Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Hulya Elmali Gulbas [a], Hale Ocak [b], Yesim Hepuzer Gursel [c] & Belkiz Bilgin-Eran [b]

[a] Department of Chemistry Technology Programme, Usak University, Banaz, Usak, Turkey

[b] Department of Chemistry, Yildiz Technical University, Esenler, Istanbul, Turkey

[c] Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey

Published online: 02 Apr 2013.

To cite this article: Hulya Elmali Gulbas, Hale Ocak, Yesim Hepuzer Gursel & Belkiz Bilgin-Eran (2013) Synthesis and Mesomorphic Properties of New Side Chain Liquid Crystalline Oligomers Containing Salicylaldimine Mesogenic Groups, Molecular Crystals and Liquid Crystals, 574:1, 40-49, DOI: 10.1080/15421406.2012.762494

To link to this article: http://dx.doi.org/10.1080/15421406.2012.762494

*Mol. Cryst. Liq. Cryst.*, Vol. 574: pp. 40–49, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.762494

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# Synthesis and Mesomorphic Properties of New Side Chain Liquid Crystalline Oligomers Containing Salicylaldimine Mesogenic Groups

HULYA ELMALI GULBAS,[1,*] HALE OCAK,[2] YESIM HEPUZER GURSEL,[3] AND BELKIZ BILGIN-ERAN[2]

[1]Department of Chemistry Technology Programme, Usak University, Banaz, Usak, Turkey
[2]Department of Chemistry, Yildiz Technical University, Esenler, Istanbul, Turkey
[3]Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey



*New liquid crystalline salicylaldimine-based homopolymers* ***PLC$_1$*** *and* ***PLC$_2$*** *have been synthesized from their corresponding monomers 5-(10-undecenyloxy)-2-[[(4-(hexyloxy)phenyl)imino]methyl]phenol (**LC$_1$**) and 5-(10-undecenyloxy)-2-[[(4-(hexyl)phenyl)imino]methyl]phenol (**LC$_2$**) via free radical polymerization. The polymers were characterized by 1H-NMR, differential scanning calorimetry (DSC) and optical microscopy in polarized light (polarizing microscope). The synthesized polymers have low molecular weights, and so are in the oligomeric domain. The oligomers behave very similarly to their monomers that exhibit smectic mesophases. Replacing the hexyloxy chain by a hexyl chain of the mesogenic unit generates an additional SmC mesophase in the temperature range of both the monomer and oligomer. All the observations suggest that the oligomerization of the liquid crystalline salicylaldimine monomers gives rise to decreased transition temperatures whereas it has no influence on the type and stability of the mesophase formed.*

**Keywords** Salicylaldimine mesogens; side chain liquid crystalline oligomers

## 1. Introduction

Side chain liquid crystalline polymers (SLCPs), which combine the liquid crystal behavior and unique properties of macromolecules, have been the subject of intensive investigation due to their potential applications such as optical data storage, nonlinear optics, electro-optic displays, and stationary phases for gas chromatography (GC), supercritical fluid chromatography (SFC), and high-performance liquid chromatography (HPLC) [1–5]. Since the SLCPs reported by Finkelmann et al. [6] and numerous systematic studies performed by Shibaev [7], several hundred SLCPs have been synthesized and investigated to understand the relation between molecular structure and mesophases exhibited. An SLCP is composed of a polymer backbone, a mesogenic unit, and a flexible spacer that links the mesogenic units to the polymeric backbone. These molecular structures chosen for the design of SLCPs play

*Address correspondence to Hulya Elmali Gulbas, Department of Chemistry Technology Programme, Usak University, TR-34220 Banaz, Usak, Turkey. Tel.: +90-276-2212150/3522; Fax: +90-276-2212151. E-mail: hulyaelmali@yahoo.com

an important role in the occurrence of desired liquid crystalline phases, thermal stability of mesophases, and physical properties of SLCPs [3,4,8,9].

SLCPs can be prepared by the introduction of a reactive group that has capability to polymerize to mesogenic molecule [10–12]. In some cases, it would be possible to use polymerizable mesogenic monomers containing a reactive group such as an olefinic group in $\omega$-position for the synthesis of mesogenic side chain polymers [10,13].

Schiff base polymers are of great interest due to their good properties such as thermal, liquid crystalline, nonlinear optical, and semiconductor properties, which provides some numerous applications [14–16]. Imine groups are widely used as a linking group in different classes of liquid crystals such as rod-like, banana-shaped, and V-shaped [17–20]. Not only do the LCs incorporating these moieties show a polymorphism of different LC phases, but also they can be coordinated to metals to obtain salicylaldimine- or imine-based metal-containing LCs exhibiting more stable mesophase. Mesophase stability in salicylaldimine-derived LCs increases because of the presence of intramoleculer hydrogen bonding [17,18].

