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Blend Electrolyte Solution Showing Smectic A for Electro-synthesis of π-Conjugated Polymer

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ABSTRACT

(*S*)-4-Cyano-4'-(4,8-dimethylnonyl)biphenyl abbreviated as DM9CB was synthesized. A chiral liquid crystal blend system (LC-blend) of octyloxycyanobiphenyl (8OCB)/DM9CB was prepared, although DM9CB shows no liquid crystal phase alone at room temperature. The LC blend shows a chessboard-like texture under polarizing microscopy (POM) observations at 43 °C. This chessboard-like texture is assigned to smectic A phase with layer structure. Electrochemical polymerization in this LC-blend system produces π-conjugated polymer having smectic order.

Keywords:liquid crystal, blend LC, electrochemical polymerization, smectic A phase, chessboard-like texture

Introduction

Liquid crystals (LCs) show middlephase with mobility and anisotropy betweencrystalphase andisotropic(liquid) phase [1]. LCs can be classified into two types, temperature (thermotropic) [2] or concentration driven phase transition (lyotropic) LC [3]. Stimuli-responsive properties of LCs have been applied for thermometer [4], pressure sensor [5], and gas detectors [6]. Polymers [7] and low-molecular weight materials having rigid structures show LC form aggregates [8], micelles [10], particles [11], ellipsoid [8], rod [9], discotic [7], rope like [12], network [10],and banana shape [13]. Liquid crystal with electro/magnetic moment can response against external field, such as electric field, magnetic field, and force field. This functionhas been applied for liquid crystal displays and liquid crystal template for chemicalreactions[14]. LC phase can be classified into nematic (including cholesteric phase) [1,15], smectic [1,16], and others [7]. However, not all the materials show LC phase between the solid phase and the liquid phase. It is difficult to predict whether a certain material has this mesophase or not. Founding of materials with liquid crystallinity is significant [8].

4-Cyano-4'-pentylbiphenyl (5CB) is a classical liquid crystal material and has been widely applied for liquid crystal displays. Here, structure modification of 5CB in molecular level can lead to develop new liquid crystals. Suzuki-Miyaura coupling reactions can be considered as a prospective method to build the biphenyl of 5CB directly using 4-bromobenzonitrile and alkyl phenylboronic acid or ester with an aid of palladium catalyst. However, the residual palladium catalyst had been mentioned as a significant problem [17].

Resultant morphology of polymer obtained via electrochemical polymerization in LC provides materials to discuss the mechanism of formation and alignment of liquid crystal because the LC morphology can be imprinted from the matrix LC template to the resultant conjugated polymers (CPs) [15]. Polymerization in cholesteric liquid crystals (CLC) provides polymers with left-hand or right-hand helical orientation. These polymers show liquid crystal like fingerprint textures [18]. However, there are few reports on polymerization in smectic liquid crystals [19].

In this research, a chiral molecule (*S*)-4-cyano-4'-(4,8-dimethylnonyl)biphenyl (DM9CB) is synthesized. DM9CB has good affinity with cyanobiphenyl based liquid crystals because similarity of the molecular structure, such as rigid form, terminal cyano group, although this molecule shows no liquid crystallinity alone. Addition of the DM9CB into octyloxycyanobiphenyl (8OCB) induced the chessboard-like texture under polarizing microscopy (POM) observation with crossed Nicol condition. After construction of such a liquid crystal system, poly(ethylenedioxythiophene) (PEDOT) was electrochemically synthesized, resulting production of the polymer having striped fan-shaped texture.

Experimental Section

4-Cyanophenylboronic acid ester and (*S*)-1-bromo-4-(4,8-dimethylnonyl)benzene was used as reactant, and alkaline ethylene diamine tetraacetic acid (EDTA) was employed to capture the palladium residual. The complex of palladium is filtrated by silica gel in the purification procedure.

To introduce alkyl group to aromatic group, two routes of coupling reaction can be considered. Coupling reaction using Grignard reagent with an aid of metal catalyst such as palladium, nickel or copper is valid [20].Multistep synthesis using Wittig reaction and subsequent reduction of the C=C double bond by hydrogen [21] are possible for it. In this research, we employ Wittig reaction for synthesis of the desired material as a suitable synthetic route, Scheme 1. A low-cost natural product (-)-β-citronellol is employed as the terminal group in the target molecule. One-pot reaction to synthesis of bromoalkane as a styrene analog form is carried out. (*S*)-1-bromo-3,7-dimethyloctane [22], (*S*)-1-bromo-4-(4,8-dimethylnon-1-en-1-yl)benzene [17] are synthesized, according to the previous reported method in the literatures.

All starting regent was purchased from Tokyo chemical industry (TCI, Tokyo), and used as received. Tetrahydrofuran (THF) was purified by distillation over sodium with benzophenone as indicator.

