



Triazine-based Dendrimers as Liquid Crystals: Synthesis and Characterization

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A B S T R A C T

Different generations of dendritic macromolecules based on triazine were synthesized by the divergent growth approach and functionalization with mesogenic units based on peripherally located dihydroxybiphenyl derivatives. Thermotropic liquid crystal dendrimers, containing poly(ethylene glycol) (PEG) as a core and triazine dendrons with peripherals mesogenic groups were synthesized. First generation (G_1) was prepared by coupling of hydroxyl group of PEG with cyanuric chloride in dichloromethane at 0-5°C. Reaction of compound G_1 with amino group of ethanolamine in dichloromethane resulted $G_{1.5}$. Second generation of linear dendritic compounds (G_2) was synthesized using coupling reaction of hydroxyl groups of compound $G_{1.5}$ and cyanuric chloride in dichloromethane. Reaction of compound G_2 with amino group of ethanolamine in water/dioxane resulted $G_{2.5}$. The growth of dendrons on the PEG core and their structures were investigated using common spectroscopy methods. In the next step, compounds C_n with different alkyl tail groups were synthesized via nucleophilic displacement of bromine from 1-bromoalkane by potassium-4,4'-biphenoxide in DMF. The mesogenic compounds 4-bromo-(4-alkyloxy-biphenyl-4'-oxy) butane (C_nC_4Br) were synthesized by reaction with C_n and 1,4-dibromobutane undergoing S_{N2} substitution. Liquid crystalline dendrimers (LCD) were synthesized via coupling of hydroxyl group of $G_{2.5}$ and bromine from mesogenic units, 4-bromo-(4-alkyloxy-biphenyl-4'-oxy) butane. The liquid crystal property of mesogenic compound has been studied in details with differential scanning calorimetry and optical polarization microscopy. The experiments showed that the thermal properties are influenced with the spacer length.

Key Words:

dendrimer;
triazine;
liquid crystal;
DSC;
polarized optical micrograph.

INTRODUCTION

In recent years, liquid crystalline supramolecular dendritic architectures have attracted the interest of many researchers [1-4]. Thermotropic liquid crystalline materials with dendritic architecture have received a lot of attention in the past decade. The monodisperse character of dendritic molecules and the shape persistence of their three-dimensional conformation

play an important role in these applications. Recently liquid crystalline dendrimers have proven to be an interesting new family of (polymeric) mesogenic compounds with dimensions and molecular weights between low molecular weight mesogens and polymers [5,6]. Dendritic properties like the absence of entanglements and the high local concentration of end

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groups, explain the interest in dendritic mesogenic molecules as potential liquid-crystalline materials with an interesting balance in viscosity and thermodynamic stability [7]. Thermotropic liquid crystals play a crucial role in everyday life (watches, calculators, mobile telephones, and notebook computers) and are essential liquid crystalline dendrimers which are interesting materials for basic studies and applications purposes. Various dendrimers have been reported such as AB₂-type dendrimers [8-10]. In 1992, Percec et al. described the first example of LC dendrimers [11]. There are two general approaches to the synthesis of this type of materials. The first one, mesogenic units are introduced within the branches in each dendrimer generation; the second synthetic approach is based on the functionality of the dendrimer terminal groups. Dendritic structure containing mesogenic groups that can display mesophase behaviour [12,13]. The mesogenic groups can be located along chains of the molecules or can occur as terminal groups. Liquid crystal dendrimers or dendromesogens behave as a specific class in the field of LCPs. The functionalization of the terminal reactive groups of dendrimers by means of promesogenic structures allows us to obtain different types of LC phases. As a new class of materials, in recent years, dendrimers have generated a great deal of interest within the scientific community [14]. One of the important features is the reactivity of the terminal groups into which we can introduce new moieties with specific functions. This makes it possible to modulate the properties of these dendrimer derivatives. Among this fascinating class of highly functional compounds, dendrimer containing thermotropic liquid crystal (LC dendrimers) is of special interest because of the possibility of creating controlled multifunctional macromolecular objects that are able to self-assemble into large organized assemblies [15]. LC dendrimers can be regarded as block molecules in analogous to block copolymers, in that the dendritic core and the functionalized terminal groups (mesogenic, promesogenic or non-mesogenic) will tend to microphase separate because of their incompatible chemical natures. The mesomorphic properties (phase type, transition temperature, and thermodynamic stability) thus highly depend on the enthalpy/entropy balance (core conformation), the

degree of chemical incompatibility, and the sizes of the different building blocks (and thus of the micro-segregated domains), as well as the structure of the mesogenic unit itself and its location in the dendrimer [16]. In general the terminal units determine the dendritic architecture being used as the scaffold only. Previously, Zhang et al. described the functionalization of pentaerythritol-based dendrimers with nitroazobenzene mesogenic groups resulting in dendritic liquid crystalline polymers showing wider mesophase region temperature comparing the primary mesogenic unit [17]. On the other hand, in recent decades, there has been interest in the synthesis and characterization of compounds containing a 1,3,5-triazine unit, owing to their interesting properties, such as liquid crystalline and non-linear optical properties as well as their applications in other fields. Liquid crystalline compound containing a 1,3,5-triazine unit has been reported by many researchers [18-20]. Lee et al. reported a new class of 2,4,6-triphenyl-1,3,5-LC-triazine derivative [21]. Meijer et al. reported star-shaped compound with a 1,3,5-triazine core and peripheral alkoxy groups represent octupolar structures. Mesophases of star-shaped triazine systems were found in the past for some dendritic compounds units [22]. From the synthetic view point, the mesogenic 1,3,5-triazine compounds with various nucleophilic side groups may be easily incorporated with the triazine ring by their reaction with cyanuric chloride, showing discotic as well as calamitic morphological behaviours depending on their structures. Recently Lai et al. reported LC dendrimers based triazine and piperazine units, which exhibit a monotropic hexagonal columnar phase [23]. Recently we reported the synthesis of barbell-like tri-block copolymers, dendritic triazine-block-(polyethylene glycol)-block-dendritic triazine and other dendritic macromolecules and investigation of their behaviours [24-28]. In this work, we have reported a divergent synthesis and the structural analysis of different generations of triazine based dendrimers with polymeric core and functionalization of these dendrimers, bearing mesogenic groups based on 4,4'-dihydroxy biphenyl derivatives with different spacer groups located peripherally. Then, we studied the liquid crystalline properties of both the mesogenic

unit and the mesogen-functionalized dendrimer that are described in details.

