

Preparation of a Ferroelectric Liquid Crystal Electrolyte Solution

Tomonori Ito¹, Tomoaki Jo¹, Jiuchao Dong¹, Hitoshi Hayashi²,
Hiromasa Goto^{1,*}

¹Graduate School of Pure and Applied Sciences, University of Tsukuba,
Tsukuba, Ibaraki 305-8573, Japan

²DENSO CORPORATION, Aichi 448-8661, Japan

*E-mail address: gotoh@ims.tsukuba.ac.jp

ABSTRACT

A ferroelectric liquid crystal was synthesised. We attempted electrochemical polymerisation in ferroelectric liquid crystal.

Keywords: electrochemical polymerisation; ferroelectric liquid crystal

1. INTRODUCTION

Polymerisation is usually carried out in liquid solvents. Because the molecules do not have a position and an orientation order in liquid state, the polymer being synthesized in the isotropic solvent does not show a certain order. Liquid crystals (LC) have fluidity, which can be used as a solvent in the polymerisation reaction.

The polymers obtained in LC have an ordered structure because of occurrences of transcription of ordered structure from LC. We achieved synthesis of conjugated polymers having molecular order of chiral nematic liquid crystal [1]. We attempt electrochemical polymerisation in a chiral nematic C (SmC*) as a ferroelectric LC. SmC* can provide chiral environment with highly ordered helical structure. In the present study, preparation of SmC*-LC for chiral electrolyte solution is carried out.

2. EXPERIMENT

2. 1. Synthesis

(S)-1-Methylheptyl 4-hydroxybiphenyl-4'-carboxylate

To a solution of triphenyl phosphine (1.794 g, 5.5 mmol), and 4-(4-hydroxyphenyl)benzoic acid (1.07 g, 5 mmol), (R)-2-octanol (0.716 g, 5.5 mmol) in THF (15 mL) was added diisopropyl azodicarboxylate (40% in toluene) (2.89 mL, 5.5 mmol) dropwise at 0 °C. After stirring for 24 h, the solvent was evaporated. The crude products were purified by silica gel column chromatography (chloroform/ethyl acetate = 9/1) to afford yellow solid (0.443 g, 1.36 mmol). Yield = 27%

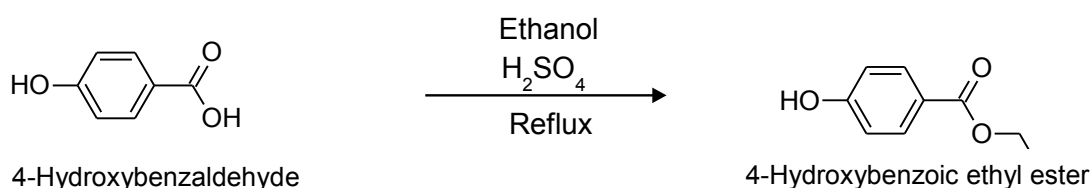


4-(4-hydroxyphenyl)benzoic acid

(S)-1-Methylheptyl
4-hydroxybiphenyl-4'-carboxylate

Scheme 1. Synthetic route for (S)-1-Methylheptyl-4-hydroxybiphenyl-4'-carboxylate.
4-Hydroxybenzoic ethyl ester.

To a solution of 4-hydroxybenzaldehyde (1.38 g, 10 mmol) and ethanol (0.58 mL, 10 mmol) was added H_2SO_4 (1 mL) dropwise. After reflux for 24 h, the solvent was evaporated, The mixture was extracted with chloroform and water, followed by drying with MgSO_4 . Then, the crude products were purified by silica gel column chromatography (chloroform/ethyl acetate = 8/2) to afford yellow solid (0.42 g, 1.29 mmol). Yield = 26%.

