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Synthesis, characterization and mesomorphic properties of side chain liquid crystalline oligomer having schiff base type mesogenic group

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ABSTRACT

A new liquid crystalline oligomer OLC was synthesized from its monomer having Schiff-base type mesogenic group MLC via free radical polymerization. The chemical structures of all compounds were confirmed using UV, FTIR, ^{1}H NMR, ^{13}C NMR and MS spectroscopy. Schiff-base type thermotropic system based on side chain oligomer containing long aliphatic branching was studied to determine the change in mesophase behaviour of the Schiff-base type mesogenic groups. A combination of differantial scanning calorimetry (DSC) and polarize optical microscopy (POM) demonstrated that the oligomer behaves similar to its monomer and both of them exhibit enantiotropic SmC and monotropic SmX mesophases. The oligomerization of the liquid crystal monomer gives rise to decreased transition temperatures whereas it has no influence on the type and stability of the mesophase formed. Namely, simply through oligomerization, we can greatly vary transition temperatures of the mesogenic groups. Copyright © 2014 VBRI press.

Keywords: Liquid crystal, schiff base, liquid crystal homopolymers, side chain liquid crystalline oligomer.

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Introduction

Side-chain liquid crystalline polymers (SLCPs), which represent a combination of liquid crystalline behavior and polymeric properties, have been the subject of intensive research during the last decade. The liquid crystallinity and physical properities of LCPs depend on the molecular structures chosen for polymer design **[1]**.

Design and synthesis of side-chain or comb-like liquid crystalline polymers containing mesogenic groups attached through a flexible spacer to the central polymer backbone attract great interest, since these polymers are regarded as materials with promising optical and electro-optical properties for potential applications in optical switching and image storage.

Various properties of Schiff base polymers, such as heat stability, catalysis, spesific separations, preconcentration of trace metal ions and semiconductor properties **[2]** have been reported **[3]**. Terminal groups are one of the important molecular fragments to form Schiff base liquid crystals. There are different terminal substituents affianced that are either a small polar substituent alkyl or alkoxy chains. It is well known that at least one alkyl or alkoxy chain is necessary for the molecular orientation necessary for liquid-crystal phase generation **[4]**. Schiff base type mesogens such as salicylaldimines are stabilized by intramoleculer hydrogen bonding **[5,6]**.

Salicylaldimine compounds have a wide variety of structural types and been employed in the synthesis of metallomesogens due to their synthetic versatility and ability to coordinate metals.**[7]** The organic salicylaldimine-based liquid crystals are thermally and hydrolytically stable on account of the presence of intramolecular hydrogen bonding between the hydroxy group and the imine group. In general, these salicylaldimine compounds that have two-ring ligand systems with two flexible chains or a lateral polar substituent and one flexible chain or three-ring systems with two flexible chains usually exhibit nematic, smectic A and smectic C mesophases.**[8–12]**

In our previous works, we reported the synthesis and characterization of several of schiff base type liquid crystals and the structure-property relationships in different molecular types **[13-15]**, for example, vinyl-terminated salicylaldimine monomers and side chain polymer containg salicylaldimine **[16]**, flourinated imine compounds **[17]**, salicyaldimine compounds and their metal complexes **[18]**.
In this paper, a new Schiff-base type thermotropic system based on side chain oligomer containing long aliphatic branching was studied to determine the change in mesophase behaviour of the Schiff-base type mesogenic groups. Their LC behaviors were studied by means of optical polarizing microscopy (POM), and differential scanning calorimetry (DSC).

Experimental

Materials

p-Nitrophenol, 2-butanon, 1-bromhexadecan, $KHCO_3$, toluene, acetone, methanol were purchased from Merck Chemical Reagent CO. Ltd., 11-brom-1-undecene (≥96%) was purchased from Alfa Aeasar Chemical Reagent CO. Ltd., 2,4-dihydroxybenzaldehyde was purchased from ABCR Chemical Reagent CO. Ltd., AIBN and Pd/C (karsted catalyst) were purchased from Aldrich Chemical Reagent CO. Ltd., all regents used as received without further purification.

Table 1. Synthesis and characterizations of oligomer[a].

Oligomer	Monomer (mol/L)	Time (Day)	Conversion (%)	M_n [b]	M_w/M_n
OLC	**MLC** (0.082)	7	72.5	1267	1.162

[a] [AIBN] = 0.012 mol/L; solvent $CHCl_3$.
[b] Determined by GPC based on polystyrene standards.

