Synthesis of Novel Glass-Forming Liquid Crystals Containing Acrylic Acid Trimer Core Unit and Mesogenic Moiety, and Their Use in Cholesteric Reflection Films

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ABSTRACT: A novel medium molecular mass liquid-crystalline (LC) material to form glassy nematic phase has been developed to provide uniformly aligned LC films. The LC material consists of an acrylic acid trimer as a core structure and a mesogenic moiety. The resulting LC trimer showed a nematic LC phase and vitrified to form mono-domain films at room temperature. This glassy LC trimer is miscible with a chiral photochromic dopant, providing monodomain, aligned, defect-free cholesteric reflection films, the color of which is tunable by UV irradiation. [doi:10.1295/polymj.PJ2006115]

KEY WORDS Glass-Forming Liquid Crystals / Acrylic Acid Trimer / Nematic Liquid Crystal / Alignment / Cholesteric Reflection Film /

In recent years, a number of studies have centered on liquid-crystalline (LC) materials with anisotropic properties. In particular, LC materials with a cholesteric structure have attracted considerable interest due to their unique optical properties and potential applications in circular polarizers, optical notch filters and reflectors, and polarized fluorescent films.¹

Polymeric cholesteric LCs have been primarily investigated with the intention of fixing the color of a cholesteric liquid crystal.² The degree of freedom of molecular motion is limited on losing fluidity by providing a high molecular weight or a crosslinked structure, and the helical molecular order is fixed.

Glass-forming liquid crystals with a high glass transition temperature, such as LC polymers, can be aligned at elevated temperatures and then stabilized by cooling below their glass transition temperatures. However, LC polymers often do not undergo fast, defect-free alignment because of their entangled molecular chains.

A good method for preparing birefringent films with complex optical functions is based on the photo-polymerization of reactive liquid crystals.^{3–5} These liquid crystals are aligned in the desired configuration in the monomeric state due to their low viscosities, and are subsequently converted into solid films through UV polymerization. Such birefringent films made with low molecular weight LCs, however, are

not stable before UV irradiation because of crystallization at room temperature.

For many optical and photonic applications, glassforming LCs represent a unique class of advanced materials that are capable of freezing the liquid-crystalline order into a solid state without crystallization. In a recent series of papers, a new molecular design concept, wherein nematic and chiral groups are chemically bonded to a volume-excluding core to prevent crystallization upon cooling, has been detailed.⁶⁻¹² These materials, however, were prepared using a multiple synthetic step and/or troublesome workup procedures. For the applications described above, materials with the highest possible glass transition temperature are needed to ensure sufficient room temperature stability of the devices. Another requirement is that the materials possess a broad nematic liquid crystal mesophase above their glass transition temperatures. Higher ordered mesophases, such as a smectic phase, are not preferred because of the difficulty in obtaining mono-domain films of these phases.¹³

In this paper, we present the design, synthesis and characterization of a novel medium molecular mass nematic liquid crystal (LC trimer), consisting of an acrylic acid trimer as the core structure and cyanobiphenyl benzoate as a mesogenic moiety. The LC trimer has an elevated glass transition temperature and exhibits both nematic and cholesteric phases with the addition of a chiral dopant.

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EXPERIMENTAL

Materials

All reagents and solvents used in the study were obtained commercially, and were used as-received. Mesogenic acrylate was prepared according to the literature.¹⁴

Synthesis of 4-(2-Tetrahydropyranyloxy ethoxy) benzoic acid

2-(2-Chloroethoxy)tetrahydro-2H-pyran (37 mL, 253 mmol) was added dropwise to a mixture of ethyl 4-hydroxylbenzoate (35.0 g, 211 mmol) and potassium carbonate (58.2 g, 421 mmol) in dry *N*-methyl-2-pyrrolidinone (NMP) (500 mL) in a nitrogen atmosphere at 135 °C. The reaction mixture was heated at 135 °C for 3 h, and was then cooled to room temperature. The solid fraction was removed by filtration, and the filtrate was diluted with ethyl acetate, washed twice with saturated aqueous ammonium chloride, saturated so-dium hydrogen carbonate, brine and dried over magnesium sulfate, and the solvent was then evaporated to dryness. The resultant pale yellow oil obtained was used without further purification in the next reaction.