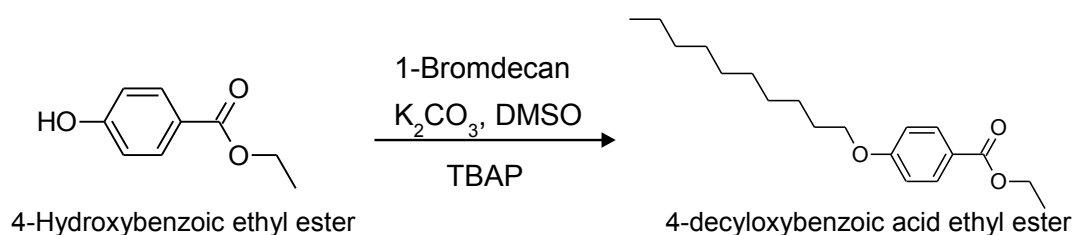


4-Hydroxybenzaldehyde

4-Hydroxybenzoic ethyl ester

Scheme 2. Synthetic route for 4-hydroxybenzoic ethyl ester.

4-Decyloxybenzoic acid ethyl ester



4-Hydroxybenzoic ethyl ester

4-decyloxybenzoic acid ethyl ester

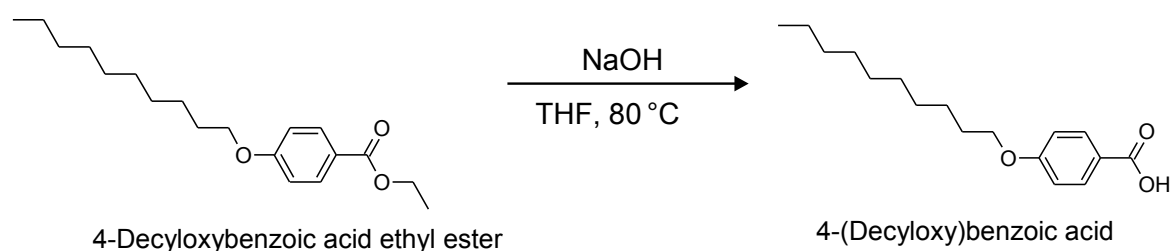
Scheme 3. Synthetic route of 4-decyloxybenzoic acid ethyl ester.

In an nitrogen flushed two neck round-bottom flask, a mixture of 4-hydroxybenzoic ethyl ester (0.9648 g, 5 mmol) in *N,N*-dimethylsulfoxide (DMSO, 1.5 mL), potassium carbonate (K_2CO_3 , 0.268 g, 1.929 mmol) and tetrabutylammonium perchlorate (TBAP, 0.0069 g, 0.015 mmol) were added, then 1-bromodecan (0.32 mL, 1.2 mmol) was drop wise added at room temperature.

After stirring for 24 h. the solvent was evaporated, the mixture was extracted with chloroform and water, followed by drying with MgSO_4 . Then, the crude products were purified by silica gel column chromatography (hexane/ethyl acetate = 4/1) to afford yellow liquid (0.479 g, 0.961 mmol). Yield = 62%.

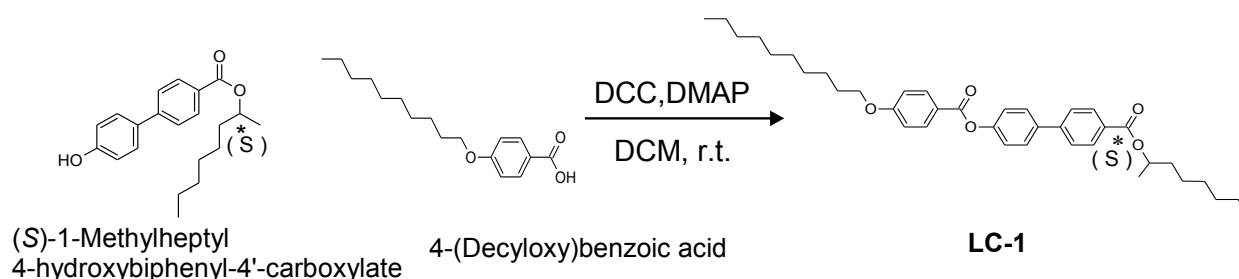
4-(Decyloxy)benzoic acid

4-Decyloxybenzoic acid ethyl ester (0.479 g, 0.961 mmol) was dissolved in 2.5 mL THF, and hydrolyzed by NaOH/water solution (2.5 mL) at 80 °C for 36 h. After the hydrolysis, the mixture was extracted with chloroform and water, followed by drying with MgSO_4 . Then purified by recrystallisation from hexane to afford white solid (0.58 g, 0.209 mmol). Yield = 22%.



