Facile Synthesis of Novel Monodisperse Liquid-crystalline Oligomers Based on Michael Adducts from Millipede Cyanoacetates

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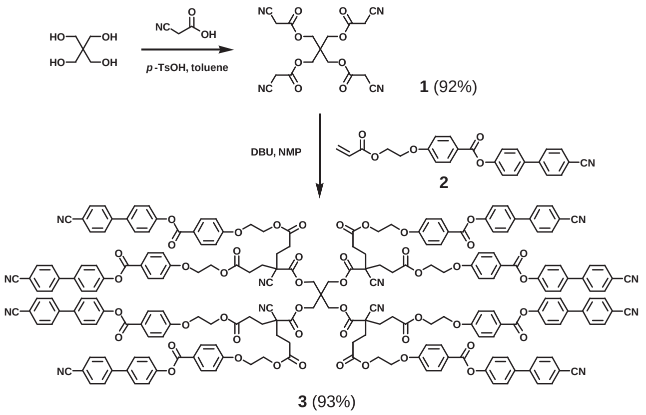
Facile synthesis of novel monodisperse liquid-crystalline (LC) oligomers was performed. The functionalization of the end group of 4 (and 6) millipede cyanoacetates with 8 (and 12) mesogenic units by Michael addition reaction produced a monodisperse LC octamer (and dodecamer) in high yields. Differential scanning calorimetry and optical polarizing microscopy revealed LC properties of the synthesized LC monodisperse oligomers. The monodisperse LC oligomers were morphologically stable glass-forming LC materials and exhibited a large variation in nematic phase temperatures in the range of approximately 80 to 300 °C.

Over the past decade, dendrimer synthesis, which is one of the core technologies in macromolecular chemistry, has undergone intense development.[1] Many reactive end groups that exist at the periphery of dendrimers easily react with various functionalities. The synthesis and characterization of liquid crystals with multiple mesogenic moieties in the periphery, such as cyclosiloxane-based liquid-crystalline (LC) materials[2] and LC dendrimers[3] have attracted considerable attention because of their similarity to side chain LC polymers.[4] Goodby and Saez have reported the synthesis of millipede oligomers in which mesogens (cyanobiphenyl and phenyl benzoate types) are connected to the pentaerythritol base core by ester bonds.[5] It is reported that LC materials in which mesogenic units are introduced via alkyl chains show thermotropic nematic, and smectic LC phases. Their low viscosity derived from their structural low chain entanglement is advantageous for fast switching optical materials.[6] However, the preparation of high-quality monodisperse LC materials is in a tedious process on a practical scale. This is because the reaction conditions require efficient removal of water and/or oxygen and tedious purification process. Ueda et al. have reported the preparation of poly(propyleneimine)-base LC dendrimers[7] by the Michael addition reaction of poly(propyleneimine) with mesogenic acrylates that are known as the precursors for LC polyacrylates. However, these amine-containing compounds are not desirable because of their color tends to change due to oxidation etc.

In this study, we perform facile synthesis of monodisperse LC oligomers by the Michael reaction[8] of millipede cyanoacetates with mesogenic acrylate **2**. We utilize the mesogenic acrylate **2** as a Michael acceptor, and not as the precursor of polyacrylates, whose synthetic process has been established, and millipede cyanoacetates as a Michael donor.

The millipede cyanoacetate **1** was synthesized by reacting pentaerythritol with excess cyanoacetic acid in the presence of *p*-toluenesulfonic acid monohydrate (Scheme 1). Further, tetra-cyanoacetate **1** was coupled with mesogenic acrylate **2**, which is responsible for LC property, by the Michael addition. The Michael addition reaction of 1 equiv. of tetra-cyanoacetate **1** and a slightly excess amount (8.1 equiv.) of mesogenic acrylate **2**[9] using an organic base catalyst 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[10] proceeded smoothly at 50 °C in 30 min. Reprecipitation was carried out twice in methanol and it produced the Michael adduct LC octamer **3** as a white powder with a high yield (93%). Although some decomposed products were produced in this basic reaction, they were removed along with the unconverted acrylate by reprecipitation. Further purifications such as column chromatography were not required. The synthetic procedures are described in detail in Supporting Information.

The formation of LC octamer **3**, which was the desired product, was confirmed by ^{1}H NMR (Figure 1), ^{13}C NMR, elemental analysis, and matrix-assister laser desorption ionization with time of flight mass spectrometer (MALDI-TOF-MS). The ^{1}H NMR spectrum of LC octamer **3** (Figure 1) showed the characteristic peaks of two methylene protons (indicated as b and c) derived from the acryl moiety for δ values in the range of 3.0–2.3. Because no peaks corresponding to the methylene (NCCH_2CO$_2$-) or methyn (NCCHRCO$_2$-) protons were observed, the methylene carbons (NCCH_2CO$_2$-) of the substrate cyanoacetate were completely converted into the quaternary carbon by the addition of the two acrylates. Thus, the octa-adduct was obtained from four-pedal alcohol through four-pedal cyanoacetate.