EXPERIMENTAL

Materials

Poly(ethylene glycol) 1000, cyanuric chloride, 4,4'-dihydroxy biphenyl, ethanolamine, 1,4-dibromobutane, 1-bromohexane, 1-bromooctane, 1-bromodecane and tetra *n*-butylammonium fluoroborate were purchased from Merck.

Instrumental Measurements

The NMR spectra were recorded on 400 MHz Bruker SP-400 AVANC in CDCl₃ and DMSO-d₆. IR spectra were measured on a Shimadzu Model FTIR-8101M spectrometer. A differential scanning calorimeter STA 625 was used to determine phase transition temperatures at heating and cooling rates of 10°C/min in air atmosphere. An optical Zeiss polarizing microscope equipped with long working distance objective was also used to observe phase transitions. The samples were heated and cooled with a TMS94 hot stage and associated temperature controller.

Synthesis

Syntheses of G₁, G_{1.5}, G₂, G_{2.5} were synthesized through divergent method using PEG (1000) as a core with a similar route reported in literature [24]. For preparation of functionalized dendrimers, first a mesogenic compound was synthesized through a modified method [26].

Synthesis of G₁ and G_{1.5}

Compound G₁ was synthesized using literature method [24]. An excess of ethanolamine (1.88 g, 3×10⁻² mol) was added dropwise to a solution of G₁ (2 g, 1.54×10⁻³ mol) in 20 mL dichloromethane at room temperature. The mixture was stirred at room temperature for 1 h and then it was refluxed for additional 8 h. After being cooled, the solvent as well as the excess ethanolamine were evaporated under vacuum. For removing traces of ethanolamine, crude product was dissolved in 3×10 mL dichloromethane, and the solution was left for 1 h before a trace of

diethanolamine being separated by decantation. Solvent was evaporated and product was separated as a colourless viscous compound with 95% yield. FTIR: ν cm⁻¹ 3358 (O-H), 2874 (C-H), 1572, 1519 (C=N), 1104 (C-O). ¹H NMR (CDCl₃): δ 3.49-3.52 (N-CH₂), 3.56-3.60 (PEG), 3.61-3.66 (-OCH₂O-triazine) 3.71 (-CH₂OH). ¹³C NMR (CDCl₃) (419, -NCH₂), (60, -CH₂OH), (69, 71, PEG, -OCH₂O-triazine), (172, triazine part).

Synthesis of G₂

A solution of G_{1.5} (2 g, 1.43×10⁻³ mol) and sodium hydroxide (0.23 g, 5.73×10⁻³ mol) in 10 mL of water was added to a solution of cyanuric chloride (5.3 g, 2.8×10⁻² mol) in 50 mL dichloromethane at 0°C. The mixture was stirred at 0°C for 1 h, and at room temperature for 2 h and it was then refluxed for additional 12 h. The resulting mixture was cooled and filtered off and the solvent was removed and crude compound was washed with THF, DMF, and methanol. The purified compound was obtained as a white solid with 4.5 g, 91% yield. FTIR: ν cm⁻¹ 2874 (C-H), 1572, 1519 (C=N), 1104 (C-O). ¹H NMR (DMSO-d₆): δ 3.64-3.65 (N-H), 3.69 (-CH₂-NH), 3.56-3.60 (PEG), 3.76-3.78 (-CH₂O-triazine). ¹³C NMR (DMSO): 41, 42 (ethanolamine portion), 71 (-CH₂O-triazine), (69, PEG), 147-157 (triazine part).

Synthesis of G_{2.5}

An excess of ethanolamine (2.45 g, 4×10⁻² mol) was added to a solution of G₂ (2 g, 1×10⁻² mol) in 40 mL of water/dioxane or water/THF dropwise at room temperature. The mixture was then stirred at room temperature for 1 h and refluxed for additional 24 h. It was cooled and the solvent was evaporated under vacuum. For purification, the crude product was dissolved in 10 mL water followed by addition of methanol and the pure product was separated as a white solid with 4.1 g, 93% yield. FTIR: ν cm⁻¹ 2920-3250 (O-H), 2874 (C-H), 1574, 1529 (C=N), 1708 (C-O) cm⁻¹. ¹H NMR (DMSO-d₆): δ 3.35-3.41 (-NH-CH₂), 3.64-3.71 (methylene proton of the interior ethanolamine part), 3.49-3.54 (PEG), 3.55-3.57 (-OCH₂O-triazine), 3.73-3.76 (N-H), 3.91-3.95 (-CH₂-OH). ¹³C NMR (CDCl₃): 40.5 (-NCH₂), 59 (-CH₂OH), 69 (PEG), (165, 169 triazine part).

Synthesis of Mesogenic Compounds

General Synthetic Procedures of 4-Hydroxy-4'-alkyloxybiphenyl (C_n)

A procedure for the synthesis of 4-hydroxy-4'-hexyloxybiphenyl through the modified method for C_6 is given in the literature, and likewise the C_8 and C_{10} compounds were synthesized and purified similar to literature route [29]. Thus a solution of 4,4'-biphenol (4.09 g, 2.3×10^{-2} mol) and potassium carbonate (1.52 g, 1.1×10^{-2} mol) in 50 mL of dry DMF was heated. 1-Bromoalkane (2.3×10^{-2} mol) was added dropwise, over a period of 30 min.

