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Synthesis and Characterization of Mono-acryl Liquid crystalline Functional Monomer

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We newly synthesized a mono-acryl liquid crystalline monomer (mono-acryl RM257) and investigated the phase behavior and the liquid crystallinity of it. The temperature range of liquid crystalline phase was broadened compering to a conventional di-acryl monomer (RM257). This result suggests that the alkylation of acryl group of RM257 increases the liquid crystallinity because less steric hindered of alkyl group enhances the interaction i.e. van der Waals and π－π interaction.

Key words: *Liquid crystal, Liquid crystalline monomer, thermal analysis, optical texture*

1. Introduction

Liquid crystals (LCs) are typical self-organized materials with a high sensitivity to external fields such as an electric field, a magnetic field, a temperature change, a mechanical strain and so on.[1] They have played significantly important roles in developing flat panel displays, optical or photonic materials, as well as other functional materials.[1] The introduction of chirality into a LC has a tremendous impact in arrangement of LC molecules. A nematic (N) phase transforms to a chiral N (N*) phase with a helical supramolecular structure by doping with a chiral molecule.[2] Blue phases are also a kind of a chiral LC phase existing between a N* phase and an isotropic liquid.[3] Three different blue phases are distinguished and denoted as BP III (nearly amorphous), BP II (simple cubic) and BP I (body center cubic), which corresponding to the sequence cooling from an isotropic phase. BPs show unique optical characteristics owing to their nature of structure, such as Bragg reflectance, non-birefringence and large electro-optical Kerr effect.[4] However, their extremely small temperature range (typically less than a few °C) was a barrier of practical use of BPs. Our previous studies have demonstrated in expanding the temperature range of BP I by more than 60 °C via *in situ* photo-polymerization of approximate amount of monomers in BP state.[5] The polymer-stabilized BP (PSBP) is expected to be applied to next-generation LC display materials because they exhibit sub-millisecond electro-optic response. Nevertheless, PSBP requires high operating voltage because of the short coherence length due to the lattice structure on a few 100 nm, the highly twisted molecular alignment of the LC and the strong interaction between the polymer and LC molecules. The investigation of the interaction between the polymer and LCs plays a key role in lowering the operating voltage of the PSBP. Preparing the substrate surface coated with a polymer allows us to evaluate the interaction between the polymer and LC molecules. The PSBP precursor mixture usually consists of host NLC, chiral molecule, mono-acryl monomer, di-acryl cross linker (RM257) and photo initiator.[5,6] Therefore, we can prepare the polymer-coated substrate surface by using the monomers as mentioned above. However, it is difficult to produce the smooth surface using cross linker monomer RM257 because the polymer prepared with RM257 is rheologically rigid owing to their highly cross-linked network structure.

The aim of this study is to provide a material which is feasible for conducting a model experiment system to evaluate the

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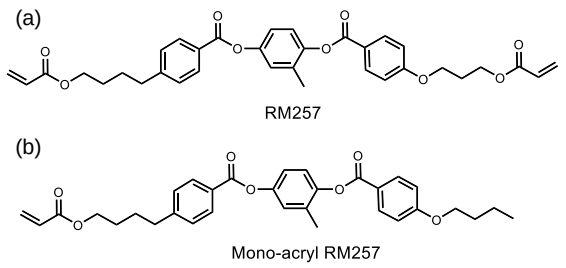

Fig. 1 Chemical structure of (a) RM257 and (b) mono-acryl RM257

intermolecular interaction between the polymer and LC molecules. In such experiment system, a monomer having simultaneously both of a targeted molecular core structure and a polymerizable mono-functional group is necessary. Therefore, we newly synthesized the mono-acryl RM257 monomer (Fig. 1b) and characterized the liquid crystallinity of the synthesized monomer by differential scanning calorimetry (DSC) measurement and by polarized optical microscopy (POM) observation.

2. Experimental procedure

2.1 General procedure

All chemical reagents were obtained from commercial suppliers and were used without further purification. Silica gel column chromatography was performed using silica gel 60N from Wako Pure Chemical Industries (irregular, 63–212 μm). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer. Tetramethylsilane was used as an internal standard (δ 0.00) for ^{1}H and $CHCl_3$ (δ 77.06) for ^{13}C. The coupling constants, *J*, are reported in hertz (Hz). Mass spectra were conducted at Kyushu University.

The phase behavior and the mesomorphic properties of synthesized monomer were characterized by DSC (DSC 1 STAR System, Mettler Toledo Inc.) and by the observation of optical textures using a polarizing optical microscope, POM (ECLIPSE E600 POL, Nikon).

2.2 Synthesis

Fig. 2 shows synthesis route of mono-acryl RM257.