A rod-like molecule consists of a rigid core with at least two aromatic rings, which are connected by linking groups and flexible terminal chains [21–23]. The type of terminal chains plays an important role to generate desired mesophases. These molecular fragments can be a small polar substituent, alkyl or alkoxy chains [24]. Replacing alkoxy chains by alkyl chains in liquid crystal molecules with different molecular geometry can lead to drastic changes on mesomorphic properties such as reduction of the mesophase stability, making narrow the mesomorphic range, or loss of liquid crystalline behavior [25–28]. The physical and optical properties of liquid crystals can also be developed by polymerization reaction.

In order to investigate how the liquid crystal properties evolve from dimers to polymers, recently a range of higher monodisperse oligomers has been characterized [29].

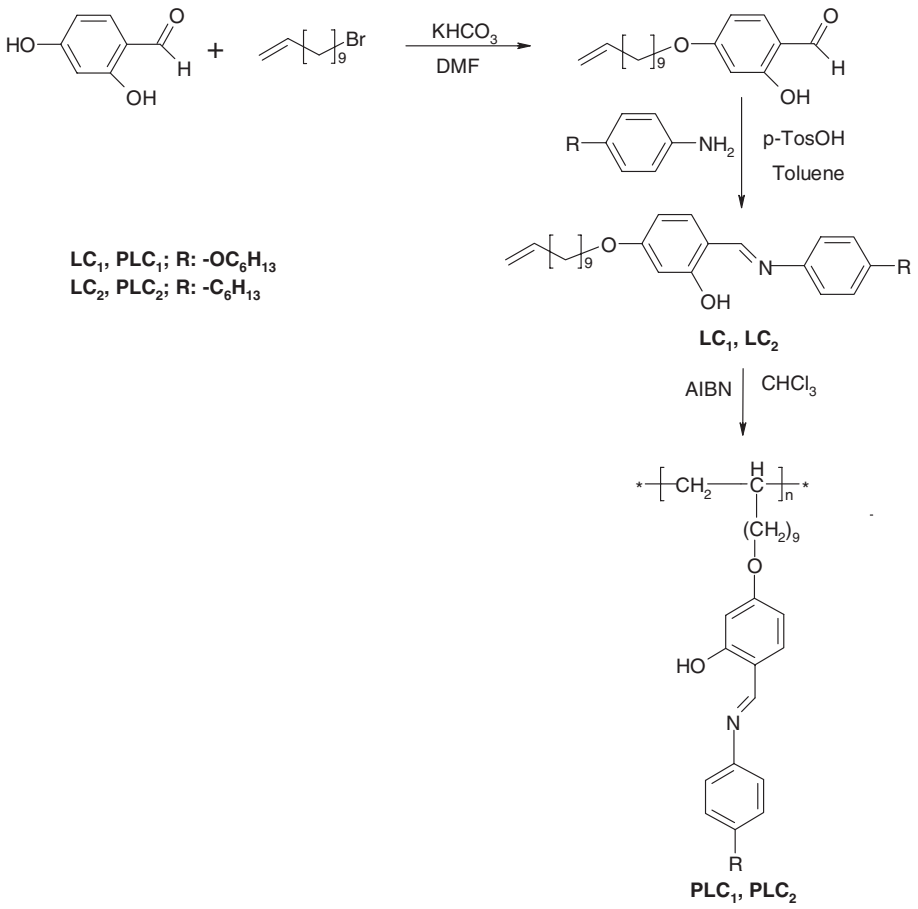
In this study, liquid crystalline oligomers were prepared in order to obtain a detailed understanding of the change of the phase behavior from the monomer to the polymer of rod-like salicylaldimine mesogenic groups. Structure–property relations in salicylaldimine monomers and their homopolymers by varying their aliphatic periphery by the replacing alkoxy chains by alkyl chains were also studied.

## 2. Results and Discussion

### *2.1 Synthesis and Characterization*

The salicylaldimine-based oligomers **PLC$_1$** and **PLC$_2$** were synthesized as shown in Scheme 1. The vinyl-terminated salicylaldimine monomers 5-(10-undecenyloxy)-2-[[(4-(hexyloxy)phenyl)imino]methyl]phenol (**LC$_1$**) and 5-(10-undecenyloxy)-2-[[(4-(hexyl)phenyl)imino]methyl]phenol (**LC$_2$**) were already reported previously and the preparation procedures and spectroscopic data for these compounds are given in Ref. [30]. The proposed structures are in full agreement with the spectroscopic data and with elemental analyses. The characterization of the synthesized compounds is based on $^1$H-NMR (Bruker Avance III 500 spectrometer in $CDCl_3$ solutions, with tetramethylsilane as internal standard). The molecular weight of the homopolymers was detected by using gel permeation chromatograpy on a Waters 996 apparatus (Evaporative Mass Detector, solvent $CHCl_3$, polystyrene standards).

