials is such wide variation of device design.

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Address correspondence to Tetsuo Tsutsui, Department of Applied Science for Electronics and Materials, Interdisciplinary Graduate School of Engineering Science, Kyushu University, Kasuga, Fukuoka 816-8580, Japan. Tel.: +81-92-583-7533, Fax: +81-92-575-2318, E-mail: tsuigz@mbox.nc.kyushu-u.ac.jp

Generally, the film preparation processes such as vacuum deposition or spin coating, are used, because the amorphous films prepared by those processes are suitable to minimize the domain boundary effects. Though the few materials which tend to be organized as a polycrystalline film such as pentacene or otiothiophene show high carrier mobility in FETs [6,7], the boundary effect can be reduced as the grain size is enlarged, in ideal case to a single crystal.

Since it is quite difficult to obtain large single crystal of organic material, it would be a substantial target of the research to fabricate a device with highly ordered molecular arrangement. It has been reported that the carrier transportation was improved owing to the high order of organic molecules in liquid crystals [8,9].

we synthesized 9,10'-Bis (4,4'-alkoxystyryl) anthracene (BSA) with long alkyl chains (Fig. 1). Among them, ones having long alkyl chains ($n > 10$) showed anisotropic domain formation in film prepared by a simple melt process. X-ray diffraction analysis of the BSA films has already revealed that the form layered structure parallel to the substrate with a layer spacing corresponding to the molecular length. In the present study, we investigated the thermal properties of the materials and films with differential scanning calorimetry (DSC), polarization micrograph, and fourier transform infrared spectroscopy (FT-IR), to discuss about the giant domain formation in BSA films.

EXPERIMENTAL SECTION

Synthesis

To examine the influence of side alkyl chain on the phase behavior, we synthesized the series of BSAs with different chain length (Fig. 1).

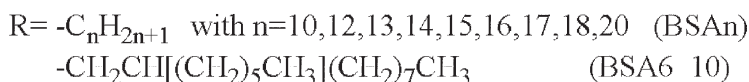
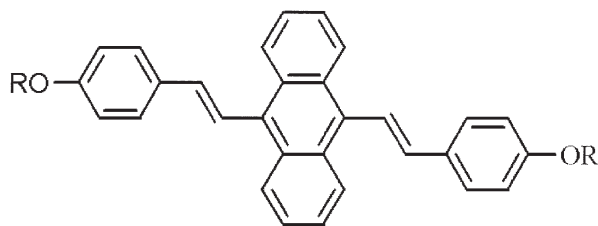
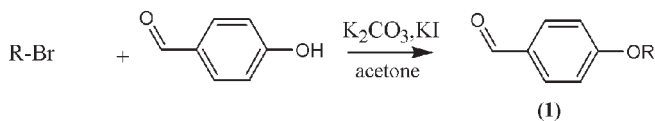


FIGURE 1 Synthesis and chemical structure of BSA.

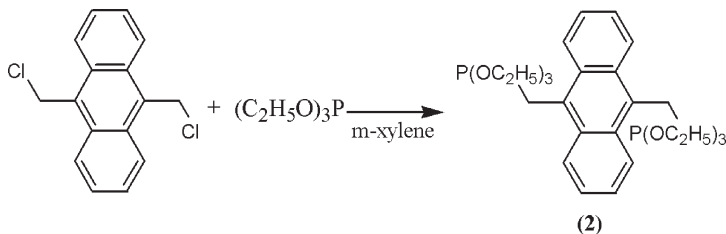
1-bromoalkane and 4-hydroxybenzaldehyde were dissolved in dry acetone. Potassium carbonate and potassium iodide were added to the solution, and refluxed under nitrogen for 24 h. Filtrated from the hot reaction mixture and the solvent was removed by evaporation. After, hexane and water were added into the condensed solution, the organic layer was washed with water several times. After purification by a silica-gel column chromatography (chloroform as eluate), the (1) was obtained. (Scheme 1) In the synthesis of BSA6_10 having 2-hexyldecyl group, the hydroxyl group of 2-hexyl-1-deanol was substituted by bromide before Scheme 1.