2.2.1 Synthesis of compound 2

Compound **1** (1.50 g, 12.0 mmol) and Et_3N (2.51 mL, 18.0 mmol) were dissolved in THF (10 mL) at 0 ºC under N_2. Then, ethyl chloroformate (1.37 mL) was added dropwise over 10 min to a solution and stirred at 0 ºC for 2 hours. The reaction mixture was filtered. The $NaBH_4$ (1.12g, 48.0 mmol) solution (15 mL)

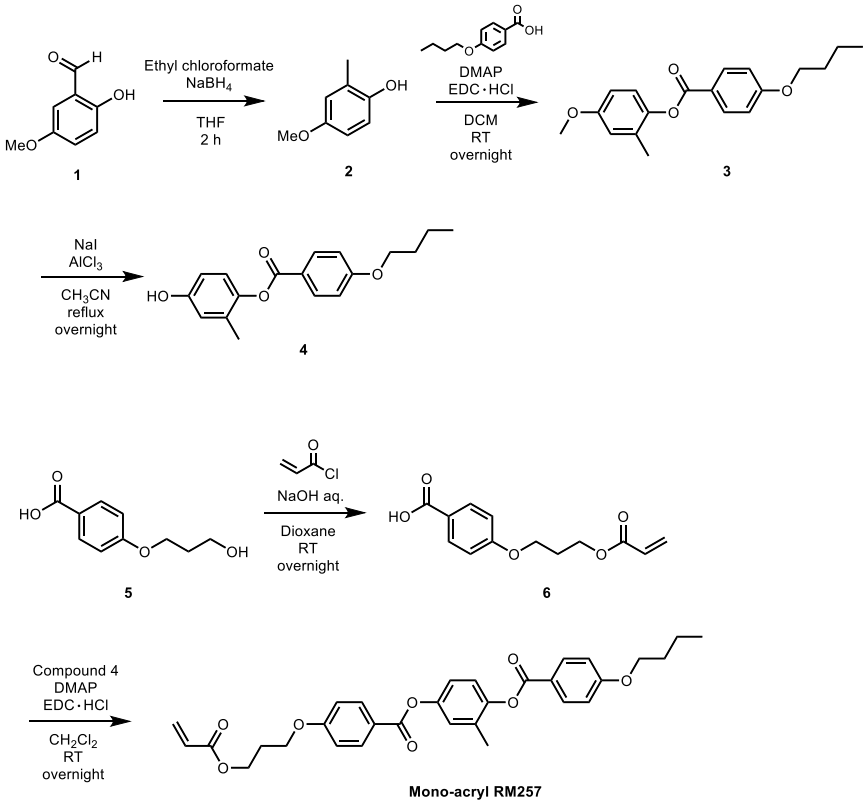

Fig. 2 Synthesis route of mono-acryl RM257

was added slowly over 45 min to a filtrate at 0 ºC and then resulting mixture was stirred at RT for 90 min. After stirring, distilled water and 2M HCl was added to adjust the pH < 2. The organic layer was extracted with ethyl acetate and dried over Na_2SO_4, filtrate, and evaporation to give a crude product, which was purified by column chromatography (CH_2Cl_2/hexane = 1/1) to yield compound **2** (994 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$); δ 6.70 (d, *J* = 8.7 Hz, 2H), 6.63 (m, 1H), 4.33 (s, 1H), 3.75 (s, 3H), 2.24 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$); δ 116.79, 115.71, 112.04, 55.92, 16.27.

2.2.2 Synthesis of compound 3

2-hydroxy-5-methoxytoluene **2** (801 mg, 5.79 mmol), 4-butoxy benzoic acid (1.35 g, 6.95 mmol), EDC·HCl (1.67 g, 8.69 mmol), and DMAP (71.7 mg, 0.58mmol) were dissolved in CH_2Cl_2 (30 mL) at RT under N_2. After stirring for 20 hours, reaction mixture was washed with distilled water (30 mL), sat. $NaHCO_3$ aq. (30 mL), and brine (30 mL). The collected organic layer was dried over Na2SO4, filtrate, and evaporation to give a crude product, which was purified by column chromatography (CH_2Cl_2) to yield compound **3** (1.51 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$); δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.78 (m, 2H), 4.05 (t, *J* = 6.3 Hz, 2H), 3.81 (s, 3H), 2.19 (s, 3H), 1.78-1.85 (m, 2H), 1.47-1.55 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$); δ 165.04, 163.52, 157.24, 143.25, 132.25, 131.43, 122.73, 121.63, 116.28, 114.33, 111.89, 68.04, 55.58, 31.18, 19.24, 16.58, 13.86.

