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Syntheses and Optical Properties of Cholesteric Liquid Crystal Polymers Utilizing *p*-Phenylene Bis-(*p*-(3-acryloxy-2-methylpropyloxy)benzoate

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We synthesized chiral choleseric liquid crystalline monomer *p*-phenylene bis-(*p*-3-acryloxy-2(S)-methylpropoxy) benzoate (**1**) and achiral nematic liquid crystalline monomer, *p*-phenylene *p*-acryloxy-6-hexyloxy-*p*-octyloxybenzoate (**2**) for the construction of cholesteric polymer network with a pitch gradient. In this research we attempted to synthesize cholesteric polymer film which have a wide reflection bandwidth in the region of visible wavelength with the synthesized chiral cholesteric monomer **1** and nematic monomer **2** under various photopolymerization conditions. We succeeded to construct cholesteric polymer film network with a pitch gradient covering more than 200 nm bandwidth in the visible wavelength by diffusion controlled photostructuring method.

key words: cholesteric liquid crystal polymer, *p*-phenylene bis-(*p*-(3-acryloxy-2-methyl propyloxy)benzoate, photopolymerization, cholesteric pitch gradient, diffusion controlled method.

INTRODUCTION

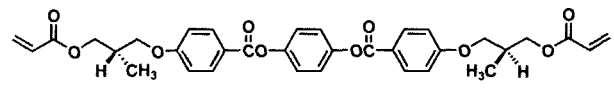
Chiral mesogene which contains the element for a chirality exhibits cholesteric phase in its liquid crystalline (LC) mesophase. The cholesteric phase has ability to selectively reflect circular light [1]. The wavelength of the circular polarized light with the maximum reflection (λ_R) is proportional to the pitch (p) of the cholesteric helix and the average refractive index (n) of cholesteric phase [2]. Cholestric phase can also be obtained by adding chiral dopants to a nematic phase where the pitch of the cholesteric helix (p) is inversely proportional to the concentration of the chiral dopant and the helical twisting power.

The stabilization of the cholesteric phase by dispersing LC mesogene in a polymer matrix [3] or by covalently linking the mesogenes in side chain LC polymer [4,5] leads to cholesteric LC with higher stability against shock and cell deformation. The stabilized cholesteric LC's have utility for optical storage [6] or electro-optical device applications [7].

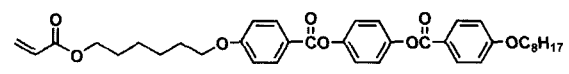
Recently Stohr [8], Broer [9,10], and Katsis [11] demonstrated successful fabrications of gradient-pitch cholesteric films by utilizing photopolymerization of mixture of a nematic acrylate and a chiral acrylate. The gradient-pitch over the cross-section of film is induced by photo-induced diffusion. The driving force is a UV intensity gradient over the film thickness in combination with a difference in reactivity between a chiral monomer and a nematic monomer. The UV-intensity gradient can be also achieved by doping a small amount of dye which absorbs in the same region as the photoinitiator. Diffusion controlled photostructuring during polymerization of a chiral-nematic monomers mixture gives rise to the formation of cholesteric networks which have the helical pitch gradient over the cross-section of the film. The cholesteric networks have ability to selectively reflect a wide bandwidth of circular polarized light which may expands over the whole visible wavelength.

The selectively cholesteric polymer network with a pitch gradient can be used as a color filter in reflective display [12] and projection systems [13] and a reflective polarizer [9].

In our initial effort to examine the possibility to construct a cholesteric polymer network with a pitch gradient which may cover over the range of visible light wavelength, we



chiral cholesteric LC monomer (1)



achiral nematic LC monomer (2)

Figure 1. Chemical structure of chiral cholesteric diacrylate (**1**) and nematic monoacrylate (**2**) monomers

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fabricated cholesteric polymer networks with mixture of a chiral cholesteric LC monomer, *p*-phenylene bis-(*p*-(3-acryloxy-2(S)-methylpropyloxy)benzoate (**1**) and a nematic LC mesogen monoacrylate, *p*-phenylene *p*-acryloxy-6-hexyloxy-*p*-octyloxybenzoate (**2**) in various ratios with different UV irradiation time and curing conditions.

The optical behavior of the synthesized cholesteric polymers was examined. The results of this effort will be reported in this paper.