This crude tetrahydropyranyloxy (THP)-protected ethyl benzoate intermediate was dissolved in ethanol (100 mL) and water (100 mL). Sodium hydroxide (25 g, 625 mmol) was added to this solution, where a mild exothermic reaction was observed. After stirring for 1 h, the solution was quenched with acetic acid and the precipitated white solid was collected by filtration, washed with water and dried under vacuum at $50\,^\circ\text{C}$ to yield THP-protected benzoic acid as a white powder (2 steps, 72% yield, 38.2 g, 152 mmol). ¹H NMR $(CDCl_3, \delta, ppm)$: 1.40–1.52 (m, 4H, CH₂ from THP), 1.60–1.65 (m, 1H, CH₂ from THP), 1.68–1.75 (m, 1H, CH₂ from THP), 3.42–3.47 (m, 1H, CH₂ from THP), 3.71–3.80 (m, 2H, –OCH₂CH₂OAr–), 3.92–3.96 (m, 1H, CH₂ from THP), 4.18–4.24 (m, 2H, –OCH₂CH₂-OAr–), 4.65–4.67 (t, 1H, J = 3.7 Hz, CH from THP), 7.02-7.06 (m, 2H, Ar), 7.88-7.91 (m, 2H, Ar), 12.65 (brs, 1H, COOH).

Synthesis of Mesogenic Alcohol

N-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDCI) (9.40 g, 49.1 mmol) was added to a solution of 4-(2-tetrahydropyranyloxy ethoxy) benzoic acid (10 g, 39.6 mmol), 4-cyano-4'-hydroxybiphenyl (6.0 g, 37.7 mmol), DPTS (*p*-toluenesulphonic acid/4-dimethylaminopyridine salt)¹⁵ (0.55 g, 1.88 mmol) and CH₂Cl₂ (100 mL). After stirring overnight, the reaction solution was evaporated and the residual solid was dissolved in THF and methanol. Concentrated hydrochloric acid was added to this clear solution. After stirred for 20 min. a white precipitate formed. After stirring for another 1 h, this white precipitate was collected by filtration, washed with water and methanol, and was then dried under vacuum at 80 °C to yield mesogenic alcohol as a white powder (2 steps, 74%, 10.0 g). This white powder was sufficiently pure, as identified and confirmed by NMR. To obtain crystals, this powder could be recrystallized from acetone/ethanol. ¹H NMR (CDCl₃, δ , ppm): 1.98 (t, 1H, J = 6.3 Hz, -OH), 4.03 (tt, 2H, J = 6.3, 4.6 Hz, HOCH₂CH₂OAr–), 4.20 (t, J = 4.6 Hz, 2H, HOCH₂CH₂OAr-), 7.02-7.04 (m, 2H, Ar), 7.32-7.35 (m, 2H, Ar), 7.62–7.66 (m, 2H, Ar), 7.68–7.71 (m, 2H, Ar), 7.72-7.76 (m, 2H, Ar), 8.16-8.20 (m, 2H, Ar). Anal. Calcd for C₂₂H₁₇NO₄: C, 73.53; H, 4.77; N, 3.90. Found: C, 73.72; H, 5.02; N, 2.97.

Synthesis of the LC Trimer

EDCI (1.86 g, 9.7 mmol) was added to a solution of 2,4,6-heptanetricarboxylic acid (tri-acid) (0.969 g, 4.2 mmol), mesogenic alcohol (3.0 g, 8.3 mmol), DPTS (0.49 g, 1.67 mmol), diisopropylethylamine (10 mL) and NMP (10 mL) at room temperature. After the solution was stirred for 4 h, aqueous hydrochloric acid and methanol were added to this clear reaction solution. The precipitate was collected by filtration, washed with water and methanol, and dried under vacuum at 70 °C to yield the LC trimer as a white powder (65% yield, 2.27 g). ¹H NMR (CDCl₃, δ , ppm): 1.15– 1.21 (m, 6H, CH₃), 1.52-2.17 (m, 4H, CH₂), 2.50-2.66 (m, 3H, CH), 4.19-4.32 (m, 6H, -OCH₂CH₂-OAr-), 4.40-4.53 (m, 6H, -OCH₂CH₂OAr-), 6.95-7.05 (m, 6H, Ar), 7.28-7.33 (m, 6H, Ar), 7.57-7.68 (m, 6H, Ar), 7.68–7.74 (m, 6H, Ar), 8.10–8.18 (m, 6H, Ar). Anal. Calcd for C₇₆H₆₁N₃O₁₅: C, 72.66; H, 4.89; N, 3.34. Found: C, 72.54; H, 4.78; N, 3.13.