9,10'-bischrolomethylantracene (purchased from Aldrich) was dissolved in m-xylene and it was refluxed with triethyl phosphite. Cooling to the room temperature, the light yellow precipitate was obtained. It was purified by recrystallization from cyclohexane to obtain product (2). (Scheme 2)

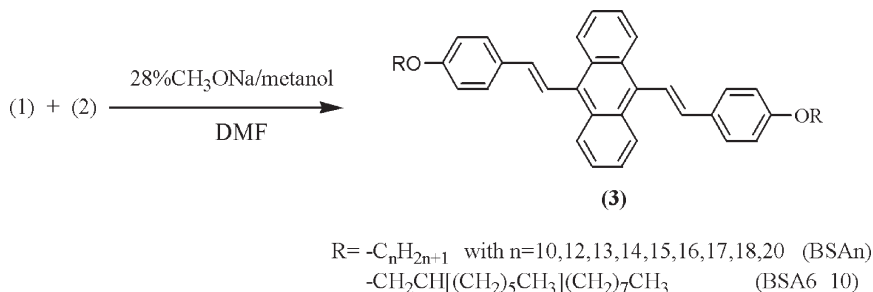
The methanolic solution of sodium methoxide was added dropwise into the mixture of product (1) and (2) in DMF. After of stirring for 12 h, the precipitate was filtered off, washed with water and dried in vacuum. The crude product was purified by silica-gel column chromatography (toluene:hexane = 4:1), and recrystallized from cyclohexane 3 times. The resulted yellow needle crystal (product (3)) was obtained. (Scheme 3) ¹HNMR spectrum was measured about each product.



SCHEME 1

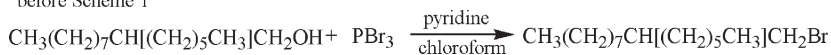


SCHEME 2



SCHEME 3

When $R = -CH_2CH[(CH_2)_5CH_3](CH_2)_7CH_3$
before Scheme 1



SCHEME 4

Differential Scanning Calorimetry (DSC) and Polarization Microscograph

DSC was measured with Seiko instruments DSC22 at a heating rate of $2^\circ\text{C}/\text{min}$ by use of aluminum pan. The measurements were repeated several times.

Thin films preparation was carried out as follows. Each BSA derivatives was heated and melt. It was sacked in between two glass plates by capilarity. The temperature was carefully controlled by Mettler Toledo FP82HT at around the melting point and gradually lowered at the rate of $0.1^\circ\text{C}/\text{min}$. The films were observed using a polarization microscope with a variable temperature hot stage under crossed nicol condition.

The polarized absorption spectra were measured on the hot stage to measure dichroic ratio. Linearly polarized light was irradiated to the film and the transmission was detected. The angle of the polarizer, which gave the weakest transmission, was defined as 0° .

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were measured in Bio-rad FTS6000 with an unpolarized incident beam perpendicular to the sample film plane. The BSA films were prepared on KBr crystal plates instead of glasses and the measurement carried out under controlled temperature by Chino DB1000.

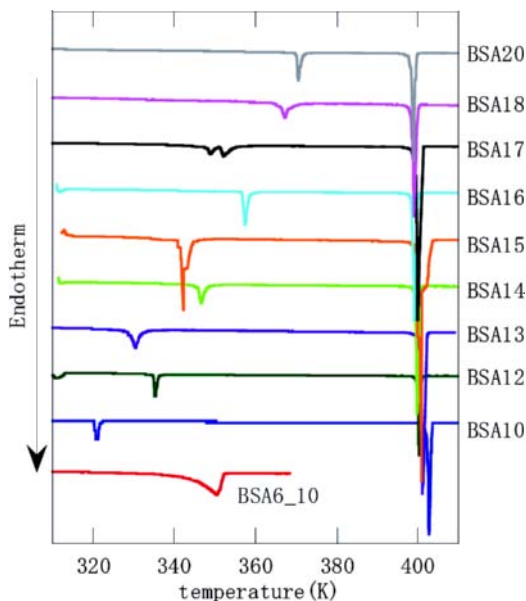


FIGURE 2 DSC curves of BSAs (the second heating).