Synthesis of vinyl-terminated Schiff's Base Monomer MLC

The vinyl-terminated Schiff-base monomer 5-(10-undecenyloxy)-2-[[[4-hexadecyloxyphenyl] imino]methly]-phenol was prepared as previously described [19]. Reaction of p-nitro phenol (30 mmol) in the presence of K_2CO_3 (30 mmol) with 1-bromhexadecan (30 mmol) in 2-Butanon (150 ml) as a solvent yielded 4-hexadecyloxynitrobenzene (1), as described previously. The reaction proceeds at 75 °C for 9 h in Ar atmosphere. Catalytic reduction of compound 1 (30 mmol) by Pd/C (karsted catalyst) (%10) in ethyl acetate (50 ml) as solvent gave corresponding aniline 2. The reaction proceeds at 40 °C for 24 h in H2 atmosphere. The compound 3 was obtained by the reaction of 2,4-dihydroxybenzaldehyde (30 mmol) with 11-brom-1-undecene (30 mmol) in the presence of $KHCO_3$ (30 mmol) as a base and 2-Butanon (150 ml) as a solvent. The reaction proceeds at 75 °C for 8 h in Ar atmosphere. p-Toluenesulfonic acid (80 mg) catalyzed condensation reaction of 2-hydroxy-4-(10-undecenyloxy) benzaldehyde (5 mmol) (3) with 4-hexadecyloxyaniline (6 mmol) (2) in toluene (50 ml) gave the Schiff -base monomer MLC. The reaction proceeds at 110 °C for 5 h in Ar atmosphere. The monomer MLC was purified by recrystallization from acetone/methanol. Yellow crystalline product was obtained and dryed. (Yellow crystals, 1,36 g, %45 yield of MLC). The synthesis of the monomer is presented in **Scheme 1**. The chemical structure of MLC was characterized by using UV, FTIR, ^{1}H NMR, ^{13}C NMR and MS spectroscopy.

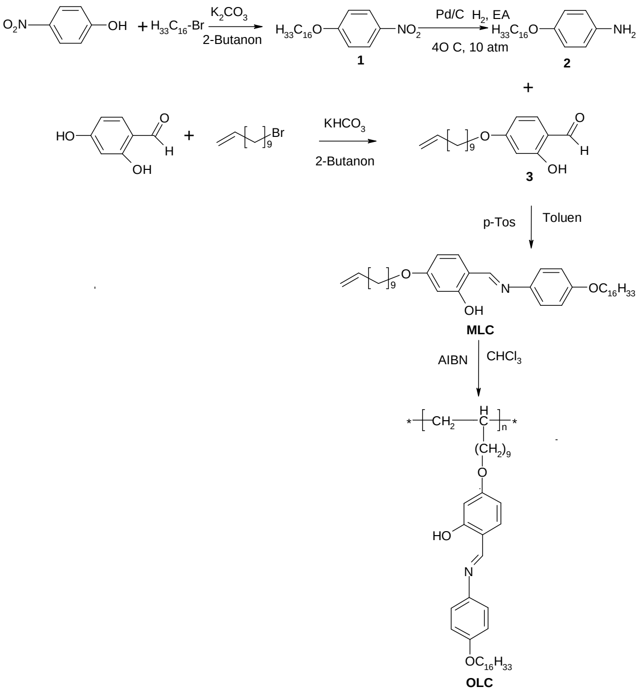
Synthesis of side chain oligomer OLC

In the polymerization reaction, predetermined quantities of MLC and 0.031 mmol of AIBN as an initiator were dissolved in chloroform and introduced in a polymerization tube and sealed in the argon atmosphere. After vigorous stirring for 7 days at 65 °C, the polymer was precipitated in methanol and filtered off. Reprecipitation in methanol yielded the side chain oligomers OLC as white precipitate. The oligomerization of Schiff's base monomer is shown in **Scheme 1**. The chemical structure of OLC was characterized by the spectroscopic methods (FTIR, 1H NMR). Polymerization conditions and results are given in **Table 1**.

Measurements

Ultra violet-visible (UV) studies were performed in quartz cell $CHCl_3$ as solvent using a Agilent 8453 spectroscope. Fourier transform infrared (FTIR) studies were performed by ATR equipment using a Perkin- Elmer FTIR spectroscope at a resolution of 4 cm^{-1}. The scanned wavenumbers range from 4,000 to 400 cm^{-1}. ^{1}H NMR measurements was conducted on Bruker 400 MHz in $CDCl_3$ as solvent with tetramethylsilane (TMS) as the internal reference.