2.2.3 Synthesis of compound 4

A suspension of aluminum chloride (6.38 g, 47.7 mmol) and NaI (7.15 g, 47.7 mmol) in CH_3CN (10 mL) was stirred at 0 ºC under N_2 and compound **3** in CH_3CN was added dropwise to a stirred mixture. The reaction mixture was refluxed for 15 hours. After cooling to RT, cold water was added to a resulting mixture and extracted with CH_2Cl_2. The separated organic layer was washed with sat. $Na_2S_2O_3$ aq. (30 mL) and brine (30 mL). The collected organic layer was dried over Na_2SO_4, filtrate, and evaporation to give a crude product. The spot of row material was removed by column chromatography (CH_2Cl_2) and purified by reprecipitation from ethyl acetate to yield compound **4** (524 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$); δ 8.10 (m, 2H), 6.93-7.00 (m, 3H), 6.67-6.74 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.18 (s, 2H), 1.82 (m, 2H), 1.48-1.58 (m, 2H), 1.00 (td, *J* = 7.5, 3.5 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$); δ 163.64, 153.42, 143.12, 132.38, 132.32, 131.55, 122.81, 121.50, 117.70, 114.39, 114.26, 113.64, 68.08, 68.03, 31.17, 19.23, 16.35, 13.84.

2.2.4 Synthesis of compound 6

4-(3-hydroxybutoxy)benzoic acid (0.66 g, 3.36 mmol) and NaOH aq. (0.36 g, 9 mmol) 6 mL was stirred at 0 ºC and acryloyl chloride (0.54 mL, 6.68 mmol) in dioxane (10 mL) was added dropwise over 10 min. After stirring 17 hours at RT, reaction mixture was evaporated and warm water was added before filtration. The residue was collected and purified by column chromatography (ethyl acetate/toluene = 1/1) to yield compound **6**. ^{1}H NMR (400 MHz, $CDCl_3$); δ 8.05 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 9.7 Hz, 2H), 6.42 (d, *J* = 17.4 Hz, 1H), 6.13 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.85 (d, *J* = 10.6 Hz, 1H), 4.77 (s, 1H), 4.38 (t, *J* = 6.3 Hz, 2H), 4.14 (t, *J* = 5.8 Hz, 2H), 2.17-2.23 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$); δ 163.22, 132.39, 131.03, 128.32, 114.25, 64.68, 61.22, 30.66, 28.58.

2.2.5 Synthesis of compound mono-acryl RM257

Compound **4** (293 mg, 0.977 mmol), compound **6** (232 mg, 0.925 mmol), EDC·HCl (274 mg, 1.43 mmol), and DMAP (11.3 mg, 0.105 mmol) were dissolved in dry CH_2Cl_2 and stirred at RT for 16 hours under N_2. The resulting mixture was washed with sat. $NaHCO_3$ aq. (30 mL), distilled water (30 mL) and brine (30 mL). The collected organic layer was dried over Na_2SO_4, filtrate, and evaporation to give a crude product, which was purified by column chromatography (CH_2Cl_2) to yield target compound (**mono-acryl RM257**). ^{1}H NMR (400 MHz, $CDCl_3$); δ 8.15 (q, *J* = 4.8 Hz, 4H), 7.07-7.19 (m, 3H), 6.98 (dd, *J* = 8.7, 1.9 Hz, 4H), 6.43 (dd, *J* = 17.4, 1.9 Hz, 1H), 6.14 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.84-5.87 (m, 1H), 4.39 (t, *J* = 5.8 Hz, 2H), 4.17 (t, *J* = 6.3 Hz, 2H), 4.06 (t, *J* = 6.8 Hz, 2H), 2.19-2.28 (m, 5H), 1.78-1.85 (m, 2H), 1.48-1.59 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 166.13, 164.87, 164.57, 163.65, 163.12, 148.42, 147.10, 132.33, 132.32, 131.81, 130.97, 128.33, 124.12, 122.95, 122.00, 121.39, 120.04, 114.40, 114.33, 68.06, 64.72, 61.20, 31.17, 28.58, 19.23, 16.46, 13.84. High resolution mass spectrum; HRMS (EI) m/z cald for $C_{31}H_{32}O_8$ (M+·), 532.2097; found, 532.2096.