Synthesis of the LC Oligomer

Mesogenic acrylate (4.13 g, 10 mmol) was dissolved in ethyl lactate (30 mL) in a 100 mL, twonecked round-bottomed flask equipped with a reflux condenser in a nitrogen atmosphere. The reaction mixture was heated at 150 °C. After the reaction mixture turned clear, azobisisobutylonitrile (AIBN) (30 mg) dissolved in ethyl lactate (3 mL) was added to the reaction mixture. After stirring for 6 h, the resulting solution was cooled to room temperature and poured into methanol (150 mL) with vigorous stirring to precipitate the oligomer. The oligomer thus obtained was purified by re-precipitation twice from THF into methanol, and was then dried under vacuum for 5 h at 70 °C to yield the LC oligomer (3.30 g, 80% yield). ¹H NMR (CDCl₃, δ , ppm): 1.5–2.2 (m, 2H, CH₂), 2.3-2.7 (m, 1H, CH), 4.1-4.3 (m, 2H, -OCH₂CH₂-

OAr-), 4.3–4.4 (m, 2H, –OCH₂CH₂OAr-), 6.9–7.1 (m, 2H, Ar), 7.3–7.4 (m, 2H, Ar), 7.5–7.8 (m, 6H, Ar), 8.0–8.2 (m, 2H, Ar).

Synthesis of Chiral-Photochromic Dopant

To a solution of 4-(4'-hydroxyphenylazo)benzoic acid (10.0 g, 41.3 mmol), potassium hydroxide (7.0 g, 123.8 mmol), potassium iodide (2.1 g g, 12.4 mmol) in ethanol (100 mL) and water (50 mL) was added 1-bromohexane (7.0 mL, 49.5 mmol) dropwise at 100 °C under nitrogen atmosphere. The flask was refluxed at 100 °C overnight and cooled to room temperature. The reaction mixture was filtered and the filtrate was diluted with dichloromethane and water. The organic layer was separated and hexane was added with vigorously stirring. The precipitated orange solid was separated, washed by hexane and dried *in vacuo* to give benzoic acid intermediate as orange solid. The resultant orange solid obtained was used without further purification in the next reaction.

To a solution of intermediate benzoic acid (3.00 g, 9.19 mmol), isosorbide (0.665 g, 4.55 mmol) and DPTS (2.82 g, 9.55 mmol) in CH₂Cl₂ (20 mL) was added EDCI (2.18 g, 11.38 mmol). After stirred overnight, the reaction solution was evaporated and the residual solid was dissolved with THF and methanol. To this clear solution was added dilute HCl and the resulting orange precipitate was filtered. The solid residue was purified by flash column chromatography on silica gel with a solvent (dichloromethane/ethyl acetate = 30/1) to give chiral-photochromic dopant. (2.80 g, 3.67 mmol, 80% yield). ¹H NMR (CDCl₃, ppm, δ) 8.3–8.2 (m, ArH, 2H), 8.2–8.1 (m, ArH, 2H), 8.0-7.8 (m, ArH, 8H), 7.1-7.0 (m, ArH, 4H), 5.6-5.5 (m, CH from isosorbide), 5.5–5.4 (m, CH from isosorbide), 5.2-5.1 (m, CH from isosorbide), 4.8-4.7 (m, CH from isosorbide), 4.2-4.0 (m, CH₂ from isosorbide and -OCH₂-CH₂-, 8H), 1.9-1.8 (m, CH₂, 4H), 1.5-1.4 (m, CH₂, 4H), 1.4-1.3 (m, CH₂, 8H), 1.0-0.9 (m, CH₃, 6H).

Measurements

¹H NMR spectra were obtained in CDCl₃ using a JEOL AL-400 spectrometer at 400 MHz. Matrixassisted laser desorption ionization with time-offlight (MALDI-TOF) mass spectra were obtained on a Kratos Konpact MALDI instrument operating in a linear detection mode to generate positive ion spectra using dithranol as the matrix, tetrahydrofuran (THF) as the solvent, and sodium trifluoroacetate as an additive agent.

Thermal transition temperatures were determined by differential scanning calorimetry (DSC) by using a Seiko Instruments Inc. DSC6200 with a continuous nitrogen purge at a scan rate of 20 °C/min.

RESULTS AND DISCUSSION

Synthesis of LC Trimer

We have previously reported that LC polymers are good candidates for optical film materials.¹⁶ These LC polymers, however, are not miscible with dopants because of phase separation. Lowering the molecular weight of the material is an effective method to obtain a defect-free film in a binary mixture. In fact, the LC oligomer, with a molecular weight of around 1,200, could be synthesized by conventional radical polymerization. By using the LC oligomer, defects in the aligned thin films were decreased in the presence of dopants. However, this was not a satisfactory solution. The LC oligomer has a molecular weight distribution (MWD) as shown in Figure 1. The average molecular weight of the oligomer was about 1,200, but this oligomer also contained various other higher molecular weight components. This appears to be the reason for the phase separation of a binary mixture of the film. Thus, LC materials without such higher molecular weight components are required.