Scheme 1. Synthesis of LC octamer **3**.

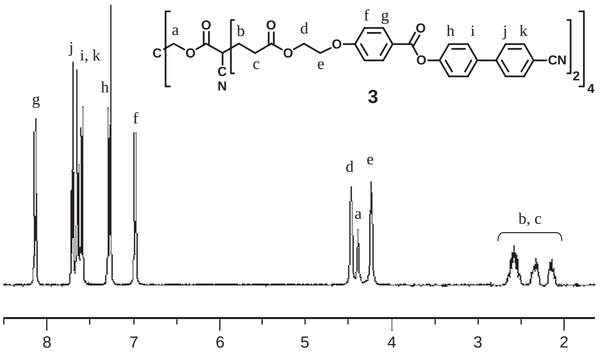


Figure 1. ^{1}H NMR spectrum of LC octamer **3**.

The methodology for obtaining multi-adducts in which the number of mesogenic moieties is twice the number of hydroxy groups of millipede alcohol through millipede cyanoacetate is further applicable to the synthesis of LC dodecamer **5** as in the case of the synthesis of LC octamer **3**. Six-pedal dipentaerythritol was selected as the precursor of the LC dodecamer. Dipentaerythritol was esterized with cyanoacetic acid to obtain six-pedal cyanoacetate **4** in 90% yield (Scheme 2). The Michael reaction of **4** (1 equiv.) and mesogenic acrylate **2** (12.5 equiv.) was carried out using DBU catalyst at 50 °C for 3 h and reprecipitation was performed twice in methanol. LC dodecamer **5** was obtained in 90% yield and it was characterized by NMR, elemental analysis, and MALDI-TOF-MS (see Supporting Information).

LC octamer **3** and dodecamer **5** were soluble in THF, cyclohexanone, dichloromethane, and amide solvents such as 1-methyl-2-pyrrolidinone (NMP) and *N*,*N*-dimethylacetamide (DMAc). The transition temperatures of these monodisperse LC oligomers were compared with those of the LC oligomer ($M_n = 4500$, $M_w/M_n = 1.26$, polystyrene as standard) that was obtained by the conventional radical polymerization of mesogenic acrylate **2** with an AIBN initiator (see Supporting Information). The transition temperatures of the LC materials were determined by DSC analysis (Seiko Instruments Inc. DSC6200) and the thermal behavior of the texture was observed using a polarizing optical microscope (Olympus BH2 polarizing microscope with a Mettler Toledo FP82 hot stage). Figure 2 shows the DSC thermograms of **3**, **5**, and the LC oligomer for the second heating scan. The scans exhibit no crystallization, thereby indicating the morphological stability of these glass-forming LC materials. The nematic phase was assigned by observing schlieren textures. The glass-transition temperature (Tg) of LC octamer **3** (78 °C) and dodecamer **5** (79 °C) were higher than those of the LC oligomer (56 °C). In contrast to a broad peak that appeared as a nematic to isotropic transition (Tc) for the LC oligomer (271 °C), sharp peaks were observed in LC octamer **3** (299 °C) and dodecamer **5** (305 °C).

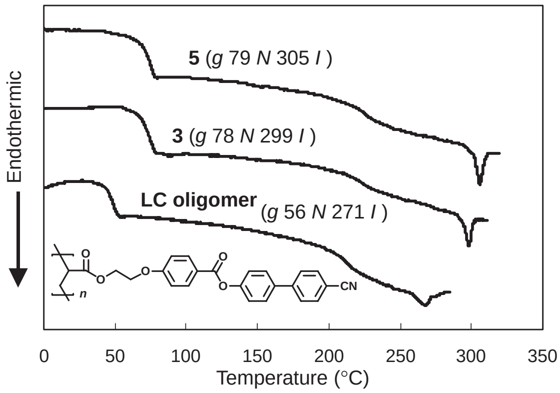
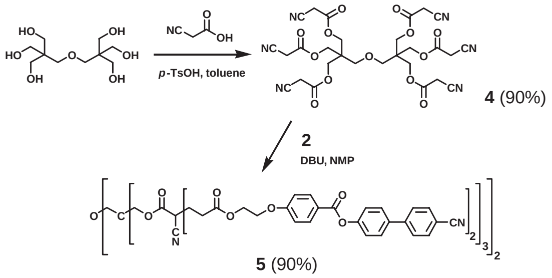


Figure 2. DSC thermograms of LC octamer **3**, dodecamer **5**, and oligomer ($M_w = 4500$, $M_w/M_n = 1.26$).



Scheme 2. Synthesis of LC dodecamer **5**.

In summary, the monodisperse LC oligomers were synthesized by the Michael addition reaction of millipede cyanoacetates (**1** and **4**) and mesogenic acrylate **2**. These oligomers are morphologically stable and have a wide nematic temperature range. This method used in this study will serve as an efficient technique for producing thin film optical components.

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References and Notes

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9 Synthetic method and characterization of the mesogenic acrylate used in this Michael reaction are described in the Supporting Information.
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