The mixture was refluxed for 12 h, after this time the white precipitate was filtered hot to ensure the complete removal of any produced potassium bromide salt and side products. The mixture was cooled, solvent was evaporated under vacuum. For purification, the crude product was washed with water and recrystallized in ethanol with 0.8 g, 70% yield, mp 158°C. FTIR (KBr) ν cm^{-1} 3286 (OH), 3041 (C-H, aromatic), 2930 (CH_2), 1612 (aromatic), 1254 to 1177 (R-O-Ar). ^1H NMR (CDCl_3): δ 7.46-7.41 (dd, 4H aromatic, *ortho* to -O), 6.92-6.95 (dd, 4H aromatic, *meta* to -O), 4.89 (s, OH phenolic), 3.98 (t, 2H, CH_2 , α to -OAr), 1.79 (m, 2H, CH_2 , β to -OAr), 1.47-1.43 (m, 2H, CH_2 , γ to -OAr), 1.34-1.28 (m, 4H, CH_2), 0.88 (t, 3H, CH_3) ppm.

4-Hydroxy-4'-octyloxybiphenyl (C_8)

Yield 0.9 g, 75% mp 152°C. FTIR (KBr): ν cm^{-1} 3284 (OH), 3041 (C-H aromatic), 2865, 2934 (CH_2), 1609 (aromatic), 1250-1177 (R-O-Ar). ^1H NMR (CDCl_3): δ 7.4-7.44 (dd, 4H aromatic, *ortho* to -O), 6.87-6.94 (dd, 4H aromatic, *meta* to -O), 4.89 (s, OH phenolic), 3.98 (t, 2H, CH_2 , α to -OAr), 1.79 (m, 2H, CH_2 , β to -OAr), 1.47-1.43 (m, 2H, CH_2 , γ to -OAr), 1.34-1.28 (m, 8H, CH_2), 0.88 (t, 3H, CH_3) ppm.

4-Hydroxy-4'-decyloxybiphenyl (C_{10})

Yield 0.8 g, 78% mp 141°C. FTIR (KBr) ν cm^{-1} 3284 (OH), 3041 (C-H, aromatic), 2934 (CH_2), 1609 (aromatic), 1250-1177 (R-O-Ar). ^1H NMR (CDCl_3): δ 7.46-7.41 (m, 4H aromatic, *ortho* to -O), 6.96-6.87 (dd, 4H aromatic, *meta* to -O), 4.89 (s, OH phenolic), 3.98 (t, 2H, CH_2 , α to -OAr), 1.79 (m, 2H, CH_2 , β to -OAr), 1.43-1.47 (m, 2H, CH_2 , γ to -OAr), 1.34-1.28 (m, 12H, CH_2), 0.88 (t, 3H, CH_3) ppm.

General Synthetic Procedures of ω -Bromo-(4-alkyloxy-biphenyl-4'-oxy)alkane ($C_nC_m\text{Br}$)

The synthesis of 4-bromo-(4-hexyloxybiphenyl-4'-oxy) butane ($C_6C_4\text{Br}$) was described in literature [30]. Compounds $C_8C_4\text{Br}$ and $C_{10}C_4\text{Br}$ were synthesized and purified by similar route.

4-Bromo-(4-hexyloxy-biphenyl-4'-oxy)butane ($C_6C_4\text{Br}$)

A volume of 1,4-dibromobutane (3.08 mL, 23×10^{-3} mol) was added to a mixture (4.9×10^{-3} mol) of C_n and (0.13 g, 0.24×10^{-3} mol) TBA and (0.62 g, 15×10^{-3} mol) sodium hydroxide in 30 mL of THF/ H_2O (1:1, v/v) over a period of 45 min under reflux condition. After 24 h the white precipitate was filtered out. The resulting mixture was concentrated, dissolved in chloroform and reprecipitated with excess of *n*-hexane. The product was recrystallized from ethanol.

Yield 0.6 g, 64%. FTIR (KBr) ν cm^{-1} 3041-3068 (C-H, aromatic), 2872-2936 (CH_2), 1607 (C=C), 1241 (R-O-Ar), 589 (C-Br). ^1H NMR (CDCl_3): δ 7.47-7.43 (dd, 4H aromatic, *ortho* to -O), 6.96-6.91 (dd, 4H aromatic, *meta* to -O), 4.02-3.97 (t, 4H, CH_2 , α to -OPh), 3.50 (t, 2H, CH_2 , α to Br), 2.1-2.05 (m, 2H, CH_2 , β to Br), 1.99-1.7 (m, 4H, CH_2 , β to -OPh), 1.48-1.32 (m, 6H, CH_2), 0.91 (t, 3H, CH_3) ppm.

4-Bromo-(4-octyloxy-biphenyl-4'-oxy)butane ($C_8C_4\text{Br}$)

Yield 0.55 g, 57%. FTIR (KBr) ν cm^{-1} 3041-3068 (C-H, aromatic), 2872-2936 (CH_2), 1607 (C=C), 1241 (R-O-Ar), 589 (C-Br). ^1H NMR (CDCl_3): δ 7.47-7.43 (dd, 4H aromatic, *ortho* to -O), 6.96-6.91 (dd, 4H aromatic, *meta* to -O), 4.02-3.97 (t, 4H, CH_2 , α to -OPh), 3.50 (t, 2H, CH_2 , α to Br), 2.1-2.05 (m, 2H, CH_2 , β to Br), 1.99-1.7 (m, 4H, CH_2 , β to -OPh), 1.48-1.32 (m, 10H, CH_2), 0.91 (t, 3H, CH_3) ppm.