MATERIALS AND METHODS

General Procedures

^{1}H nuclear magnetic resonance (NMR) and spectra were recorded using 200 MHz spectrometers and chemical shifts are reported in parts per million downfield from tetramethylsilane employed as an internal standard; abbreviations used are s (singlet), d (doublet), t (triplet), br (broad) and m (multiplet). Transmission spectra were recorded using UV-VIS-NIR spectrometer.

Synthesis of achiral nematic monomer

Synthesis of Octyl methanesulfonate (**4**)

To a solution of octanol **3** (9.29 mL, 7.68 mmol) and triethylamine (1.06 mL, 7.68 mmol) in 100mL of acetonitrille was added methanesulfonyl chloride (0.59 mL, 7.68 mmol) dropwise at 0°C. The reaction mixture was stirred for 2h at room temperature. The mixture was extracted with $CHCl_3$ solution was washed with water, dried and concentrated *in vacuo* to give 1.46g (91%) of **4**. ^{1}H-NMR($CDCl_3$) δ 0.80 (t, 3H, J=6Hz, $C\underline{H}_3(CH_2)_7OMs$), 1.20-1.51 (m, 10H, $CH_3(C\underline{H}_2)_5CH_2CH_2OMs$), 160-1.78 (m, 2H, $CH_3(CH_2)_5C\underline{H}_2CH_2OMs$), 2.93 (s, 3H, $SO_2C\underline{H}_3$), 4.14 (t, 2H, J=6.6Hz, $C\underline{H}_2OMs$), ^{13}C-NMR($CDCl_3$) 13.8, 22.4, 25.6, 28.7, 29.2, 31.6, 32.6, 37.0 and 70.2 ($SO_2\underline{C}H_3$)

Synthesis of Ethyl 4-octyloxybenzoate (**6**)

To a solution of sodium hydride (0.23 g, 5.76 mmol) in DMF (30mL) was added ethyl 4-hydroxybenzoate **5** (0.96 g, 5.76 mmol) in DMF (10mL). And then octyl methanesulfonate **4** (1g, 4.90 mmol) was added and the reaction mixture was stirred for 8h at 80°C. After removal of DMF *in vacuo*, the residue was dissolved in CH_2Cl_2 and filtered. The filtered solution was subjected to column chromatography (ethyl acetate: methylene chloride : hexane = 1: 1: 20) to give 1.31g (82%) of **6**. ^{1}H-NMR($CDCl_3$) 0.87 (t, 3H, J=6Hz, $C\underline{H}_3$), 1.33-1.56 (m, 10H, $CH_3(C\underline{H}_2)_5CH_2CH_2O$), 170-1.82 (m, 2H, $CH_3(CH_2)_5C\underline{H}_2CH_2O$), 3.96 (t, 2H, J=3Hz, $C\underline{H}_2O$), 4.33 (q, 2H, J=3Hz, $CO_2C\underline{H}_2CH_3$), 6.88 (d, 2H, J=9Hz, aromatic), 7.97 (d, 2H, J=9Hz, aromatic) : ^{13}C-NMR($CDCl_3$) 14.0 ($CO_2CH_2\underline{C}H_3$), 14.3 (CH_3), 22.6, 26.0, 29.1, 29.2, 29.3, 31.8 (CH_2), 60.5 ($CO_2\underline{C}H_2CH_3$), 68.1 (CH_2), 113.9, 122.6, 131.4, 162.8 (aromatic) and 166.4 ($\underline{C}O_2CH_2CH_3$)

Synthesis of 4-Octyloxybenzoic acid (**7**)

To a solution of **6** (1 g, 3.59 mmol) in methanol was added 2.24M KOH solution (6 mL). The reaction mixture was stirred for 3h. After removal of methanol, add 20mL of water and acidified with conc. HCl. The white precipitate of **7** was filtered off and washed with water. Recrystallization from ethyl acetate gave 0.76g (85%) of white crystal **7**. mp 87-89 °C ^{1}H-NMR($CDCl_3$) 0.87 (t, 3H, J=6Hz, $C\underline{H}_3$), 1.25-1.73 (m, 10H, $CH_3(C\underline{H}_2)_5CH_2CH_2O$), 1.77-1.82 (m, 2H, $CH_3(CH_2)_5C\underline{H}_2CH_2O$), 4.02 (t, 2H, J=6.6Hz, CH_2O), 6.92 (d, 2H, J= 9.8Hz, aromatic), 8.05 (d, 2H, J=9.8Hz, aromatic) : ^{13}C-NMR($CDCl_3$) 14.1 (CH_3), 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 68.3 (CH_2), 114.2, 121.4, 132.3, 163.7 (aromatic), 172.1 (COOH)