Scheme 4. Synthetic route of 4-(decyloxy)benzoic acid.

(S)-1-Methylheptyl-4'-(4-n-decyloxybenzoyloxy)biphenyl-4-carboxylate (LC-1)



Scheme 5. Synthetic route of LC-1.

In an argon atmosphere, two neck round-bottom flask, a mixture of (S)-1-methylheptyl-4-hydroxybiphenyl-4'-carboxylate (0.072 g, 0.22 mmol), DMAP (0.027 g, 0.22 mmol), 4-(decyloxy)benzoic acid (0.058 g, 0.21 mmol), DCC (0.047 g, 0.22 mmol) and DCM was stirred at room temperature for 20 h.

The solvent was evaporated, then purified by silica gel column chromatography (hexane/ethyl acetate = 1/4) to afford white solid (0.099 g, 0.016 mmol). Yield = 76%. ^1H NMR (400 Hz; CDCl_3 TMS): δ 0.794 - 0.853 (m, 7H), 1.183 - 1.496 (m, 30H), 1.719 - 1.779 (m, 3H), 3.964-3.996 (t, 2H), 5.080 - 5.111 (q, 2H), 6.897-6.926 (d, 2H), 7.214-7.236 (t, 2H), 7.568 - 7.607 (m, 4H), 8.019-8.0951 (q, 4H). ^1H NMR result shows in Figure 1.