^{13}C NMR measurements was conducted on Bruker 400 MHz in $CDCl_3$ as solvent with tetramethylsilane (TMS) as the internal reference. The mass of Schiff's base monomer was studied by using Varian MAT-711 or Inctectra GmbH, AMD-402 spectroscope. DSC (Perkin-Elmer DSC-7) measurements were performed at a heating and cooling rate of 10 °C/min up to 130 °C. The textures of the monomer and its oligomer were observed by using a Leitz Laborlux 12 polarising microscope, equipped with Linkam THMS 600 hot stage and Linkam TMS93 temperature controller. The molecular weight of the homopolymer was detected by using gel permeation chromatograpy (GPC) on a Waters 996 apparatus equipped with Evaporative Mass Detector, $CHCl_3$ solvent with polystyrene standards.



Scheme 1. Synthesis of Schiff-base monomer and oligomer.

Results and discussion

Synthesis and characterization of vinyl-terminated schiff's base monomer MLC

The vinyl-terminated Schiff- base monomer MLC was prepared by the p-toluenesulfonic acid catalized condensation of the 2-hydroxy-4-(10-undecenyloxy)benzaldehyde (3) with 4-hexadecyloxyaniline (2), respectively. The general reaction scheme for the synthesis of vinyl-terminated Schiff- base monomer is given in **Scheme 1**. The chemical structure of the MLC was confirmed by UV, FTIR, ^{1}H NMR, ^{13}C NMR and MS. The proposed structures are full agreement with the all spectroscopic data. The resonance of the vinyl-terminated Schiff-base monomer MLC was observed at 13.90, 8.42, 5.95-4.76 ppm which was assigned to –O$\underline{H}$, $\underline{H}$C=N and -C$\underline{H}$=C$\underline{H}_2$, respectively.

The spectroscopic data of vinyl-terminated Schiff-base monomer (MLC) 5-(10-Undecyloxy)-2-[[(4-(hexadecyloxy) phenly)imino]methyl]phenol ($C_{40}H_{61}NO_3$; 605.94 g/mol); UV: λ(nm) = 244.5, 285.9, 349.1. FTIR: γ(cm^{-1}) = 3076 (H_2C=CH), 1617 (C=N).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 13.80 (s; OH), 8.50 (s; HC=N), 7.20-7.13 (m; 3H, ArH), 6.85 (d, J ≈ 8.8; 2H, ArH), 6.48-6.37 (m; 2H, ArH), 5.80-5.70 (m; 1H, H_2C=C$\underline{H}$), 4.97-4.83 (m; 2H, $\underline{H_2}$C=CH), 3.95-3.87 (m; 4H, OC$\underline{H_2}$), 2.10-1.95 (m; H_2C=CH-C$\underline{H_2}$), 1.76-1.68 (m; 4H, OCH_2-C$\underline{H_2}$), 1.43-1.13 (m; 38H, CH_2), 0.82 (t, J ≈ 7.0 Hz; CH_3).

^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) =163.91, 163.39, 158.09, 139.92, 112.89 (5s; 5 Ar-C), 159.31 (d, HC=N), 139.23 (d; H_2C=$\underline{C}$H), 133.27, 121.92, 115.21, 107.60, 101.60 (5d, 7 Ar-$\underline{C}$H), 114.14 (t; $H_2\underline{C}$=CH), 68.37-68.27 (2t; 2 O$\underline{C}H_2$), 33.82, 31.94, 29.68, 29.62, 29.60, 29.50, 29.42, 29.38, 29.35, 29.28, 29.12, 29.09, 28.94, 26.05, 25.99, 22.71 (16t; 22C, CH_2), 14.13, (q; CH_3).
MS (EI): m/z (%) = 605 (100) [M$^+$], 453 (30) [M - $C_{11}H_{21}$], 381 (35) [M$^+$ - $C_{16}H_{33}$], 228 (55) [M$^+$ – $C_{16}H_{33}$, - $C_{11}H_{21}$]
EA: Calculated (%): C, 79.29; H, 10.48; N, 2.31; Found (%): C, 79.37; H, 10.48; N, 2.2. The ^{1}H-NMR spectrum of MLC is given in **Fig. 1.**

Synthesis and characterization of side chain liquid crystalline oligomer OLC

The general reaction scheme for the synthesis of side chain oligomer is given in **Scheme 1**. The synthesis of side chain liquid crystalline oligomers OLC was carried out by free radical polymerization of the corresponding Schiff-base monomer (MLC) in the presence of azobisisobutyronitrile (AIBN) as an initiator.