Synthesis of 4-Hydroxyphenyl 4-octyloxybenzoate (**8**)

To a solution of **7** (1.77 g, 7 mmol) in benzene was added thionyl chloride (15.5 mL, 212 mmol). The mixture was refluxed at 80°C for 8h. The solvent and excess $SOCl_2$ were removed by evaporation under reduced pressure, and then 1,4-hydroquinone (5.5 g, 49 mmol) and triethylamine (0.79 mL, 7 mmol) and 30mL of THF were added and stirred for 3h. After removal of THF, the reaction mixture was poured into excess water and extracted with methylene chloride. The combined organic layers were washed several times further with water, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed by evaporation under reduced pressure. The crude product was purified by column chromatography (ethyl acetate : hexane = 1: 4) to give 1.30 g (54%) of **8**. mp 96-97°C ^{1}H-NMR($CDCl_3$) 0.85-1.79 (m, 14H, alkyl chain), 4.04 (t, 2H, -CH_2O-), 6.85 (d, 2H, aromatic), 6.95 (d, 2H, aromatic), 7.07 (d, 2H, aromatic), 8.10 (d, 2H, aromatic)

Synthesis of 4-(6-Hydroxyhexyloxy)benzoic acid (**11**)

To a solution of 4-hydroxybenzoic acid **10** (3 g, 22 mmol) and KOH (2.92 g, 52 mmol) in ethanol was added 6-bromo-1-hexanol **9** (3.98 g, 22 mmol) and the reaction mixture was stirred for 12h. After removal of ethanol, add 50mL of water and acidified with 6M HCl. The white precipitate was filtered off and washed with water. Recrystallization from ethyl acetate gave 3.04g (59%) of white crystal **11**. mp 125-127°C ^{1}H-NMR(DMSO) 1.35 (m, 6H, alkyl chain), 1.68 (q, 2H, -$CH_2C\underline{H}_2CH_2$-), 3.33 (t, 2H, -CH_2O-), 3.98 (t, 2H, -CH_2-O-), 4.31 (t, 1H, -OH), 6.95 (d, 2H, aromatic), 7.82 (d, 2H, aromatic)

Synthesis of 4-(6-Acryloxyhexyloxy)benzoic acid (**12**)

To a solution of **11** (3.8g, 16 mmol) and triethylamine (3.55 g, 35 mmol) in 30mL of 1,4-dioxane was added acryloyl chloride (3.65 g, 18 mmol) dropwise. The reaction mixture was stirred for 4h at room temperature. The mixture was extracted with ethyl acetate, dried and concentrated *in vacuo*. The residue was subjected to column chromatography (ethyl acetate: hexane = 1: 4) to give 1.48g (34%) of **12**. ^{1}H-NMR($CDCl_3$) 1.35 (m, 4H, alkyl chain), 1.75 (m, 4H, alkyl

chain), 4.04 (t, 2H, -CH_2-O-), 4.18 (t, 2H, -CH_2-O-), 5.8-6.4 (m, 3H, vinylic), 6.95 (d, 2H, aromatic), 7.82 (d, 2H, aromatic)

Synthesis of 4-[4-(6-Acryloxyhexyloxy)benzoyl]phenyl 4-octyloxybenzoate **(2)**

To a solution of **12** (7 g, 24 mmol) in benzene was added thionyl chloride (52.4 mL, 71 mmol). The mixture was refluxed at 80°C for 8h. The solvent and excess $SOCl_2$ were removed by evaporation under reduced pressure, and then **8** (5.5 g, 49 mmol) and 100mL of dichloromethane were added and stirred for 3h. The reaction mixture was poured into excess water and extracted with methylene chloride. The combined organic layers were washed several times further with water, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed by evaporation under reduced pressure. The crude product was purified by column chromatography (ethyl acetate : methylene chloride : hexane = 1: 1: 8) to give 9.2 g (58%) of **2**. mp 83-84°C ^{1}H-NMR($CDCl_3$) 0.85-1.82 (m, 23H, alkyl chain), 4.08 (t, 4H, -CH_2O-), 4.19 (t, 2H,-CH_2O-), 5.8-6.4 (m, 3H, vinylic), 6.98 (d, 4H, aromatic) ,7.24 (d, 4H, aromatic), 8.15 (d, 4H, aromatic)