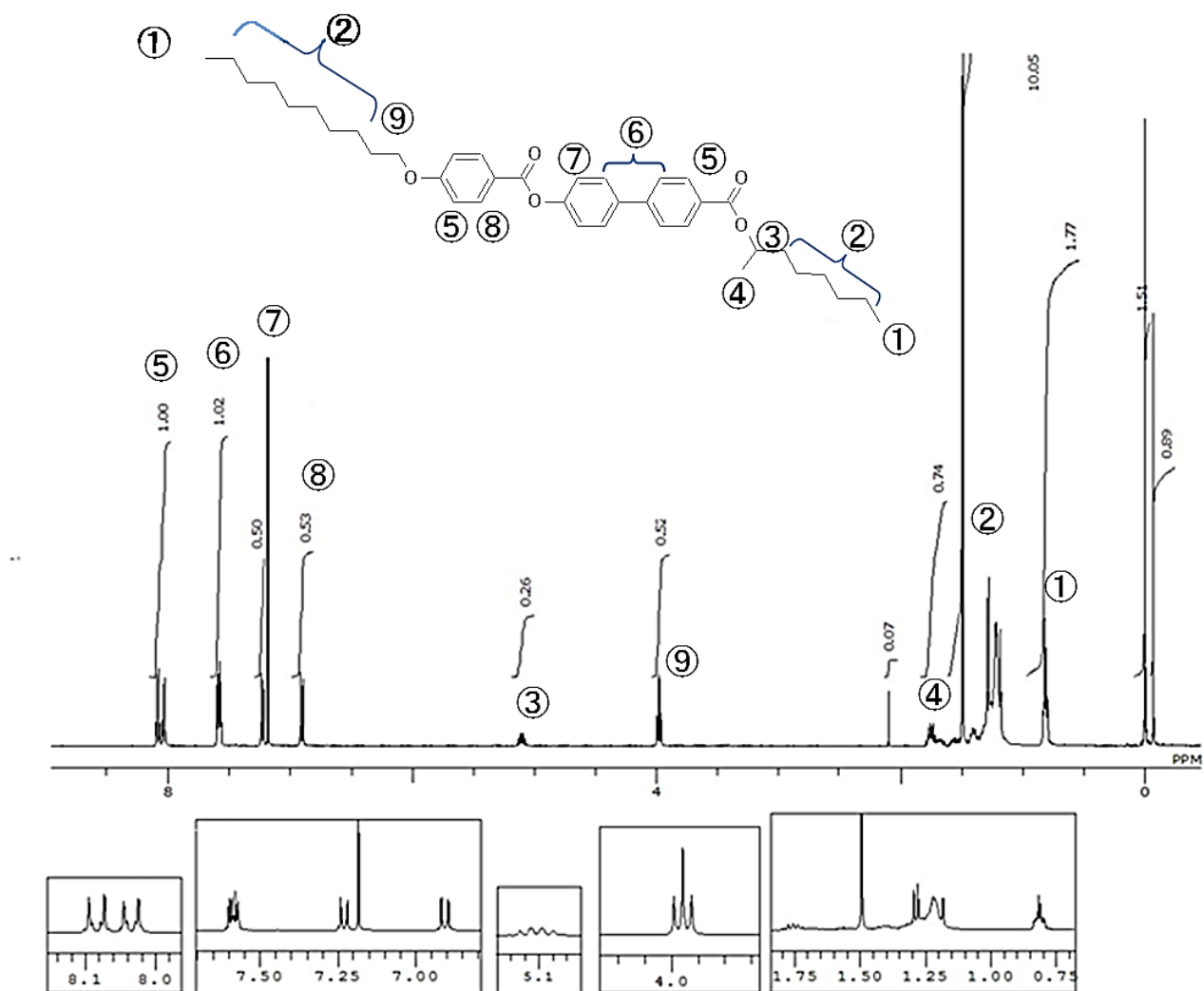


Figure 1. ^1H NMR of LC-1.

2. 2. Phase transition

Differential scanning calorimetry (DSC) measurement result is shown in Figure 2. Phase transition in 110 °C (isotropic*-smecticA* (SmA^*)) and 44 °C (SmC^* - SmC_A^*) transition were observed on cooling. A transition of SmC^* - SmC_A^* was not clearly observed due to second-order transition.

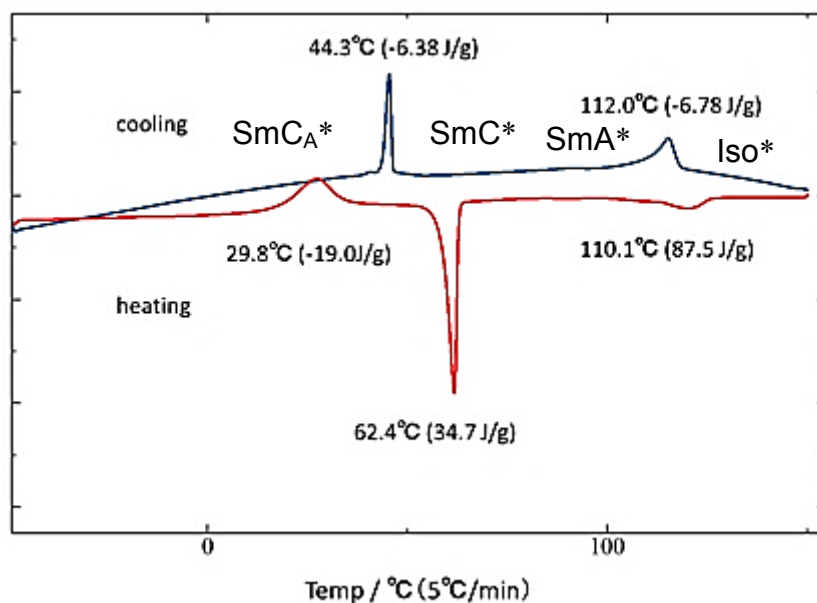


Figure 2. DSC curves of LC-1. Iso* = isotropic, SmA* = chiral smectic A phase, SmC* = chiral smectic C, SmC_A* = anti-ferroelectric phase of SmC*.