The structure of the LC trimer is based on a central scaffold made up of an acrylic acid trimer unit linked together with cyanobiphenyl benzoate as a mesogenic moiety (Figure 2). This trimer is, in a sense, a miniature model of polyacrylate oligomers.



Figure 1. MWD of the LC oligomer measured by MALDI-TOFMS.



Figure 2. Chemical structure and molecular weights of LC oligomer and LC trimer.





Figure 3. ¹H NMR spectrum of the LC trimer.

The central scaffold triacid (2,4,6-heptanetricarboxylic acid) of the LC trimer was prepared *via* the Michael reaction of methyl cyanoacetate with methyl methacrylate followed by hydrolysis (Scheme 1).¹⁷ Both the starting materials are inexpensive reagents. The mesogenic moiety with an aliphatic alcohol terminal group [4-(2-hydroxyethoxy) benzoic acid 4'cyanobiphenyl-4-yl ester] was prepared from 4-hydroxybenzoate in two steps, as depicted in Scheme 2.

The condensation of triacid with mesogenic alcohol in the presence of EDCI and diisopropylethylamine in NMP formed the LC trimer with a 65% yield. Figure 3 shows the ¹H NMR spectrum of the LC trimer. The benzoyl and biphenyl units yielded peaks at δ 8.14, 7.71, 7.61, 7.30. Two peaks assigned to the methylene protons adjacent to ester and ether groups were observed at δ 4.46 and 4.26 respectively. The methyn and methyl protons on the acrylic trimer core were found at δ 2.58 and 1.18. The methylene protons of the acrylic trimer core were observed as four separated peaks at δ 2.17–1.52. These protons, derived from the acrylic trimer core, are seen as multiplet



Figure 4. MALDI-TOFMS spectrum of the LC trimer with a theoretical molecular weight of 1255.

peaks since this trimer is a mixture of stereoisomers.¹⁷ As shown in Figure 1, the LC oligomer has a MWD $(M_w/M_n = 1.32)$, while the LC trimer has a distinct molecular weight $(M_w/M_n = 1)$. This was measured and verified using the MALDI-TOFMS analysis (Figure 4). A single signal was observed at m/z ([M + Na])+) = 1278.40, indicating the formation of the trimer (calcd mass 1255.41).



Figure 5. Optical texture of the LC trimer using POM with crossed polarizers (40 x). The sample was heated to $150 \,^{\circ}$ C.



Figure 6. DSC thermograms for the LC trimer and LC oligomer on the second heating scan $(20 \,^{\circ}C/\text{min})$.



Scheme 3. Synthesis of chiral-photochromic dopant.

Comparison of LC Trimer with LC Oligomer

The mesomorphic properties of the macromolecular materials prepared were investigated by polarized light optical microscopy (POM), and the defect textures of the compounds were examined. On cooling from the isotropic state, the LC trimer developed schlieren texture characteristics of the nematic phase (Figure 5). No further textural changes were observed upon cooling. Remarkably, upon further cooling the sample froze into a glass, but still retained its mesophase texture, *i.e.*, a glassy nematic phase was formed. Glassification probably occurs due to the disordering influence of the central scaffold, preventing the mesogenic units from readily packing together to form a crystalline solid. Figure 6 shows the DSC thermograms of the LC trimer and the LC oligomer for the second heating scan, where the LC order prevails below the glass transition temperature (T_g) . The scans exhibit no crystallization, indicating the morphological stability of these glass-forming LC materials. From the heating scans shown in Figure 6, $T_{\rm g}$ and $T_{\rm c}$ (nematic to isotropic transition temperature) for



Figure 7. Reflection color of the cholesteric films composed of a binary mixture of LC trimer and the chiral photochromic dopant. Trimer/dopant mass ratios are 100/7.5(Blue), 100/6.4(Green), 100/5.5(Red).

the LC oligomer ($M_n = 1260$, $M_w/M_n = 1.32$) are at 55 and 272 °C, and at 58 and 232 °C for the LC trimer ($M_w = 1255$), respectively. The T_c of the LC trimer is lower than that of the LC oligomer, both LC materials showed no tendency to crystallize or for smectic mesomorphism.