(*S*)-3,7-Dimethyloctan-1-ol was synthesized as follow. Under a hydrogen atmosphere, (-)-β-citronellol was dissolved in methanol. This solution was stirred in the presence of 5 wt% of palladium/carbon (10 wt%). After 2 days, the mixture was filtrated. Then, the solvent (methanol) was removed by evaporation. The desired material is a form of colorless oil (Y = 95%).

DM9CB was synthesized by reflux of the mixture containing 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (1 eq.), (*S*)-1-bromo-4-(4,8-dimethylnonyl)benzene (1 eq.), potassium carbonate (1.5 eq.), and $Pd(PPh_3)_4$ (0.03 eq.) in THF for 24 h under an argon atmosphere. The solution was poured into large volume of water, and extracted by hexane. The organic layer was washed by alkaline (sodium hydroxide: 2 eq.), EDTA (1 eq.) solution. The organic layer was extracted again, and the solvent was evaporated. The product was purified using silica gel column chromatography (eluent: hexane/dichloromethane = 1/1), subsequent dry in vacuum afforded to yield brown oil. (Y = 73%)

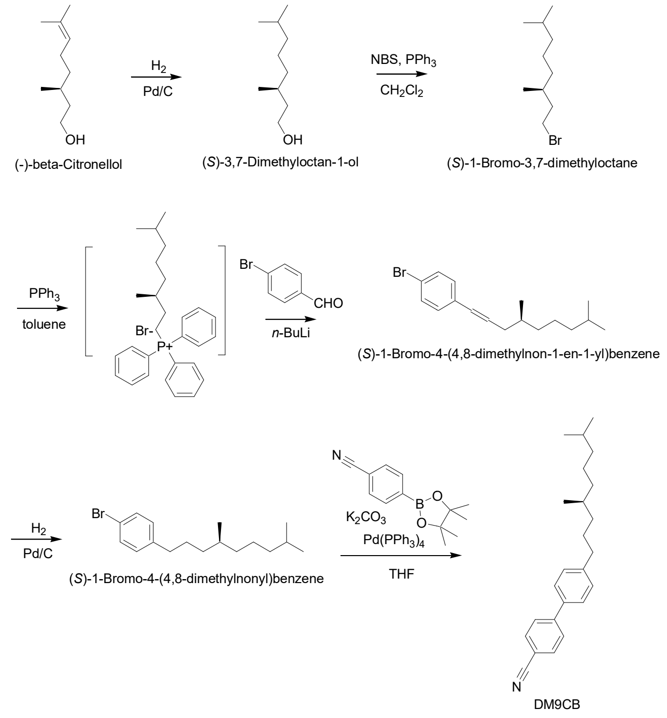
Electrochemical polymerization of 2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxine (bisEDOT) as a monomer in the liquid crystal was carried out, according to the procedure in the literature[18]. Two pieces of ITO glass were used as electrodes. A tetrafluoroethylene film (0.2 mm, ‘U’-shaped) was used as the spacer between the ITO glasses. The blend electrolyte (monomer: 5 wt%, tetrabutylammonium perchlorate: 0.5 wt%, DM9CB: 5 wt%, 8OCB: remaining percentage) has been injected into the 0.2mm ‘U’-shaped space at 120 °C. A direct current (3.0 V) was then applied across the ITO electrodes to initiate electrochemical polymerization.

Results and Discussion

Chemical structure of the product was confirmed with ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, Fig. 1-2. In the ^{1}H NMR spectrum, the peaks from 1.5 to 1.0 ppm show complicated multi-coupling. While, ^{13}C NMR show clear 11 signals from 0 ppm to 45 ppm. They can be attributed to 11 kinds of carbons on the alkyl chain. Electrospray ionization mass (ESI-MS) spectroscopy measurement indicates no impurity of palladium (m/z = 105.90) and shows the signal of monomer (m/z = 356.24), dimer (m/z = 689.49) and trimer (m/z = 1022.74) of DM9CB. DM9CB has the similar structure as the well-known liquid crystal 5CB but have a chiral structure. Liquid crystallinity research on DM9CB seems significant.

DM9CB shows no liquid crystallinity from the room temperature to -5 °C. A blend liquid crystal, 5 wt% of DM9CB in 8OCB was prepared. Differential scanning calorimetry (DSC) measurement was carried out to determine transition temperatures, Fig. 3.

In the heating process, this liquid crystal system shows three phase transition signals. The range from 48.78 °C to 65.71 °C is attributed to the smectic phase, from 65.71 °C to 76.16 °C is nematic phase. In the cooling process, the phase transition temperature shifts toward lower range, especially transition point from smectic phase to crystal.