2. 3. Polarising optical microscopy observation

The results of polarising optical microscopy (POM) observation are shown in Figure 3-5. Figure 3 displays typical fan-shaped structure at 94 °C on cooling, indicating SmA* phase.

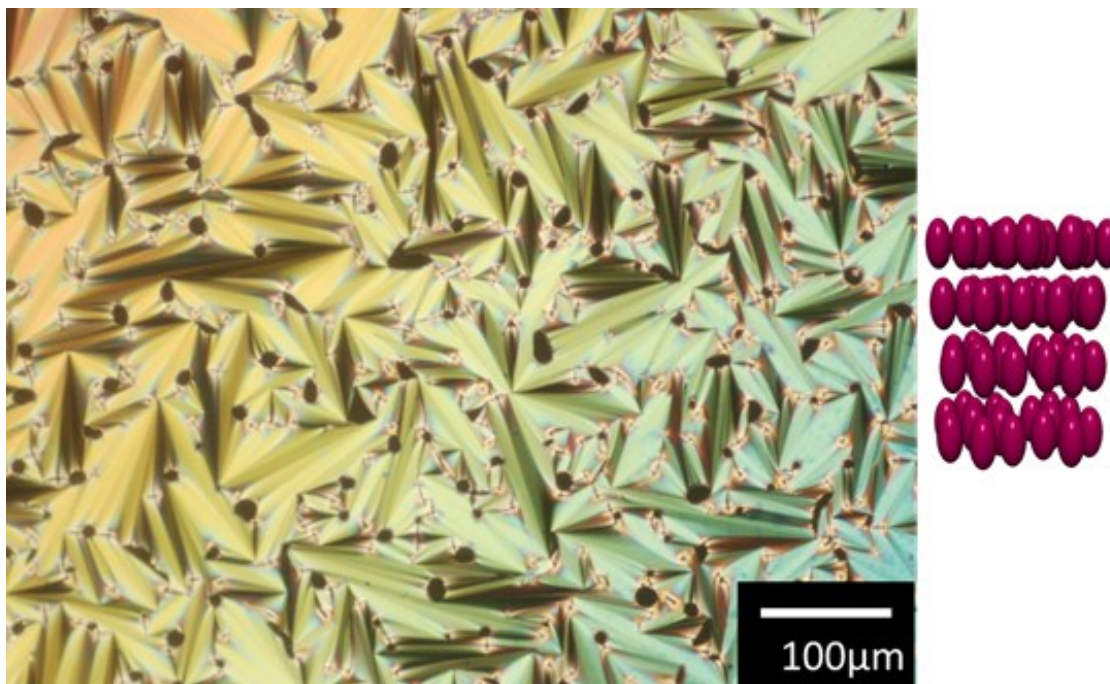


Figure 3. Polarising optical microscopy (POM) image of LC-1 at 94 °C on cooling.