The synthesis of side chain liquid crystalline oligomers **PLC$_1$** and **PLC$_2$** was carried out by free radical polymerization of the corresponding salicylaldimine monomers (**LC$_1$** and **LC$_2$**) in the presence of azobisisobutyronitrile (AIBN) Aldrich as an initiator.




**Scheme 1.** Synthesis of salicylaldimine monomers and oligomers.

In the polymerization reaction, predetermined quantities of **$LC_1$** or **$LC_2$** and 0.031 mmol of AIBN 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 into methanol yielded the new side chain homopolymers **$PLC_1$** and **$PLC_2$** as white precipitate. Polymerization conditions and results are given in Table 1.

**Table 1.** Synthesis and characterizations of oligomers[a]

| Oligomer | Monomer (mol/L) | Time (day) | Conversion (%) | $M_n$[b] (g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|
| **$PLC_1$** | $LC_1$ (0.21) | 7 | 40.5 | 1182 | 1.162 |
| **$PLC_2$** | $LC_1$ (0.21) | 7 | 44.1 | 1155 | 1.141 |

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

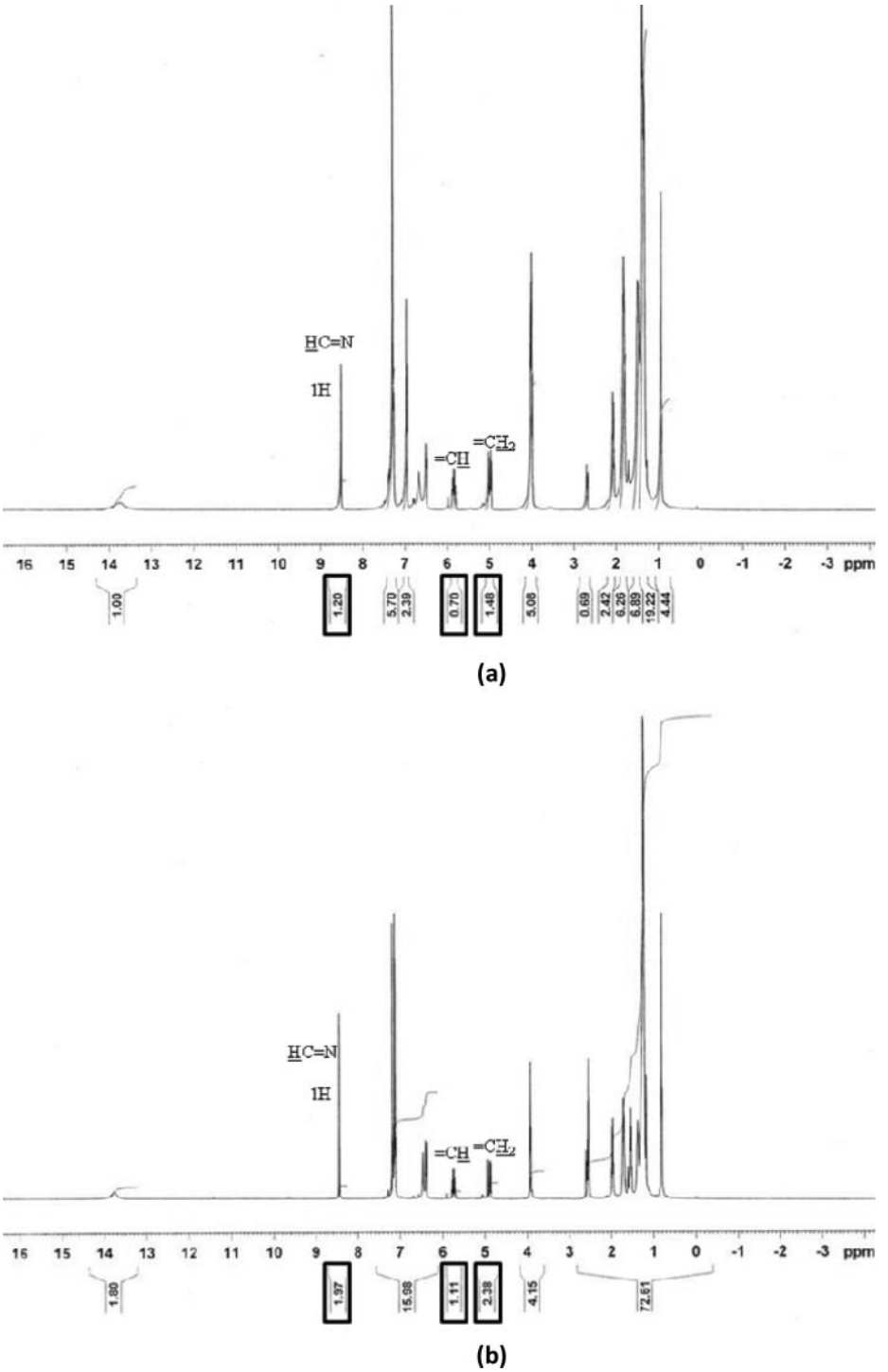



**Figure 1.** $^{1}$H-NMR spectrum (500 MHz, $CDCl_3$) for (a) **PLC$_1$** and (b) **PLC$_2$**.

**PLC$_1$:** $^1$H-NMR (500 MHz, $CDCl_3$, $\delta$ ppm): 13.80 (s; O<u>H</u>), 8.53 (s; <u>H</u>C=N), 7.36–7.23 (m; 7 Ar-<u>H</u>), 4.03, 3.97 (2t, $J \approx 6.5$ Hz; OC<u>H</u>$_2$).

**PLC$_2$:** $^1$H-NMR (500 MHz, $CDCl_3$, $\delta$ ppm): 13.80 (s; O<u>H</u>), 8.46 (s; <u>H</u>C=N), 7.24–7.10 (m; 7 Ar-<u>H</u>), 3.94 (t, $J \approx 6.5$ Hz; OC<u>H</u>$_2$).

The formation of the oligomers can be identified by comparing the $^1$H-NMR spectra of monomers and corresponding oligomers. $^1$H-NMR spectra of salicylaldimine monomers **LC$_1$** and **LC$_2$** revealed two multiplets in the range of 5.84–5.76 and 5.01–4.91 ppm [30] and a singlet peak at 8.50–8.49 ppm, corresponding to the olefinic protons (1H, =CH and 2H, =$CH_2$) and imine proton (1H, <u>H</u>C=N), respectively.