Synthesis of chiral cholesteric monomer

Methyl 2-methyl-3-(tetrahydro-2H-pyran-2-yloxy)propanoate **(14)**

p-Toluenesulfonic acid was added to a solution of methyl (R)-(-)-3-hydroxy-2-methyl- propionate **13** (1g, 8.46 mmol) and 3,4-dihydro-2*H*-pyran (1.1mL, 11.9 mmol) in dry THF. The mixture was stirred overnight at room temperature. It was then poured into ice-water and extracted with ether. The ether solution was washed with saturated aq $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo* to give 1.50g (88%) of **14**. ^{1}H-NMR($CDCl_3$) δ 1.16 (d, 3H, J=7Hz, CH_3), 1.25-1.90 (br, 6H, $C\underline{H}_2C\underline{H}_2C\underline{H}_2CHO_2$ of THPO), 2.30-2.90 (m, 1H, CH), 3.00-3.90 (m, 2H, CH_2), 3.65 (s, 3H, CO_2CH_3), 4.56 (br.t, 1H, $C\underline{H}O_2$ of THPO)

2-Methyl-3-(tetrahydro-2H-pyran-2-yloxy)-1-propanol **(15)**

A solution of **14** (1 g, 4.95 mmol) in dry ether (30mL) was added dropwise during 40 min to a stirred and ice cooled suspension of lithium aluminum hydride (0.22g, 5.94 mmol) in dry ether. The solution was stirred overnight at room temperature. The excess LAH as decomposed by the successive addition of water (8mL), 15% NaOH solution (8mL) and water (24mL) to the stirred and ice-cooled mixture. After stirring for 10 min at room temperature, the mixture was filtered. The filtrate was dried over Na_2SO_4 and concentrated *in vacuo* to give 0.87g (85%) of **15**.

^{1}H-NMR($CDCl_3$) δ 0.89 (d, 3H, J=7Hz, CH_3), 1.30-2.20 (m, 7H, CH), 2.80-4.20 (m, 7H, THPO), 4.54 (br.t, 1H, $C\underline{H}O_2$ of THPO)

2-Methyl-3-(tetrahydro-2H-pyran-2-yloxy)propyl 4-methylbenzenesulfonate **(16)**

To a solution of **15** (1g, 5.81 mmol) and triethylamine (1.22 mL, 8.71 mmol) in 30mL of acetonitrille was added *p*-toluenesulfonyl chloride (1.66 g 8.71 mmol) dropwise in 10mL acetonitrille for 30min. The reaction mixture was stirred for 5h at 50°C. The mixture was extracted with CH_2Cl_2. The organic solution was washed with water, dried and concentrated *in vacuo*. The residue was subjected to column chromatography (ethyl acetate: methylene chloride : hexane = 1: 1: 8) to give 1.49g (78%) of **16**. ^{1}H-NMR ($CDCl_3$) δ 0.89 (d, 3H, J=7Hz, CH_3), 1.00-2.20 (m, 7H, CH), 2.38 (s, 3H, OTs), 2.90-4.30 (m, 6H, THPO), 4.40 (br, 1H), 7.34 (d, 2H, J=8Hz, aromatic), 7.80 (d, 2H, J=8Hz, aromatic)

Ethyl 4-[2-methyl-3-(tetrahydro-2H-pyran-2-yloxy)propoxy] benzoate **(17)**

To a solution of sodium hydride (0.18 g, 4.57 mmol) in DMF (30mL) was added ethyl 4-hydroxybenzoate (0.76 g, 4.57 mmol) in DMF (10mL). And then chiral tosylate **16** (1g, 3.04 mmol) was added and the reaction mixture was stirred for 8h at 80. After removal of DMF *in vacuo*, the residue was dissolved in CH_2Cl_2 and filtered. The filtered solution was subjected to column chromatography (ethyl acetate: methylene chloride : hexane = 1: 1: 20) to give 1.73g (74%) of **17**. ^{1}H-NMR($CDCl_3$) δ 1.08 (d, 3H, J=7Hz, CH_3), 1.37 (t, 3H, J=7.1Hz, $CO_2CH_2C\underline{H}_3$), 1.41-1.76 (m, 6H, THPO), 2.23-2.27 (m, 1H, CH), 3.35-4.04 (m, 6H), 4.33 (q, 2H, J=7.3Hz, $CO_2C\underline{H}_2CH_3$), 4.57 (t, 1H, J=2.9Hz), 6.90 (d, 2H, J=11.7Hz, aromatic), 7.90 (d, 2H, J=11.7Hz, aromatic): ^{13}C-NMR($CDCl_3$) 13.5 (CH_3), 35.5, 65.0, 70.4 (CH_2), 114.1, 121.7, 132.2, 163.2 (aromatic) and 171.1 ($\underline{C}O_2Et$)