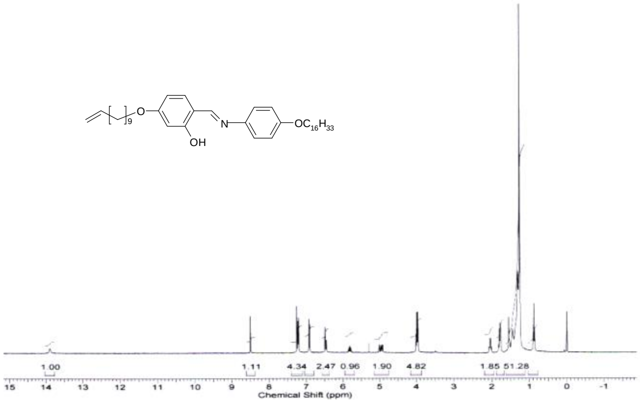


Fig. 1. The ^{1}H-NMR spectrum of MLC.

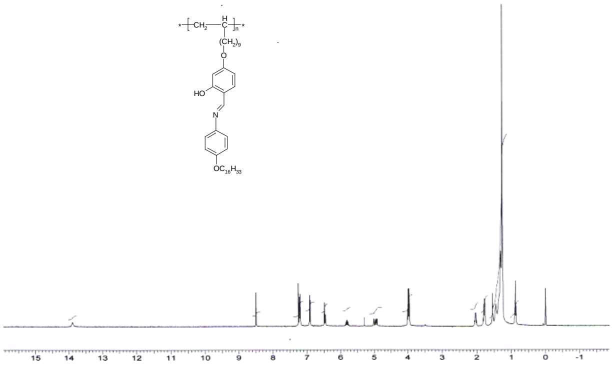


Fig. 2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) for OLC.

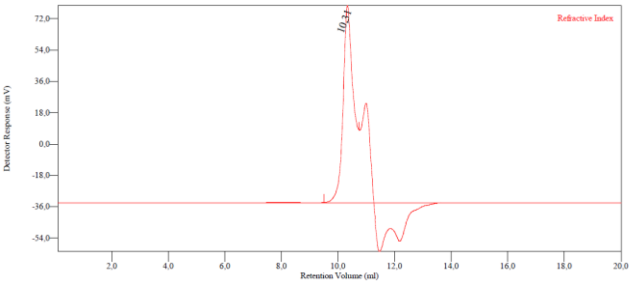


Fig. 3. GPC curve of the OLC.

The chemical structure of the OLC was confirmed by standart methods: FT-IR, ^{1}H NMR. The proposed structures are full agreement with the all spectroscopic data. The ^{1}H-NMR spectrum of OLC is shown in **Fig. 2**.

Table 2. Phase transition temperatures T ($^{\circ}$C) and associated transition enthalpies ΔH (kJ mol^{-1}) of the vinyl-terminated Schiff-base monomers (MLC) and the corresponding side chain liquid crystalline oligomers (OLC)^a

Compound	T (°C) _H (kJ mol−1)
MLC	K 84.06 (73.8) [SmX 70.34 (4.3)] SmC 117.75 (12.3) Iso
OLC	K 75.62 (92.5) [SmX 67.70 (6.7)] SmC 112.44 (18.2) Iso

^{a}*Cr: crystalline, Sm: smectic, and Iso: isotropic liquid phase; transition temperatures and enthalpy values were determined by DSC (Perkin-Elmer DSC-7; heating rates 10 K min^{-1}).*

The spectroscopic data of Side Chain Oligomer (OLC); FTIR**:** γ(cm^{-1}) = 1618 (C=N).

^{1}H NMR**:** (400 MHz, $CDCl_3$): δ (ppm) = 13.80 (s; OH), 8.50 (s; HC=N), 7.20-7.12 (m; 3H, ArH), 6.85 (d, $J \approx$ 8.8; 2H, ArH), 6.48-6.37 (m; 2H, ArH), 3.94-3.85 (m; 4H, $OC\underline{H}_2$), 1.78-1.69 (m; 4H, OCH_2-$C\underline{H}_2$).