4-Bromo-(4-decyloxy-biphenyl-4'-oxy)butane ($C_{10}C_4\text{Br}$)

Yield 0.52 g, 53%. FTIR (KBr) ν cm^{-1} 3041-3068 (C-H, aromatic), 2872-2936 (CH_2), 1607 (C=C), 1241 (R-O-Ar), 589 (C-Br). ^1H NMR (CDCl_3): δ 7.47-7.43 (dd, 4H aromatic, *ortho* to -O), 6.96-6.91 (dd, 4H aromatic, *meta* to -O), 4.02-3.97 (t, 4H, CH_2 , α to O), 3.50 (t, 2H, CH_2 , α to Br), 2.1-2.05 (m, 2H,

CH₂, β to Br), 1.99-1.7 (m, 2H, CH₂, β to -OPh), 1.48-1.32 (m, 14H, CH₂), 0.91 (t, 3H, CH₃) ppm.

Synthesis of Functionalized LC Dendrimer Compounds

General Synthetic Procedures of LCD-C_nC_m

C_nC_mBr (23 × 10⁻³ mol) in 5 mL dichloromethane was added dropwise to a mixture of solution of G_{2.5} (0.41 g, 2.3 × 10⁻⁴ mol) and sodium hydroxide (1.52 g, 1.1 × 10⁻² mol) in 50 mL of THF/H₂O/CH₂Cl₂ or water/dioxane/CH₂Cl₂ (1:1:1 v/v/v) and (0.13 g, 0.24 mmol) TBA and then was refluxed for additional 24 h. This mixture was cooled and the solvent was evaporated. The crude product was dissolved in 10 mL THF/CH₂Cl₂ and was precipitated in diethyl ether at 0°C four times. The purified product was obtained as a white solid.

General Synthetic Procedures of LCD-C₄C₆

Yield 1.5 g, 70%. FTIR (KBr) ν cm⁻¹ 3041-3068 (C-H, aromatic), 2872-2936 (CH₂), 1708 (C-O), 1607 (C=C), 1574, 1529 (C=N). ¹H NMR (DMSO-d₆): δ 7.44 (d, C-H aromatic, *ortho* to -O), 6.92 (d, C-H aromatic, *meta* to -O), 3.61-4.01 (b, methylene proton of ethanolamine, CH₂, α to O-Ar), 3.49-3.54 (PEG), 3.35-3.41 (-NH-CH₂), 3.31 (CH₂, α to O), 1.67-1.75 (m, CH₂, β to -OPh), 1.30-1.41 (m, CH₂), 0.89 (m, CH₃) ppm. ¹³C NMR (CDCl₃): 69.1 (PEG), (165.4, 169.7 triazine part), 156.29, 152.35, 146.76, 142, 68, 126.05, 124.97, 122.45, 111.70 (aromatic part), 58, 21, 53.38, 41.5, 58.6, 27.30, 25.23, 24.88, 20.76.

General Synthetic Procedures of LCD-C₄C₈

Yield 1.2 g, 67 %. FTIR (KBr) ν cm⁻¹ 3043-3060 (C-H, aromatic), 2869-2931 (CH₂), 1712 (C-O), 1607 (C=C), 1574, 1529 (C=N). ¹H NMR (DMSO-d₆): δ 7.38 (d, C-H aromatic, *ortho* to -O), 6.87 (d, C-H aromatic, *meta* to -O), 3.64-4.05 (b, methylene protons of ethanolamine, CH₂, α to O-Ar), 3.49-3.54 (PEG), 3.35-3.41 (-NH-CH₂), 3.28 (CH₂, α to O), 1.63-1.70 (m, CH₂, β to -OPh), 1.34-1.45 (m, CH₂), 0.89 (m, CH₃) ppm. ¹³C NMR (CDCl₃): 69.1 (PEG), (165.4, 169.7 triazine part), 155.74, 153.87, 148.06, 145.97, 141.93, 125.52, 123.94, 120.66, 110.58 (aromatic part), 63.71, 60.28, 57.44, 53.51, 33.36, 29.91, 28.77, 27.65, 23.43 (CH₂).