RESULTS AND DISCUSSIONS

Thermal Property

In the DSC measurements, BSA10, 12, 13, 14, 15, 16, 18, 20 showed two endothermic peaks (Fig. 2). Those phase which indicate that there are two phases (K1, K2) before isotropic melting. Even in the mesophase between two peaks, it showed no fluidity. Figure 3 shows the dependence of phase transition temperatures on the chain length, n . The temperature of K1-K2 phase transition, was changed linearly along with a solid line in $n = 10, 12, 14, 16, 18, 20$ or along with a dotted line in $n = 13, 15$. This odd-even effect suggests the direction of the chain-end could affect the transition behavior. Since the films have been revealed to take layer structure where the chain-ends are facing each other, the chain-end direction may play an important role for inter layer interaction.

The BSA17 showed three peaks; another phase (K2') was observed between the K1 and the K2 phase. Since it may be caused by impurities, the recrystallization was repeated several times and the purity was checked by ^1H NMR and HPLC. No sign of impurities detected. About BSA6_10, no phase was shown from one crystalline phase to isotropic phase, even if it lowered temperature to -100°C , though the mesophase of BSA6_10 was

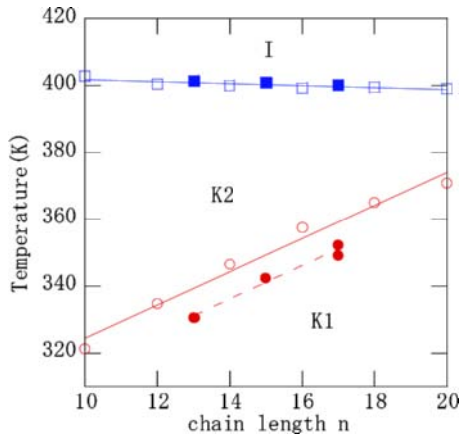


FIGURE 3 The dependence of phase transition temperature on the chain length, n .

expected to be lowered to room temperature. It should be concluded that the branched BSA has no mesophase as the BSAs with shorter chain length ($n < 10$).

The giant anisotropic domains appeared at the transition temperature from I to K2 phase under polarized microscope. Moreover, when the temperature was lowered more gradually, it was observed that a nuclear into an mm-scale mono-domain (Fig. 4). At the K2-K1 transition temperature, the angle of the polarizer which gave the darkest image of the domain under the crossed nicol conduction changed in 8 degree, and some crack appeared in the film. The axis of the refractive index ellipsoid of the BSA

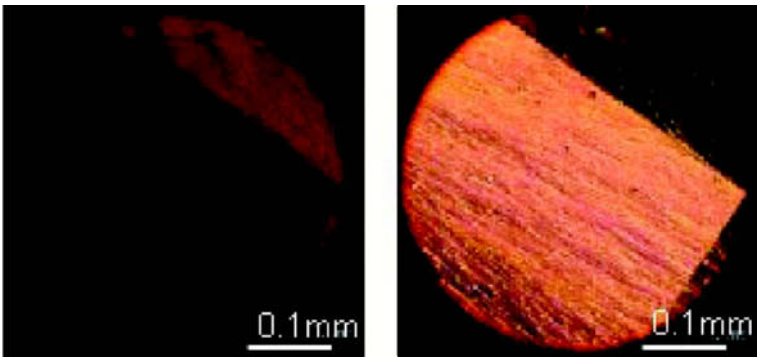


FIGURE 4 Polarization micrograph of BSA16 film under crossed nicol.