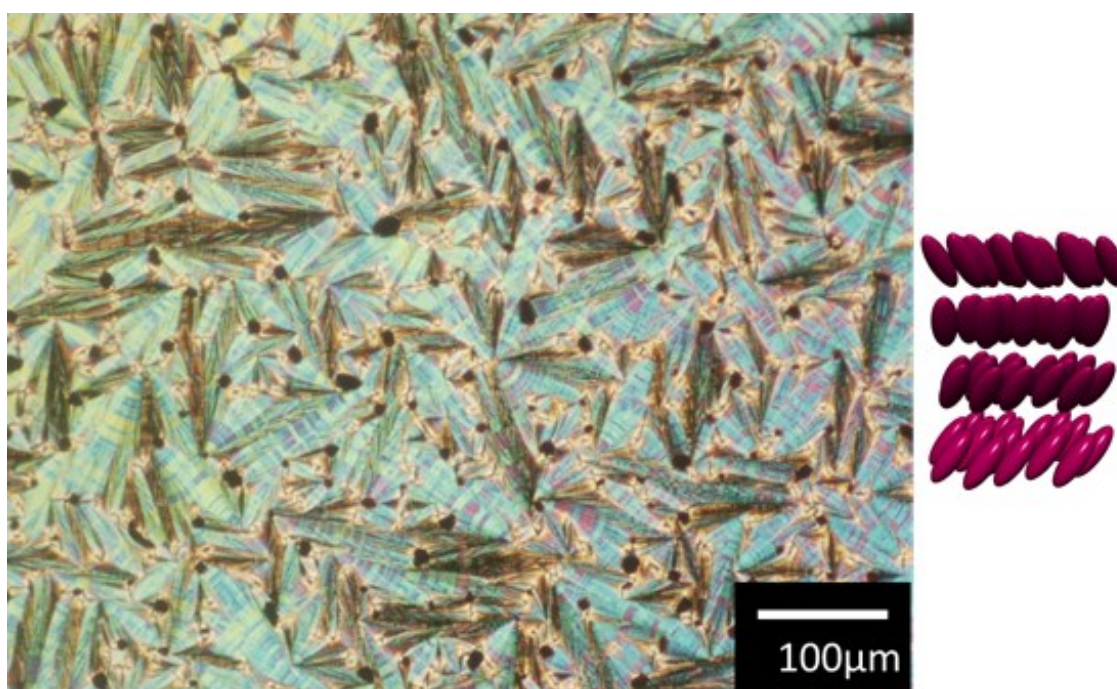


Figure 4. POM image of LC-1at 55 °C on cooling.

Figure 4 shows broken fan-shape structure in 55 °C on cooling, indicating SmC* phase. The wrinkle appeared at 55 °C, and the texture was changed to fan-shaped texture at 38.9 °C on cooling, indicating LC-1 shows SmC_A* phase.

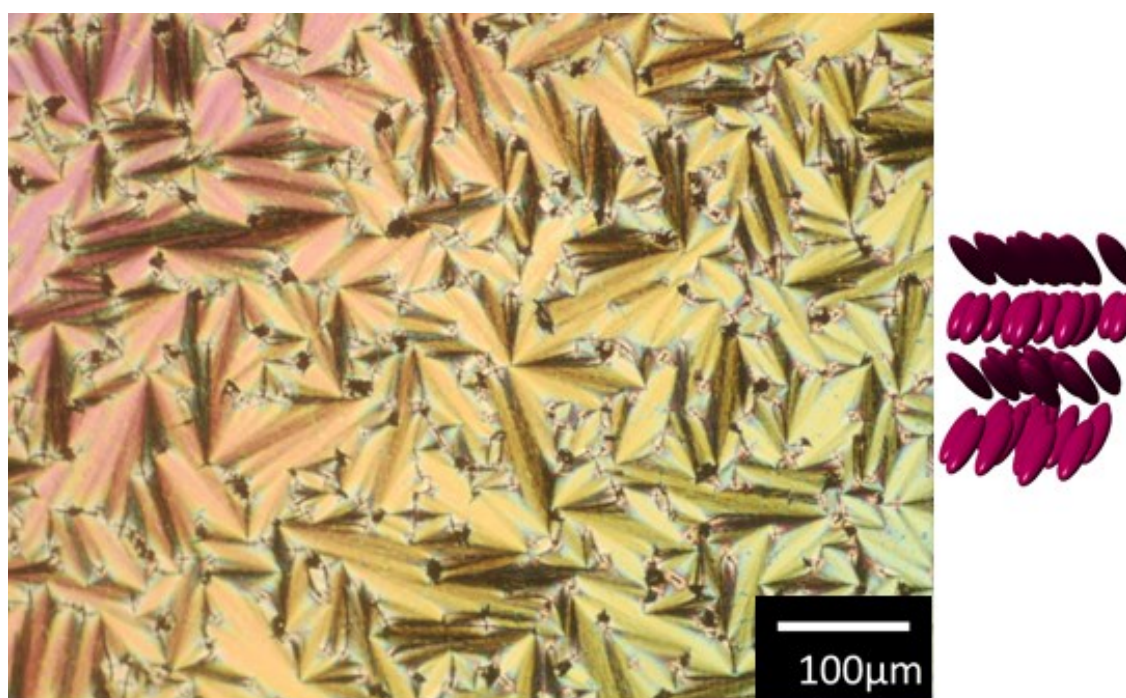
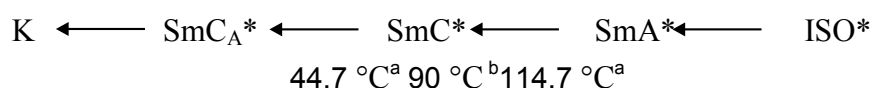