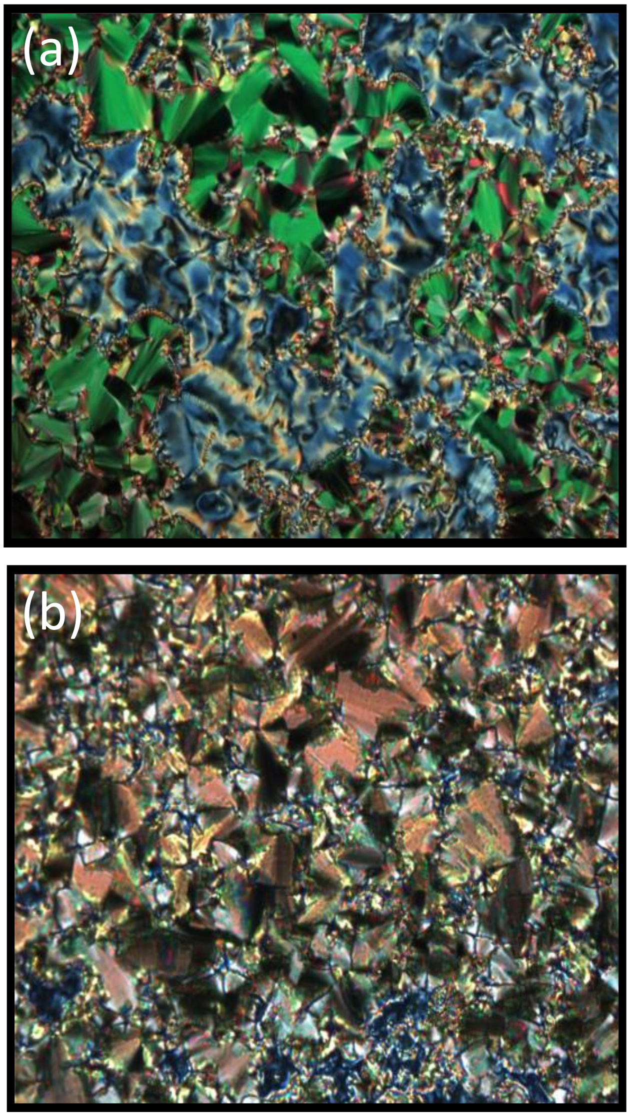


Fig. 4. PM photomicrographs as observed on cooling for the (a) the SmC mesophase of MLC at T = 75◦C; (b)SmX mesophase of MLC at T = 63°C.

The formation of the oligomer can be identified by comparing the ^{1}H NMR spectra of monomers and its oligomer. ^{1}H NMR spectra of vinyl-terminated Schiff's base monomers MLC revealed two multiplets in the range of 5.80–5.70 and 4.97–4.83 ppm and a singlet peak at 8.50 ppm, corresponding to the olefinic protons (1H, CH and 2H, CH_2) and imine proton (1H, HC=N), respectively. As seen in ^{1}H NMR spectra of OLC (**Fig. 2**), olefinic protons in the range of 5.80-4.83 ppm are observed. Since the chemical properties of the monomers are similar to its oligomer, unreacted monomer cannot be removed from the resulting oligomer. Comparison of peak integration of olefinic protons and imine proton on the polymeric chain revealed that side chain liquid crystalline oligomers OLC was achived with a yield of 72%. It is well known that especially vinly monomer's polymer reactions cannot proceed by 100% conversion **[13]**. Molecular weight of the oligomer was evaluated by gel permeation chromatography. The molecular weight and molecular weight distribution of the oligomer is given in **Table 1.** The GPC plots of OLC is shown in **Fig. 3.**