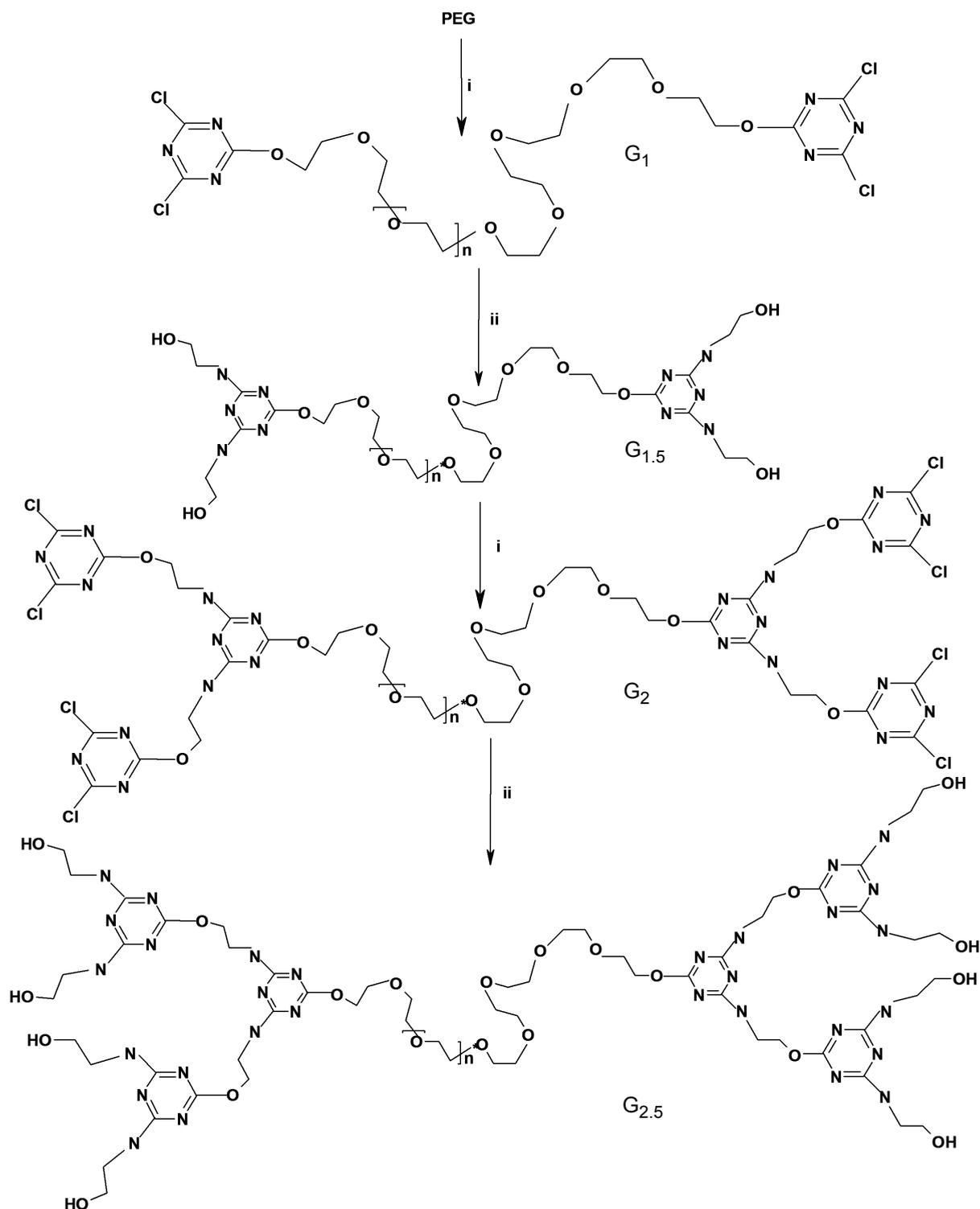
General Synthetic Procedures of LCD-C₄C₁₀

Yield 0.9 g, 50 %. FTIR (KBr) ν cm⁻¹ 3039 -3058 (C-H, aromatic), 2867-2924 (CH₂), 1710(C-O), 1605 (C=C), 1571, 1530 (C=N). ¹H NMR (DMSO-d₆): δ 7.40 (d, C-H aromatic, *ortho* to -O), 6.88 (d, C-H aromatic, *meta* to -O), 3.67-3.99 (b, methylene protons of ethanolamine, CH₂, α to O-Ar), 3.51-3.60 (PEG), 3.35-3.41 (-NH-CH₂), 3.33 (CH₂, α to O), 1.65-1.77 (m, CH₂, β to -OPh), 1.30-1.41 (m, CH₂), 0.89 (m, CH₃) ppm. ¹³C NMR (CDCl₃) 69.5 (PEG), (164.7, 169.2 triazine part), 165.30, 155.38, 146.75, 146.12, 126.07, 125.50, 124.98, 123.17, 122.30, 111.71 (aromatic part), 34.82, 30.45, 29.02, 27.30, 25.23, 24.88, 20.76 (CH₂).

RESULTS AND DISCUSSION

Compound G₁ was synthesized through a divergent method reported in literature [24] and compounds G_{1.5}, G₂ and G_{2.5}, were synthesized using similar method. Compound G₁ was synthesized using PEG (1000) as a core and cyanuric chloride in the presence of sodium hydroxide in dichloromethane as a solvent. Compound G_{1.5} was synthesized by reaction between compound G₁ and ethanolamine. The molecular structures of supramolecular dendrimers are depicted in Scheme I. For preparation of mesogenic compound, C₆ was synthesized via nucleophilic displacement of bromine from 1-bromohexane by potassium-4,4'-biphenoxide [29]. The mesogenic compound C₆C₄Br was synthesized by reaction with C₆ and 1,4-dibromobutane undergoing S_N2 substitution and purified with modified route reported [30]. The mesogenic compounds C₈, C₁₀, C₈C₄Br and C₁₀C₄Br were successfully synthesized by similar route. The structures of C_n and C_nC₄Br (Scheme II) compounds were characterized using FTIR, ¹H NMR, and ¹³C NMR. Synthetic route of O-substituted dendrimers with mesogenic group is shown in Scheme III. LC-dendrimers were synthesized via nucleophilic displacement of bromine from C_nC₄Br by hydroxyl end group of dendrimer in the presence of sodium hydroxide in mixture of solvents.