4-(3-Hydroxy-2-methylpropoxy)benzoic acid **(18)**

To a solution of **17** (1 g, 3.10 mmol) in methanol was added 2.24M KOH solution (6 mL). The reaction mixture was stirred for 3h. After removal of methanol, 20mL of water was added and acidified with conc. HCl. The white precipitate of **18** was filtered off and washed with water. Recrystallization from ethyl acetate gave 0.55g (85%) of white crystal **18**. mp 111-113°C ^{1}H-NMR($CDCl_3$) δ 1.06 (d, 3H, J=7Hz, CH_3), 2.11-2.29 (m, 1H, CH), 3.72 (d, 2H, J=5Hz, CH_2), 4.01 (d, 2H, J=6Hz, CH_2), 6.94 (d, 2H, J=9Hz, aromatic), 8.03 (d, 2H, J=9Hz, aromatic): ^{13}C-NMR($CDCl_3$) 13.5 (CH_3), 35.4 (CH), 65.0, 70.4 (CH_2), 114.1, 121.2, 132.2, 163.2 (aromatic) and 171.1 (COOH)

4-(3-Acryloxy-2-methylpropoxy)benzoic acid **(19)**

To a solution of **18** (1g, 4.76 mmol) and triethylamine (0.80 mL, 5.71 mmol) in 30mL of THF was added acryloyl chloride (0.46 mL, 5.71mmol) dropwise in 10mL THF for 30min at -30°C. The reaction mixture was stirred for 1h at -30°C. The mixture was extracted with ethyl acetate, dried and concentrated in vacuo. The residue was subjected to column chromatography (ethyl acetate: methylene chloride : hexane = 1: 1: 3) to give 0.44g (35%) of **19**. ^{1}H-NMR

($CDCl_3$) δ 1.13 (d, 3H, J=7Hz, CH_3), 2.38-2.51 (m, 1H, CH), 4.12 (d, 2H, J=5.9Hz, CH_2), 4.24 (d, 2H, J=5.5Hz, CH_2), 5.84 (d, 1H, vinylic), 6.13 (dd, 1H, vinylic), 6.37 (d, 1H, vinylic), 6.94 (d, 2H, J=9.2Hz, aromatic), 8.04 (d, 2H, J=9.2Hz, aromatic): ^{13}C-NMR($CDCl_3$) 13.9 (CH_3), 33.0 (CH), 65.9, 69.6 (CH_2), 114.1, 121.7, 128.2, 131.0, 132.3, 163.3, 166.1 (vinylic, aromatic) and 171.8 (COOH)

1,4-Phenylene bis[4-(3-acryloxy-2-methylpropoxy)benzoate] **(1)**

To a solution of **19** (1g, 3.78 mmol) and 1,3-dicyclohexyl carbodiimide (0.78 g, 3.78 mmol) and N,N-dimethylamino-pyridine (0.01g) in methylene chloride was added hydroquinone (0.21 g, 1.89 mmol) and the reaction mixture was stirred for 24h at room temperature. The mixture was extracted with CH_2Cl_2, dried and concentrated in vacuo. The residue was subjected to column chromatography (ethyl acetate: methylene chloride: hexane = 1: 1: 3) to give 0.33g (29%) of **1**.

mp 120-121°C ^{1}H-NMR($CDCl_3$) 1.14 (d, 4H, J=7Hz, CH_3), 2.35- 2.46 (m, 2H, CH), 3.97-3.99 (m, 4H, CH_2), 4.01 (d, 4H, J=3Hz, CH_2), 5.84 (d, 2H, vinylic), 6.14 (dd, 2H, vinylic), 6.42 (d, 2H, vinylic), 6.97 (d, 4H, J=8.8Hz, aromatic), 7.25 (s, 4H, aromatic), 8.14 (d, 4H, J=8.8Hz, aromatic): ^{13}C-NMR($CDCl_3$) 13.9, 33.0, 65.9, 69.7, 114.3, 122.6, 128.2, 131.0, 132.3, 148.4, 163.2, 164.8 and 166.1