Figure 5. POM image of LC-1 at 38.9 °C on cooling.

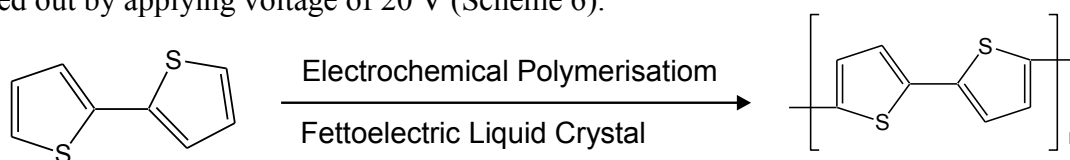
Phase sequence of LC-1 was determined by results from the DSC and observation of POM, as follows.



^a DSC observation, ^bPOM observation

2. 4. Polymerisation in SmC*

We prepared electrolyte solution consisting of LC-1, *n*-tetrabutyl ammonium perchlorate (TBAP), and bithiophene. The mixture was injected to indium-tin-oxide (ITO) coated glass sandwich cell with thin Teflon spacer. Electrochemical polymerization was then carried out by applying voltage of 20 V (Scheme 6).



Scheme 6. Polymerisation in liquid crystal.

We observed optical textures of the electrolyte solution during the electrochemical polymerisation by using POM. The results are shown in Figure 6. Color of the polymerisation cell changed periodically yellow-red- yellow in every one minute (Figure 6 A-C).

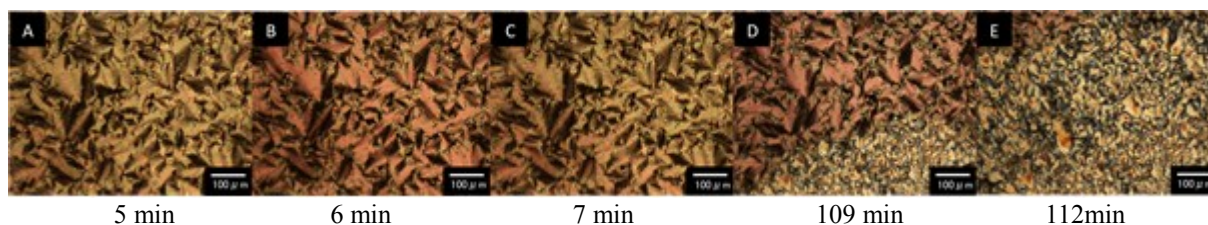


Figure 6. POM observation of the reaction mixture during electrochemical polymerisation.

3. CONCLUSIONS

A ferroelectric liquid crystal was synthesised. Subsequently, electrochemical polymerisation was carried out in the liquid crystal. Orientation of molecules did not change in the polymerisation cell during the electrochemical polymerisation. The ferroelectric liquid crystals form spontaneous polarisation with gold stone mode [2]. In the future work, electrical interaction of the monomer and the ferroelectric LC at the anode interface needs to be examined.

Acknowledgement

NMR and DSC measurements were carried out in Research Facility Centre for science and Technology University of Tsukuba.

References

- [1] H. Goto, *IOP Conf. Ser.: Mater. Sci. Eng.* 54 (2014) 012013.
- [2] Editorial committee of Liquid Crystal Handbook, *Liquid Crystal Handbook*, Maruzen, Tokyo, 2000.

(Received 30 December 2014; accepted 14 January 2015)