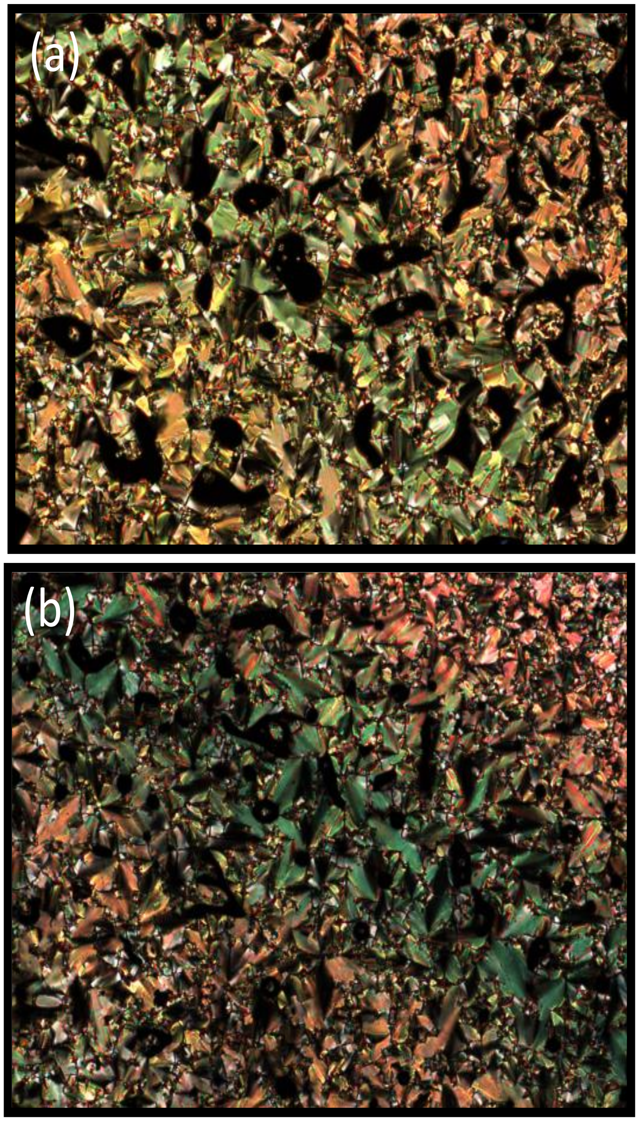


Fig. 5. PM photomicrographs as observed on cooling for the **a.** the SmC mesophase of OLC at *T = 71◦C;* ***b.*** *SmX mesophase of* MLC at *T = 60◦C.*

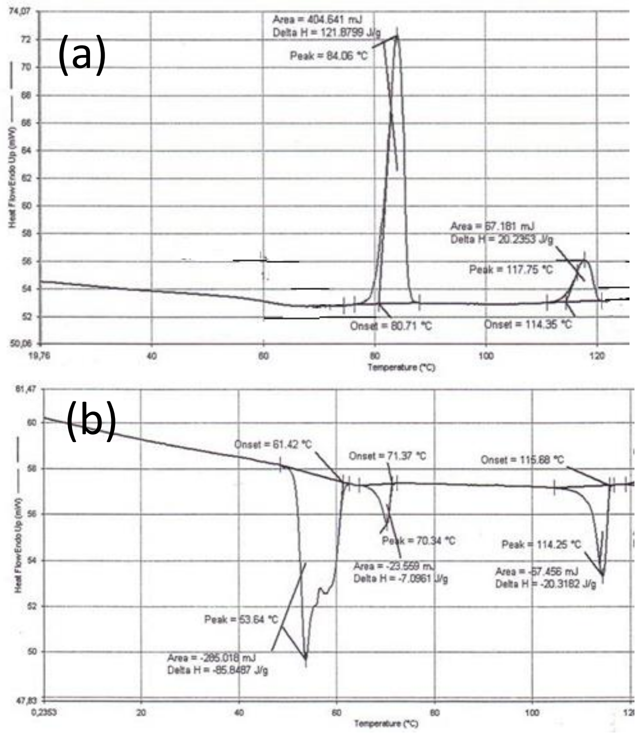


Fig. 6. (a) DSC thermograms during the second heating process and (b) DSC thermograms during the second cooling process for MLC **(**10 K·min^{-1}) (GPC).