Preparation and Characterization of a Photocured Chiral-Nematic Film

Mixtures containing chiral cholesteric LC diacrylate monomer **1** and achiral nematic LC monoacrylate monomer **2** in the ratios of 70:30, 60:40, 50:50, 40:60 and 30:70 along with 1wt% photoinitiator (Irgacure 907, Ciba-Geigy) were dissolved in toluene in 20wt%. The toluene solution was dropped onto a glass plate with a rubbed polyimide (DOCDA-DA) coating. The glass plate was stayed at room temperature for 2-3h avoiding incident light until solvent toluene become evaporated. The film thickness was controlled to be 13 μm, was heated on a hot plate to 100° or 120°, and was photocured with 365nm mercury lamp at a power intensity of 2mW/cm^2 with a glass covered. The transmittance of the photocured films on glass plate was recorded using a UV-VIS-NIR spectrometer.

RESULT AND DISCUSSION

Preparation of Liquid Crystal Momomers

Achiral nematic monomer **2** was synthesized and purified by following literature procedures as summarized in Figure 1. [14] The key synthetic intermediates the hydroxyphenyl **8** and the benzoic acid **12** were obtained in moderate to good yields starting from octanol **3** and 6-bromohexanol **9** respectively. The nematic monoacrylate monomer **2** could be finally synthesized by esterification of 4-(6-acryloxyhexyloxy) benzoic acid **12** with 4-hydroxyphenyl-4-octyloxybenzoate **8**.

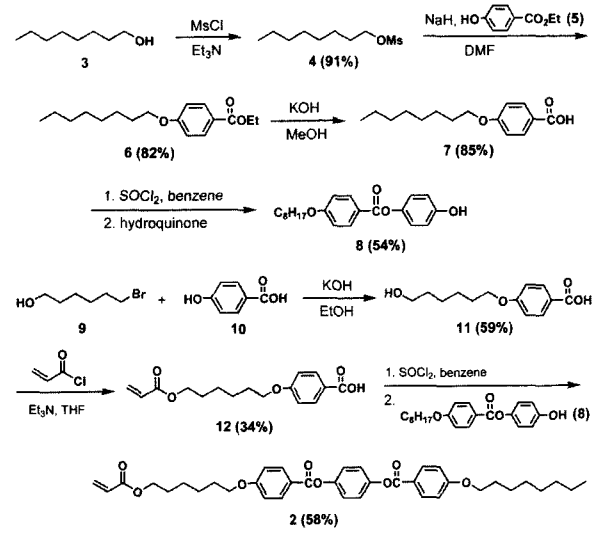

Figure 2. Synthetic scheme of nematic monoacrylate.

The chiral cholesteric liquid crystal monomer **1** was synthesized through a synthetic route outlined in Figure 3 starting with (R)-methyl 3-hydroxy-2-methylpropionate **13** which ensures the retention of the configuration without appreciable reduction of the optical purity of the starting material **13**. The hydroxyl group of **13** was protected with 2-tetrahydropyranyl group in **14**. Lithium aluminium hydride reduction of the ester group of **14** and tosylation of the resulting alcohol **15** at the below 60°C led to the generation of the chiral tosylate **16**. The tosylate **16** was used to form the corresponding benzoic acid **18** by reaction with ethyl 4-hydroxybenzoate, followed by alkaline hydrolysis to cleave tetrahydropyranyl protecting group. The chiral hydroxyl benzoic acid **18** was converted to 4-(3-acryloxy-2-methylpropoxy) benzoic aicd **19** in low to moderate yield by treating with acryloyl chloride at below -30°C. We observed the generation of undesired bis-acrylated product in a significant amount and the amount increases when the reaction temperature keeps above -30°C. The monoacrylated acid **19** was condensed with a half equivalent of hydroquinone in the presence of dehydrating reagent DCC to synthesize the final 1,4-phenylene bis-4-(3-acryloxy-2-methylpropoxy)benzoate **1** in low to moderate yield.