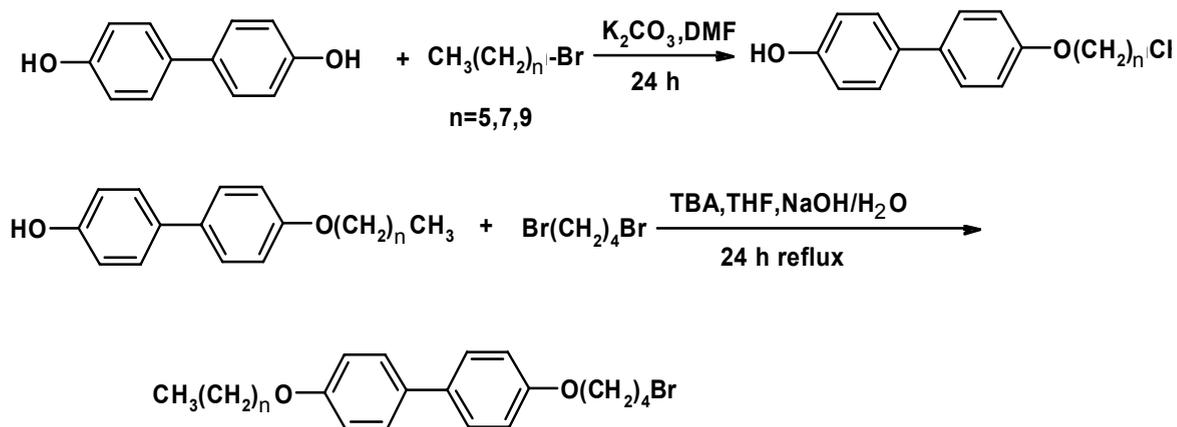
The degree of substitution calculated from ¹H NMR signals in regions 6.9-7.8 and 3.5-3.6 ppm corresponds to aromatic rings of mesogenic units and



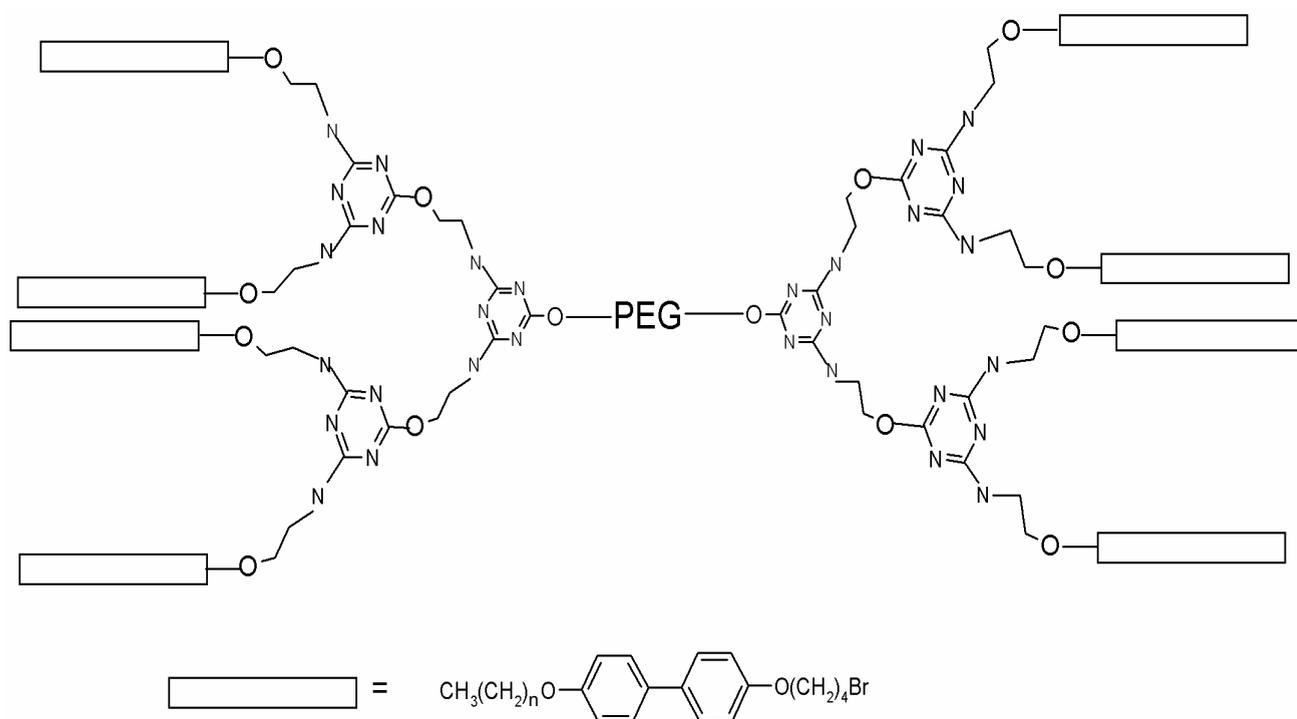
Scheme I. Synthesis of supramolecular dendrimers, (i): NaOH, triazine, CH_2Cl_2 , (ii): ethanolamine, CH_2Cl_2 .

PEG (for example, Figure 1). ^1H NMR signals at 7.49-7.51 and 3.49-3.56 ppm correspond to the newly formed terminally substituted biphenyl group on C_nC_4 -dendrimer. The ratio of ^1H NMR signals in

region 7.49-7.51 ppm (corresponding to C-H aromatic, *ortho* to -OPh) to 3.49-3.56 (corresponding to PEG protons) gives the degree of substitution. The degree of substitution calculated from ^1H NMR showed all



Scheme II. Synthesis of mesogenic units.



Scheme III. Synthesis of liquid crystal dendrimer.

LCDs having 8 peripheral mesogenic groups.