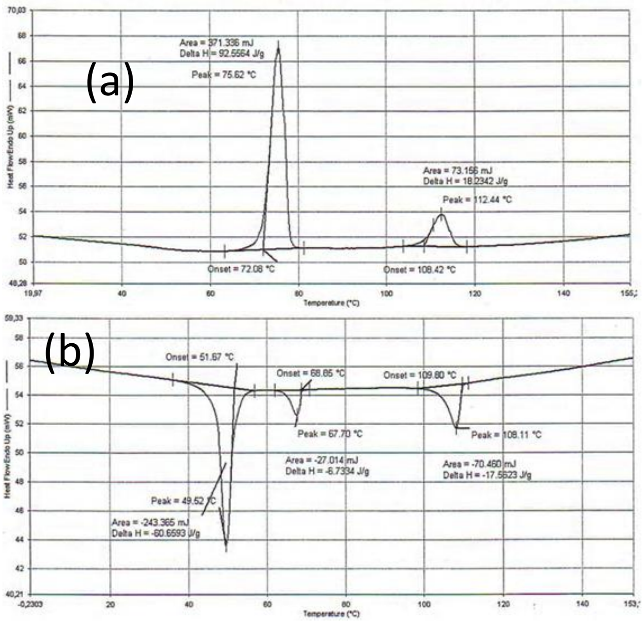


Fig. 7. (a) DSC thermograms during the second heating process and (b)DSC thermograms during the second cooling process for OLC (10 K·min^{-1}).

Liquid crystalline properties of vinyl-terminated schiff-base monomer MLC and side chain oligomers OLC

The liquid crystal properties of MLC and OLC have been investigated by using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Transition temperatures were measured using a Mettler FP-82 HT hot stage and control unit in conjunction with a Leica polarizing microscope (PM) and these were confirmed using differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7, heating and cooling rate: 10°C min^{-1}).

The Schiff's base vinyl monomer MLC and its oligomer OLC show thermotropic mesomorphic behavior and exhibit smectic mesophases. The oligomers behave similar to its monomer. MLC and OLC exhibit an enantiotropic SmC mesophase with broken fan shaped texture and Schlierin textures, respectively. On cooling compounds MLC and OLC a transtion to a monotropic SmX phase takes place at 70 °C and 67 °C respectively. The phase temperatures are decreased by polimerization. The texture of the SmC and SmX mesophase of compound MLC and OLC are shown in **Fig. 4a, 4b** and **Fig. 5a, 5b**, respectivly. The transition temperature, corresponding enthalpy values and mesophase type observed for the MLC and OLC are summarized in **Table 2**.

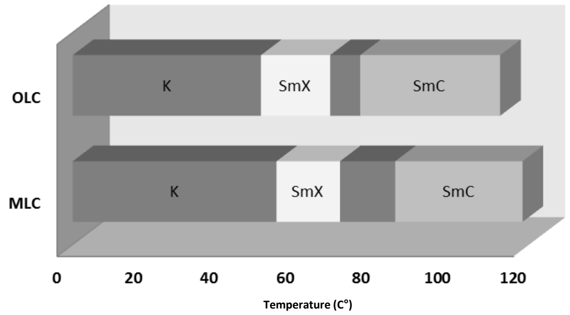


Fig. 8. Comparison of the thermal behavior of monomer MLC and its oligomer OLC**.**

The DSC (second heating) thermograms for MLC and OLC are given in **Fig. 6a** and **6b.** MLC exhibits an endothermic peak at 117 °C, which was assigned as a SmC-Iso transition and OLC exhibits an endothermic peaks at 112 °C assignedas a SmC-Iso transitions, respectively. The DSC (second cooling) thermograms for MLC and OLC are given in **Fig. 7a** and **7b**. MLC exhibits two exothermic peaks at 114 °C and 70 °C, which were assigned as Iso-SmC and SmC-SmX transtition, respectivly. OLC exhibits two exothermic peaks at 108 °C and 67 °C, which were assigned as Iso-SmC and SmC-SmX transtition, respectivly.which was assigned as a SmC-Iso transition and OLC exhibits an endothermic peaks at 112 °C assigned as a SmC-Iso transitions, respectively. A comparison of the mesomorphic properties of the monomer MLC with its oligomer OLC shows that the melting point and clearing points are significantly reduced whereas the mesophases remain the same after oligomerization. **Fig. 8** gives a graphical overview of the behavior of the monomer and their corresponding oligomer.

Conclusion

We synthesized a novel liquid crystalline vinyl monomer and its side chain liquid crystalline oligomer having Schiff-base type mesogenic group with longer terminal aliphatic substituent than those reported before in our previous work **[16]** to understand the structure-property relationships in mesogens having different terminal groups. Side chain liquid crystalline oligomer OLC behaves very similarly to their vinyl-terminated Schiff base monomer MLC. As a result of oligomerization, the melting and clearing points are significantly decreased whereas mesophases exhibited by monomers remain the same. According to the result, the effect of terminal group on the mesomorfic behaviour of the monomer and its oligomer is relatively minor.

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