Photopolymerization of cholesteric-nematic liquid crystal monomer mixture to cholesteric polymer networks

Recently Broer [9,10] and Stohr [8] demonstrated that the pitch of the helix of a cholesteric polymer network can be varied continuously over the film thickness so that the bandwidth of cholesteric reflection becomes broadened from the single pitch value of about 40nm to one which expands over the whole visible spectrum of 400nm wavelength–span by using photo-induced diffusion method. UV-intensity gradient over the film thickness generated in irradiation in

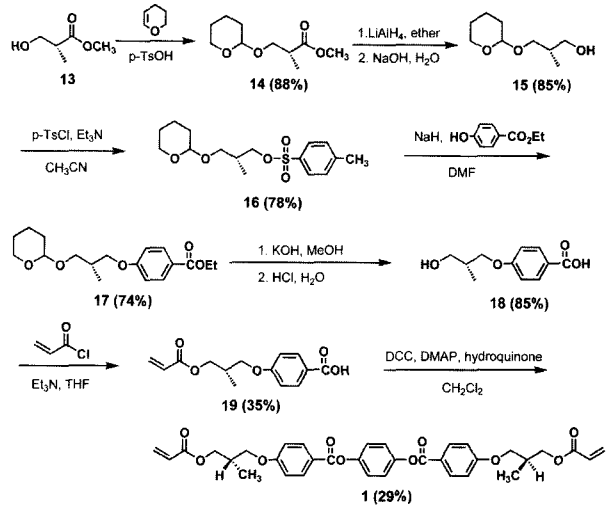

Figure 3. Synthetic scheme of chiral diacrylate.

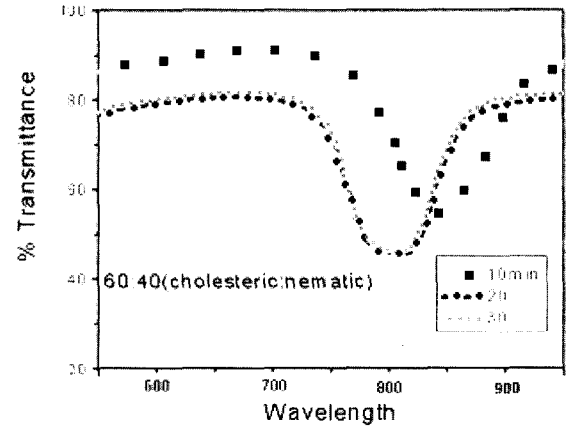

Figure 4. Transmission spectra of Cholesteric LC polymer film depending on the UV irradiation time. (Ch **1**:Ne **2**=60:40, temperature 100°C)

combination with different reactivity between a helix-winding chiral monomer and a helix-unwinding nematic monomer have proved to work as the driving force for the diffusion.

In present study we examined photopolymerization conditions for the construction of cholesteric polymer network with a pitch gradient which can reflect a wide band of circular polarized light in the region of visible wavelength utilizing the synthesized chiral cholesteric monomer **1** and achiral nematic monomer **2**.

For the fabrication of cholesteric polymer network, mixtures containing cholesteric diacrylate monomer **1** and nematic monoacrylate monomer **2** in various compositions were spin-coated on a polyimide (DOCDA-DA)-aligned plate and were photocured at polymerization temperature 100°C or 120°C in the presence of photoinitiator (Iraqacure 907) with UV irradiations.

The wavelength of light with maximum reflection (λ_R) on the photocured cholesteric film which was synthesized with mixture of chiral diacrylate **1** and nematic monoacrylate **2** in a ration of 60:40 is observed to undergo hypsochromic shift from 850nm to 800nm varying the photocured time from 10 min to 30min as seen in the transmission spectra in Figure 4.

The average bandwidth of the reflected light is around 80 nm. The hypsochromic shift of maximum reflection wavelength on a longer 20min-irradiation indicates that UV-irradiation for less than 20 min is not sufficient enough for inducing cholesteric helix winding in full extent.

Further a prolonged UV-irradiation for 30min does not induce any further hypsochromic shift which indicates that 20 min UV-irradiation is sufficient for full helix winding under the photopolymerization conditions.

We further studied change in the bandwidth of light reflection by cholesteric polymer films fabricated with mixtures of chiral cholesteric diacrylate **1** and nematic monoacrylate **2** in different ratios, 70:30, 50:50 40:60, and 70:30. Figure 5 shows transmission spectra of the two cholesteric polymer films fabricated with compositions of chiral diacrylate **1** and nematic monoacrylate **2** in 60:40 and 70:30 which allow bandwidth of reflection in the region of visible wavelength. When the relative content of chiral diacrylate **1** increases, the reflection wavelength bands undergo blue-shift and *vice versa*.