The thermal behaviours, melting temperature (T_m), and isotropization temperature (T_i) of these compounds were studied using polarizing optical microscopy (POM) with a heating stage and differential scanning calorimetry (DSC). The DSC thermogram of the $\text{C}_8\text{C}_4\text{Br}$ exhibits a melting temperature of 115°C . On cooling $\text{C}_8\text{C}_4\text{Br}$, two exothermic transitions are observed at 113°C and 78°C corresponding to the isotropic-mesophase and crystallization transitions, respectively. Furthermore,

polarizing microscopic observation confirms the S_A liquid crystalline phase for $\text{C}_8\text{C}_4\text{Br}$ on cooling process. The focal conic texture formation of the smectic phase is observed from isotropic phase in cooling process. The heating process of $\text{C}_{10}\text{C}_4\text{Br}$ showed two endothermic peaks at 58°C and 109°C . The peak appearing at the lower temperature might be associated with a solid-solid transition. The endothermic peaks positioned at the higher temperatures were found to undergo isotropization. On cooling $\text{C}_{10}\text{C}_4\text{Br}$ it seemed that two exothermic peaks are appeared at

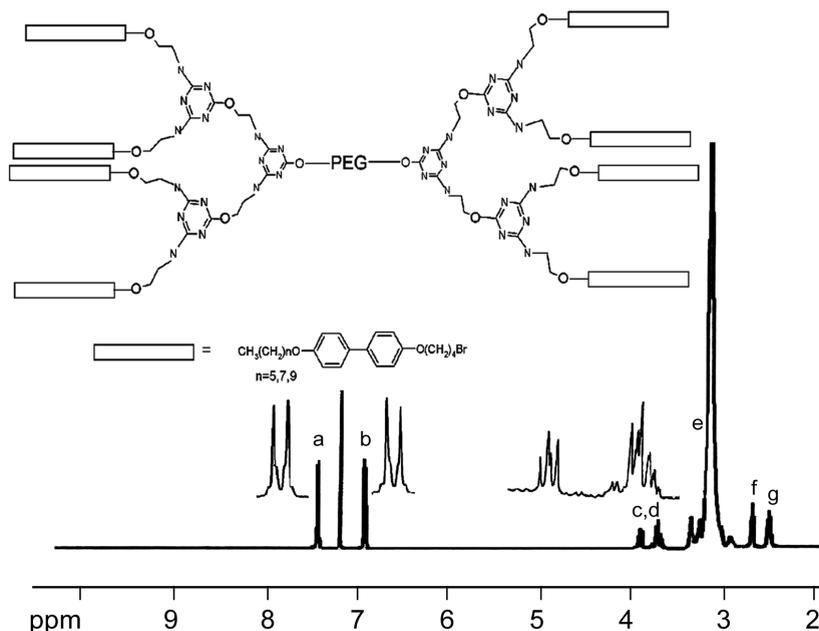


Figure 1. ¹H NMR spectrum of LCD-C₄C₈ in CDCl₃.

95°C and a fairly small exothermic peak at 61°C. The first broad peak corresponds to overlapped isotropic-mesophase and crystallization transitions and the second to solid-solid transition. The polarizing microscopic observation of C₁₀C₄Br showed the texture formation of the smectic phase. Transition temperatures of C₁₀C₄Br and C₆C₄Br are presented in Table 1.

The transition temperatures of all dendrimers were determined by DSC measurements at a heating rate of 10°C/min and examined under an optical polarized microscope to confirm the existence of the liquid crystalline phase.

Table 1. Phase transition temperatures of the C_nC₄Br and LCD-C₄C_n determined by DSC at a scan rate of 10°C/min on the first heating and cooling scans and microscope observation.

Sample	First heating (°C)	First cooling (°C)
C ₆ C ₄ Br ^[30]	K 116 S _A 119 I	I 115 S _A 111 K
C ₈ C ₄ Br	K 114 I	I 113 S _A 78 K
C ₁₀ C ₄ Br	K 58 K 109 I	I 95 S _A 89* K 61 K
LCD-C ₄ C ₆	K 97 S 106 N 145 I	I 143 N 90 S 74 K
LCD-C ₄ C ₈	K 91 S 109 N 141 I	I 139 N 97 S 69 K
LCD-C ₄ C ₁₀	K 84 S 102 N 138 I	I 136 N 89 S 60 K

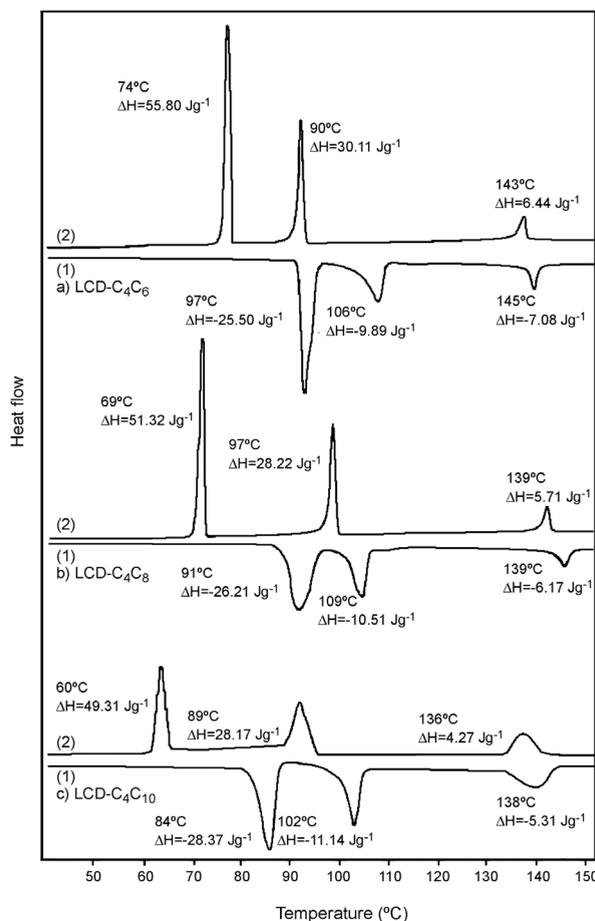


Figure 2. DSC thermograms for LCD-C₄C_n with a heating rate of 10°C/min: (1) heating and (2) cooling.