Scheme 1. Synthetic route for (*S*)-4-cyano-4'-(4,8-dimethylnonyl)biphenyl (DM9CB). PPh_3 = triphenylphosphine. THF = tetrahydrofuran. NBS = *N*-bromosuccinimide.

Figs. 4 (a,b) show polarizing optical microscopy (POM) images of two liquid crystal (LC) phases of the LC-blend. The POM image shows typical fingerprint texture, which is attributed to cholesteric phase, Fig. 4(a). In the temperature range of smectic A phase (SmA), some parts of this mixture show grid pattern under the POM observation, Fig. 4(b).

Gypsum first order red plate (optical phase plate) was used in the POM observations to discuss the further character of this grid pattern texture, Figs. 4 (c,d). Figure 4(c) shows the POM image of this grid pattern texture upon insertion of the optical phase plate between the sample and the polarizer. In this condition, the grid pattern texture is colored with blue and red alternately. The texture on the chessboard is colored with black and white alternately. Rotation of the plate with 90 deg in clockwise changes the area of the color. It suggests that the domain have different optical directions, which is typical character of SmA.

Electrochemical polymerization is carried out in LC-blend in SmA. Optical texture of the LC transfers to the resultant polymer in the solid state. Fig. 5shows the POM image of the polyEDOT film. In this picture, the texture shows typical smectic like fan-shaped structure. However, this fan-shape domain has stripes. Scanning electron microscopy (SEM) observation reveals that the polymer forms fibril structure along the SmA like domains, Fig. 6.

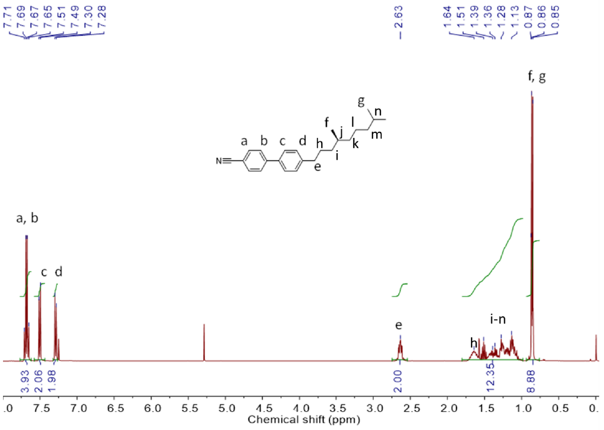


Figure 1. ^1H NMR spectrum of DM9CB in $CDCl_3$.

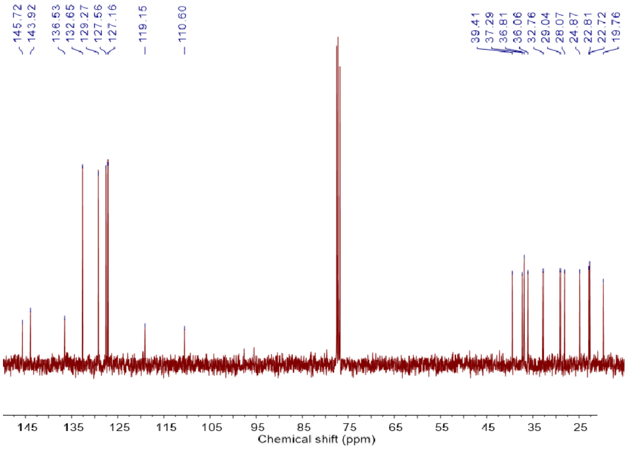


Figure 2. ^{13}C NMR spectrum of DM9CB in $CDCl_3$.

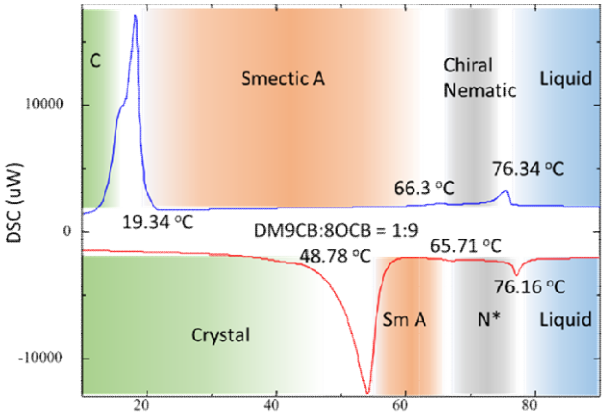


Figure 3. Differential scanning calorimetry (DSC) result of the blend liquid crystal (5 wt% of DM9CB in 8OCB).