We prepared homogenious aligned retardation films

of the LC materials. To obtain oriented films, the LC materials were dissolved in cyclopentanone (30 wt %), and a small portion of the resultant solution was spincast on a glass substrate with a polyvinyl alcohol alignment layer (about 0.1 µm thick) that had been rubbed in order to align the liquid crystals by spin coating. Homogeneously aligned films were obtained after baking at 160 °C for 60 s. The thickness of the aligned films was measured with a surface profiler (Veeco Instruments Inc., Dectak 3ST). The LC films became opaque immediately after heating, but turned transparent in ten seconds, which indicates that the LC material was oriented, and a retardation film was formed. The maximum thickness of the retardation films without defects is 3.5 µm for the LC oligomer and 8.0 µm for the LC trimer. Thus, the advantage of the LC trimer compared to the LC oligomer for making optical films is obvious.

Cholesteric Reflection Film

Dissolving a chiral dopant in a nematic LC causes helix formation of the cholesteric LC resulting in the selective reflection of circular light corresponding to the helical pitch. A wide variety of cholesteric LC materials have been developed, including low molecular weight materials, lyotropic and thermotropic polymers, liquid crystal/polymer composites, and glassy liquid crystals.¹⁸ Although glassy liquid crystals, wherein nematic and chiral units are introduced into single molecules, are very promising, the synthesis of such binary component materials is tedious. On the other hand, the structure of the LC trimer is simple and is anticipated to have good miscibility with a dopant. For the example of a dopant, the chiral photochromic dopant which contains isosorbide and azobenzene moieties (shown in Scheme 3)¹⁹ was selected because of its high helical twisting power against the nematic liquid crystal. The chiral photochromic dopant was synthesized by etherification of 4-(4'-hydroxyphenylazo)benzoic acid with 1-bromohexane followed by esterification with isosorbide in the presence of EDCI. The dopant dissolved in the LC trimer without phase separation, but did not dissolve completely in the LC oligomer.

A binary mixture of the LC trimer and the chiral photochromic dopant was spin-coated to form a $3 \mu m$ thick film, yielding selective reflection in the visible light region. Cholesteric films prepared with mixtures with LC trimer/dopant mass ratios of 100/7.5, 100/ 6.4, and 100/5.5 were obtained. These selective reflection colors correspond to blue, green and red color (Figure 7) and their selective reflection bands centered at 400, 520, 650 nm respectively (Figure 8). The blue light reflection film was isolated from the substrate and the cross-section was imaged by the trans-



Figure 8. Reflection spectra of a cholesteric films composed of a binary mixture of LC trimer and the chiral photochromic dopant. Trimer/dopant mass ratios are 100/7.5(Blue), 100/6.4(Green), 100/5.5(Red).

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Figure 9. Cross-sectional TEM image of the cholesteric film with blue reflection.

mission electron microscope (TEM) in Figure 9. As seen in this microscopy, the texture of Grandjean orientation derived from a helical stack of quasi-nematic layers was observed. There was no phase separation from a microscopic view.

These films show long-term morphological stability at room temperature for 1 year.

Tunable Cholesteric Reflection Film

The selective reflections are tunable by UV-irradiation without destruction of the helix structure. We used the chiral dopant shown in Scheme 3 for the photochromic control and fixation of cholesteric pitch. In this chiral dopant, a photochromic azobenzene moiety is incorporated. A thin film with 3 µm thickness in the cholesteric phase reflecting red light was UV-irradiated (30 mW/cm²) at a temperature (150 °C) above its T_g . The reflection color of the film changed from red to blue passing through green in several seconds (Figure 10). The thin film solidified by cooling to room temperature retained the reflection color. A different color is fixed depending on the energy of the irradiated UV light.



Figure 10. Shift of reflection spectra for the cholesteric film by UV irradiation.

The iridescent color of the solid film is stable for at least 2 months at room temperature, and furthermore, it is also stable upon UV-irradiation at room temperature because of the high T_g of the glassy material. When the solid film is heated at above 160 °C, the cholesteric structure melts and the azobenzene unit isomerizes from *cis* to *trans* to yield the original reflection color.

CONCLUSIONS

The LC trimer (miniature of the LC polymer) has good miscibility with the chiral photochromic dopant and has the advantage of forming thick and large-area defect-free aligned films compared to the LC oligomer. Unlike other reported glass-forming LCs, the synthesis of this LC trimer is easy to scale-up. This miniaturization methodology is applicable to all polyacrylate LC materials without skeletal change. This material has good photoresponse in addition to filmforming ability, so the application of this technology promises to create new high performance peripheral materials, not only for passive optical devices but also for active devices, such as for nondestructive rewritable optical storage and photonic switching. Acknowledgment. This work was supported by the New Energy and Development Organization (NEDO) through a grant for "Project on Nanostructured Polymeric Materials" under the Nanotechnology Program.

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