3. Results and discussion

The mono-acryl RM257 was chemically synthesized through 5 steps (Fig. 2). The methylation of aldehyde of compound **1** using ethyl chloroformate resulted compound **2**. Dehydration condensation between compound **2** and 4-butoxy benzoic acid gave compound **3**. Next, we conducted the demethylation of compound **3**. It is known that BBr_3 is a good reagent for demethylation reaction. However, the compound was broken when BBr_3 was used for demethylation reaction in this study. It is considered that hydrogen bromine was formed by adding water at the quench of the reaction and hydrolysis of the material occurred. Therefore, demethylation reaction of compound **3** was conducted via mild condition using aluminum chloride and sodium iodide in CH_3CN. The Schotten-Baumann reaction of compound **5** resulted compound **6**. Finally, we successfully obtained mono-acryl RM257 via dehydration condensation between compound **4** and **6**. The total yield was 3.0%.

The liquid crystallinity of mono-acryl RM257 was characterized by DSC measurement and POM observation. As a reference experiment, DCS measurement and POM observation of the conventional cross linker monomer RM257 was conducted. The DSC charts were shown in Figs. 3a and b. The DSC chart of RM257 exhibits two major endothermic peaks at 71.7 and 126.2 ºC and weak minor peak at around 42 ºC. The weak broad peak at 42 ºC was attributed to be a non-equilibrium melting of crystal. The optical texture of RM257 were displayed in Fig. 3c. The crystalline, nematic, and isotropic phase can be identified at 40.1, 105, and 129 ºC, respectively. This observation suggests that the peak at 71.7 ºC corresponds to the crystal－nematic transition, and the highest peak at 126.2 ºC is due to nematic－isotropic transition. The supercooling was observed in the measurement temperature range. In contrast, the optical textures of mono-acryl RM257, crystalline, nematic, and isotropic phase can be identified at 47.3, 80.0, and 165 ºC, respectively. This observation suggests that mono-acryl RM257 exhibits the nematic phase between 72.0 and 153.0 ºC and supercooling of the nematic phase was observed below 152.7 ºC in the measurement temperature range. The crystal － nematic transition temperature is mostly the same between RM257 and mono-acryl RM257. However, interestingly, the temperature range of nematic phase of mono-acryl RM257 was significantly larger than that of RM257. This behavior could be due to alkylation of one side of acryl group of RM257. This implies that lack of the symmetry of the molecular structure and less of the steric hindered of alkyl group increase molecular interaction i.e. van der Waals and π－π interaction between alkyl chains and aromatic moieties, respectively.

4. Conclusion

In conclusion, we have newly synthesized a liquid crystalline mono-acryl RM257. The temperature range of nematic phase in mono-acryl RM257 is broadened comparing to the conventional cross linker RM257. We believe that the mono-acryl RM257 will be applied to a monomer for preparation of a smooth substrate surface modified with a

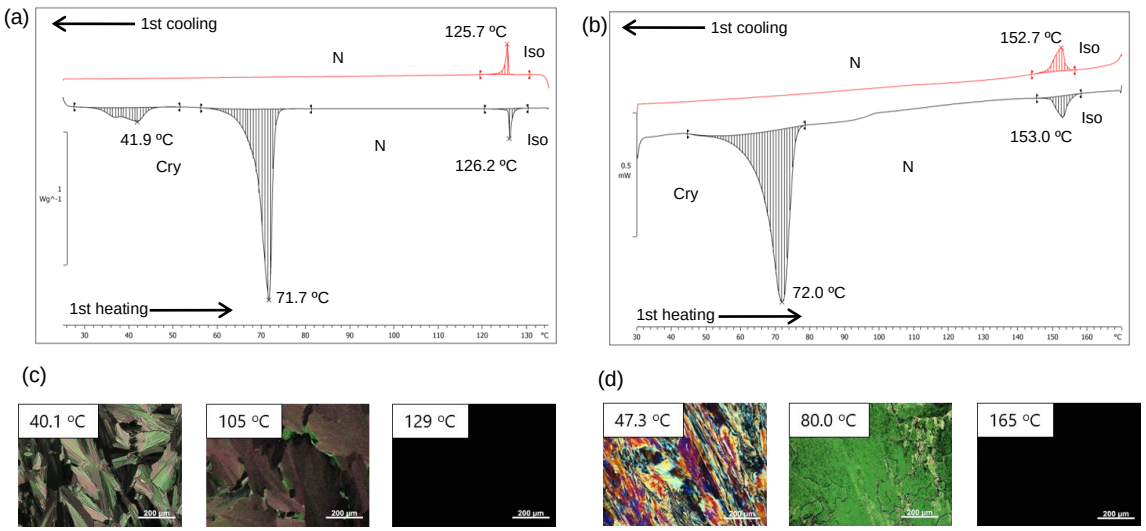

Fig. 3 DSC chart of (a) RM257 and (b) mono-acryl RM257 and POM images of (c) RM257 and (d) mono-acryl RM257

target polymer feasible for investigating the interaction between the polymer and LC molecules.

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