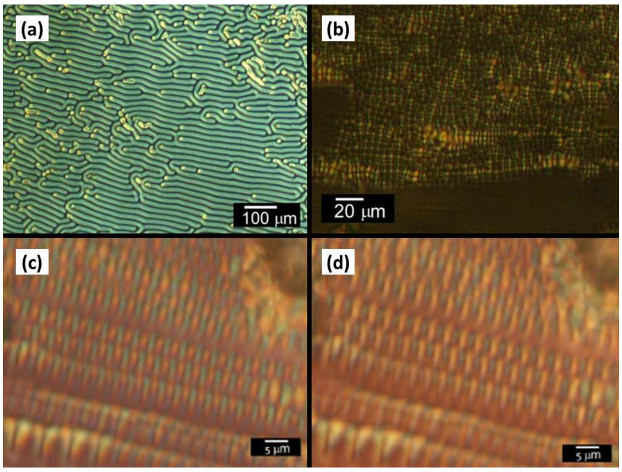


Figure 4. Polarizing optical microscopy (POM) images of 5wt% of DM9CB in 8OCB. (a) Cooling process at 70 °C. (b-d) Heating process at 55 °C. (c,d) POM images with insertion of gypsum first order red plate.

Figure 5. POM image of resultant polymer prepared in SmA liquid crystal.

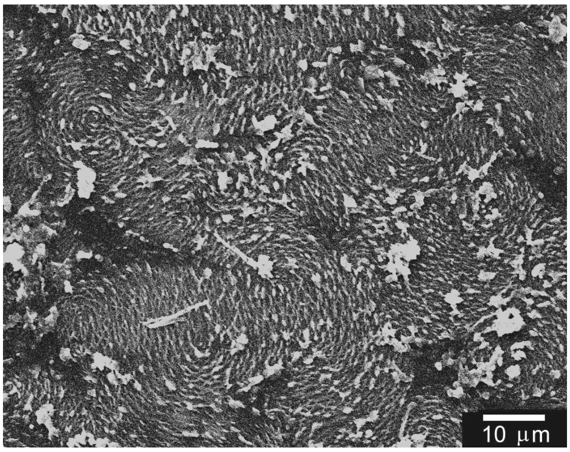


Figure 6. Scanning electron microscopy (SEM) image of resultant polymer prepared in SmA liquid crystal.

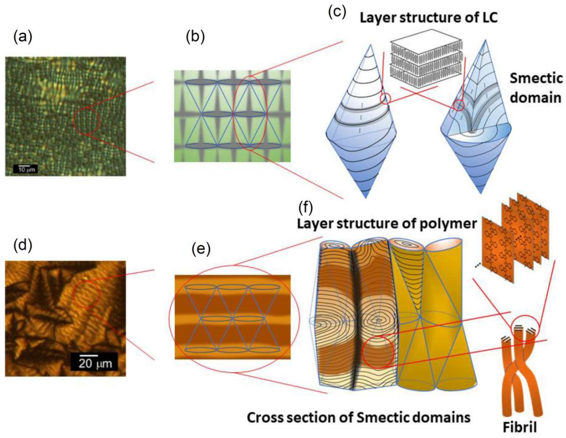


Figure 7. (a) POM image of the electrolyte LC, (b) possible domain structure of LC, (c) layer structure of LC-blend in smectic A phase [23]. (d) POM image of the polymer (polyEDOT) synthesized in the LC-blend, (e) possible domain structure of the polymer, (f) layer structure and fibril structure of the polymer.

Possible structure of PEDOT prepared in SmA LC-blend is shown in Fig. 7(e). Fig. 7(f) displays fibril structure consisting of layer structure of PEDOT as textile like aggregates. Plausible layer structure of the PEDOT prepare in the blend LC is indicated in Figs. 7(e,f). The stripes are attributed to the cross section of SmA domain. Polymerization may be terminated in the cross section due to the low conductivity between layer structures of SmA phase. No polymerization in frustrated chessboard-like texture could be carried out at the present stage. The blend method for preparation of SmA liquid crystals decreases viscosity of the liquid crystal electrolyte solution.

Decrease of viscosity of the liquid crystal electrolyte solution for electropolymerization by the LC blend technique is valid because mobility of ions from supporting electrolyte increases. This blend-LC electrolyte solution can be applied for monomer with low electro-activity to obtain good film form having SmA order.

Conclusions

(*S*)-4-Cyano-4'-(4,8-dimethylnonyl)biphenyl (DM9CB) was synthesized via Wittig reaction, and Miyaura-Suzuki coupling reaction. Chemical structure of this product was confirmed by ^{1}H and ^{13}C NMR. The LC-blend of DM9CB in matrix liquid crystal shows SmA and cholesteric phase. The POM observation revealeduniquegrid pattern texture of the LC-blend. Electrochemical polymerization in the LC-blend in SmA phase yielded striated fan-shaped texture. The resultant polymer has both characters of liquid crystal and polymer bundles. The blend system provides low viscosity and good ionic mobility of supporting salt. This condition is valid for electrochemical polymerization in smectic liquid crystal.

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