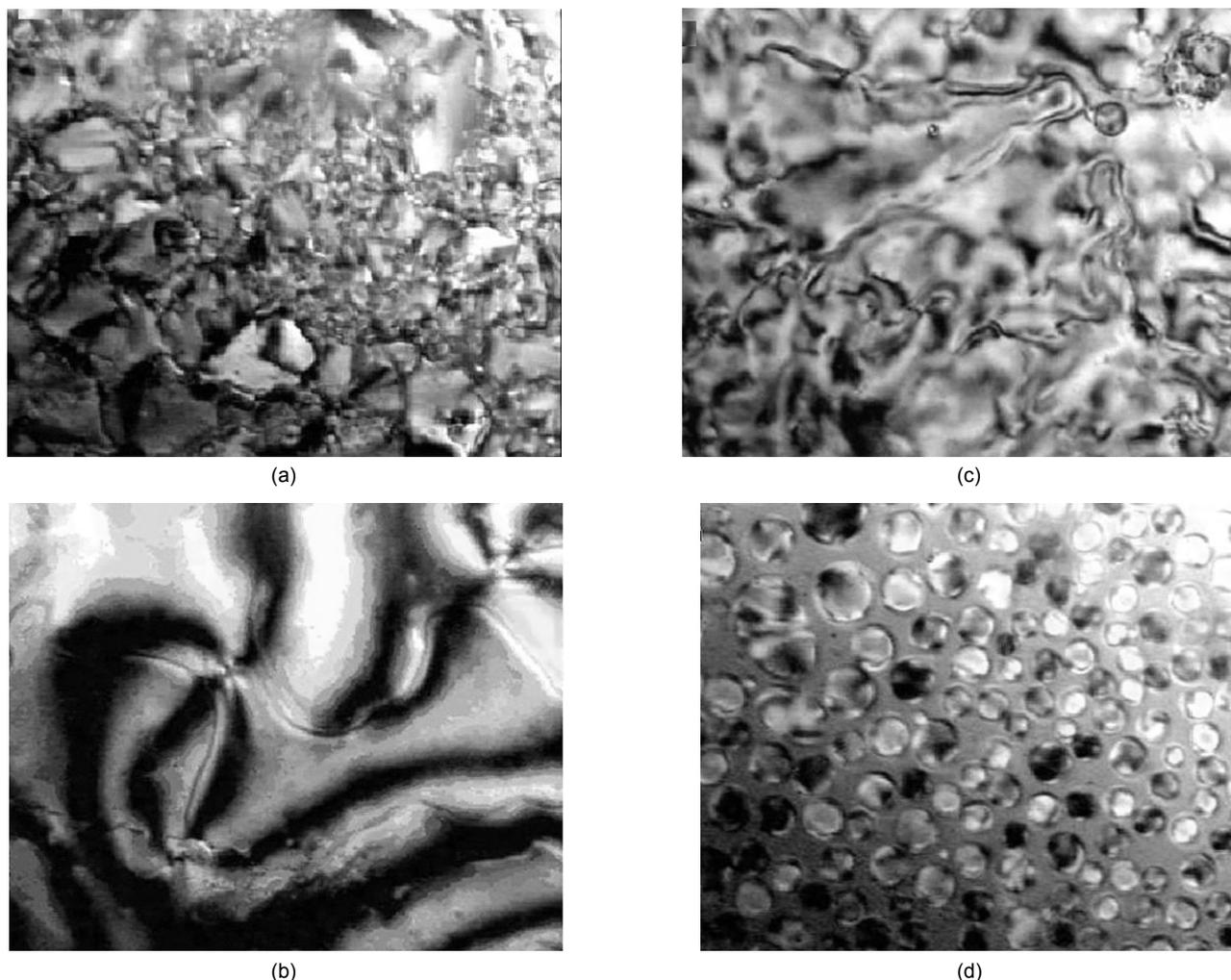


Figure 3. Optical polarized micrographs for LCD- C_4C_6 on cooling at: (a) 108°C and (b) 138°C , (c) LCD- C_4C_8 on heating at 106°C , and (d) LCD- C_4C_{10} on cooling at 138°C .

The DSC thermograms (Figure 2) of liquid crystalline dendrimer with peripherally substituted C_4C_6 -mesogenic group showed three exothermic transitions at 97°C , 106°C , and 145°C corresponding to crystal-mesophase, mesophase-mesophase, and isotropization transitions. The peaks were also observed on cooling process at 143°C , 90°C , and 74°C . The first small peak corresponds to isotropic-mesophase, mesophase-mesophase, and the third to the crystallization transitions. The polarizing microscopic observation of LCD- C_4C_6 showed the fan-shaped texture formation of S_A phase on cooling at 109°C and Schliere texture formation of nematic phase on cooling processes at 140°C . Figure 3 illustrates the textures of LCD- C_4C_6 . Transition temperatures and DSC thermograms of $C_{10}C_4$ -

dendrimer and C_8C_4 -dendrimer are presented in Table 1 and Figure 2.

Comparing the mesophase region temperature of mesogen-functionalized dendrimer wider than the mesogenic unit. For example, mesophase region temperature of dendrimer in LCD- C_4C_6 is about 45°C , while the mesogenic unit is 6°C .

CONCLUSION

The new low molecular weight liquid crystalline compounds, 4-bromo-(4-octyloxy-biphenyl-4'-oxy) butane ($C_8C_4\text{Br}$), 4-bromo-(4-decyloxy-biphenyl-4'-oxy) butane ($C_{10}C_4\text{Br}$), and new series of thermotropic liquid crystalline dendrimers containing

peripheral biphenyl mesogenic group, LCD-C₄C₆, LCD-C₄C₈, and LCD-C₄C₁₀ were synthesized and characterized. The results of DSC thermograms and POM observation showed focal conic texture formation of smectic A phase for C₈C₄Br, C₁₀C₄Br, and Schlirene texture and fan-shaped texture characteristic of smectic phase and nematic phase for LCD-C₄C₆, LCD-C₄C₈ and LCD-C₄C₁₀.

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