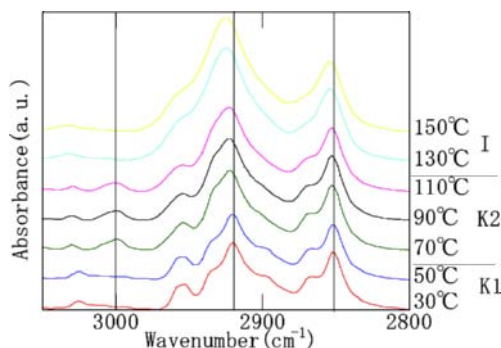


FIGURE 5 Temperature dependence of FT-IR spectra (BSA14 film).

film moved and the domain shrunk at K1-K2 phase transition. On the other hand, BSA6_10 film became turbid, which indicates microcrystalline formation, at the transition temperature from the isotropic to the crystalline phase as BSAs of short chain ($n < 10$).

The FT-IR spectra of BSA films showed significant temperature dependence (Fig. 5). The absorption peaks ascribed in antisymmetric $V_{as}(CH_2)$ and symmetric $V_s(CH_2)$ stretching vibration appeared around 2919–2926 and 2851–2855 cm^{-1} respectively.

The peak position plotted against the temperature are shown in Figure 6. Both the $V_{as}(CH_2)$ and $V_s(CH_2)$ vibration frequencies were observed at around 2920 and 2851 cm^{-1} at K1 phase, which corresponding to an all-trans conformation [10]. While both shifted to higher frequency at K2

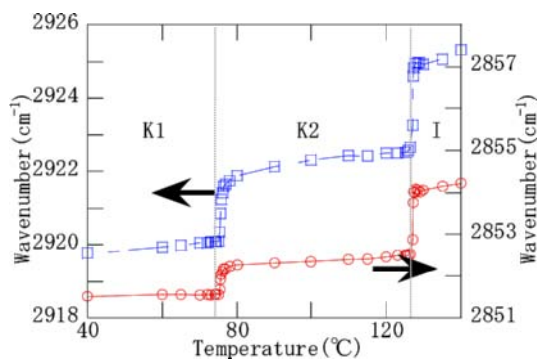


FIGURE 6 Temperature dependence of the CH_2 stretching absorption band frequencies.

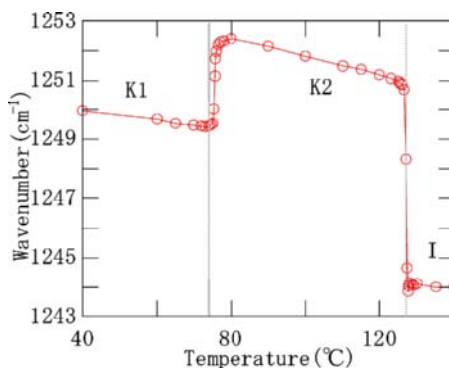


FIGURE 7 Temperature dependence of the C-O-C stretching absorption band frequencies.

phase (at 2922 and 2853 cm^{-1} respectively), indicating the gauche conformation content become larger. Both shifted to far higher at the I phase (at 2925 and 2854 cm^{-1} respectively), indicating all alkyl chains are in a disordered state [10,11].

In the spectra at the K2 phase, a small peak was observed at 3000 cm^{-1} , which can be ascribed to olefinic CH stretching vibration. It is suggesting that the orientation of olefin hydrocarbon bonds in the aromatic core as changed at the K1-K2 phase transition. The peak around 1250 cm^{-1} ascribed to C-O-C stretching vibration shows significant temperature dependence (Fig. 7). It shifted to higher frequency at the transition from K1 to K2 phase, but shifted reversely to lower from K2 to I. It indicates that the environmental condition around CO bond was drastically changed at the K2 phase. Probably CO bond should suffer stranger stress at K2 phase than at the other phases.

CONCLUSIONS

It has been revealed that the thin film having highly ordered molecular arrangement can be prepared from the BSAs other than BSA6_10 by the simple melt process. They showed mesophase before melting.

The alkyl chains took all-trans conformation at K1 phase, and the gauche content increased at K2 phase.

In this study, we conclude that the mesophase should be indispensable for the giant domain formation. The film at the K2 phase showed no fluidity and the domain size did not changed at the transition from K2 to K1.

More detail study such as temperature dependent X-ray crystallography is required for making a conclusion whether K2 is liquid crystalline state or crystalline state.

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