The reflection bandwidth of cholesteric polymer film with composition of diacrylate **1** and monoacrylate **2** in 60:40 is observed to be about 180nm where as the bandwidth of film in a higher ratio 70:30 to be a narrower 100nm. The result indicates that the mixture containing higher content 70% of helix-winding more reactive cholesteric diacrylate undergo photopoly merization so fast that full diffusion of helix-unwinding nematic monoacrylate **2** can not occur cross the film thickness.

Since cholesteric polymer films obtained with compositions of diacrylate **1** and monoacrylate **2** in ratios of 70:30 and 60:40 provide reflection band in visible region, we attempted to get a cholesteric polymer network of a wider reflection bandwidth with the two mixture compositions under varying photocuring temperature and varying UV irradiation intensity by applying photomask.

Increase in photocuring temperature from 100° to 120° gives rise to a hypsochromic shift of reflection maximum from 800nm to 760nm and leads to somewhat reduction of reflection bandwidth (130nm→120nm in the average bandwidth) in the case of cholesteric polymer film with the composition of 60:40 (Figure 6).

The cholesteric film formation with additional photomask at 120° provides a cholesteric network with a much wider reflection bandwidth, around 200nm of average reflection band (Figure 6), even though the efficiency of reflection significantly becomes reduced probably due to the increased scattering by the generation of focal conic phase at high near to isotropic temperature. The result obtained by applying

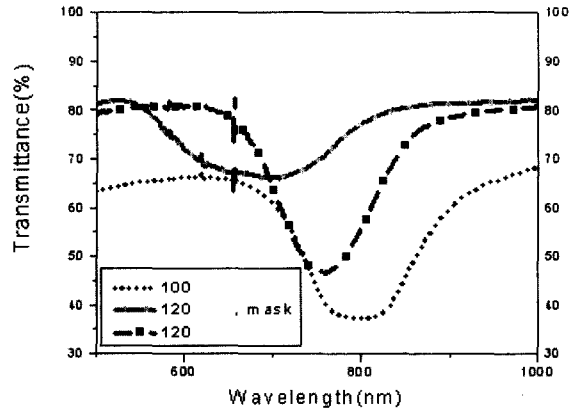

Figure 6. Transmission spectra of the Cholesteric LC film depending on the curing condition (Ch **1**:Ne **2**=60:40)

mask indicates that reduced UV-intensity with photomask allows better diffusion probability of helix-unwinding nematic monoacrylate **2** across the film thickness and leads to a wider reflection bandwidth of about 200nm.

The effect of applying photomask in the photopolymerization of cholesteric and nematic acrylate mixture is also similarly observed in the case of the composition with a ratio of 70:30 as seen in Figure 7.

The maximum reflection wavelength is shifted to a shorter wavelength 600 nm comparing with that of 60:40 composition at around 700 nm. Also transmission spectrum of the cholesteric polymer film obtained with mixture of 70:30 ratio and applying of photomask shows significantly different reflection intensity along the region of wavelength which might be improved by applying a more densely patterned photomask.

In summary we synthesized chiral cholesteric LC monomer *p*-phenylene bis-(*p*-3-acryloxy-2(S)-methylpropoxy)benzoate and achiral nematic LC monomer *p*-phenylene *p*-acryloxy-6-hexyloxy-*p*-octyloxybenzoate with which we constructed

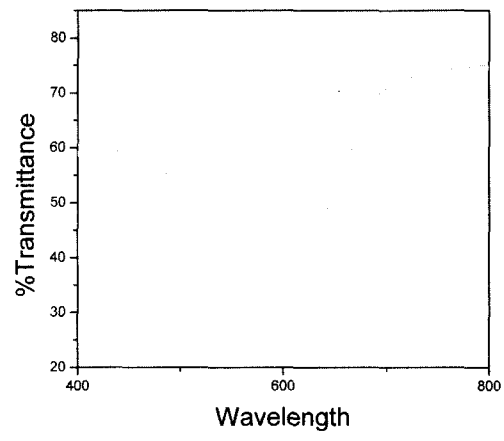

Figure 7. Transmission spectrum of the Cholesteric LC film (Ch **1**: Ne **2**=70:30)

cholesteric polymer film network with a pitch gradient covering more than 200 nm band width in the visible wavelength by diffusion controlled photostructuring method.

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