As seen in $^1$H-NMR spectra of **PLC$_1$** and **PLC$_2$** (Fig. 1), olefinic protons in the range of 4.91–5.84 ppm are observed. Since the chemical properties of the monomers are similar to those of corresponding oligomers, 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 **PLC$_1$** and **PLC$_2$** were achived with a yield of 41% and 44%, respectively.

It is well known that polymer reactions cannot proceed by 100% conversion [31,32] and polymerizability of the allyl monomers is significantly low [13,33].

Molecular weight of the oligomers was evaluated by gel permeation chromatography (GPC). The molecular weight and molecular weight distribution of the oligomers are given in Table 1. The GPC plots of **PLC$_1$** and **PLC$_2$** are shown in Figs. 2 and 3.

### *2.2 Liquid Crystalline Properties of Salicylaldimine-Based Oligomers PLC$_1$ and PLC$_2$*

Transition temperatures were measured using a Mettler FP-82 HT hot stage and control unit in conjunction with a Leica polarizing microscope (PM). The associated enthalpies were obtained from DSC-thermograms that were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10°C min$^{-1}$.

Investigations by PM show that **PLC$_1$** exhibits only a smectic A phase (see Fig. 4). Replacing the alkoxy chain by alkyl chain clearly leads to the same influence on the mesomorphic properties of monomers and homopolymers. **PLC$_2$** containing a terminal hexyl

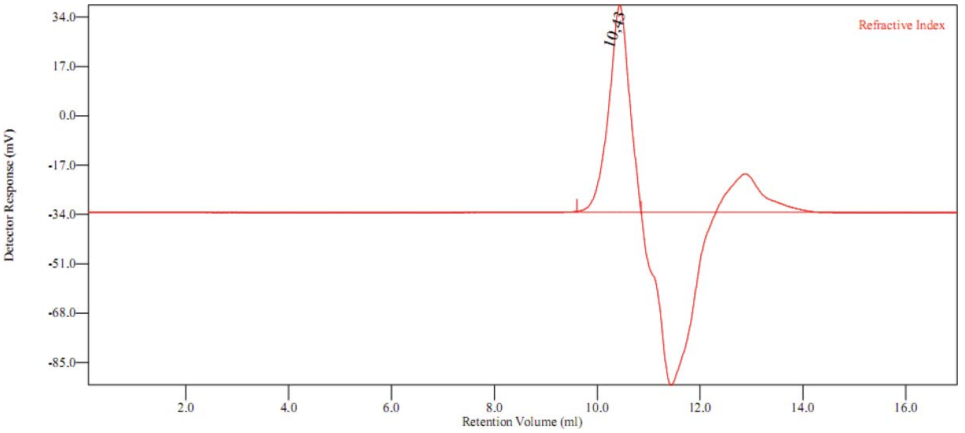



**Figure 2.** GPC curve of the **PLC$_1$**.

**Table 2.** Phase transition temperatures $T$ (°C) and associated transition enthalpies $\Delta H$ (kJ mol$^{-1}$) of the terminated salicylaldimine monomers (**LC$_1$** and **LC$_2$**) and the corresponding side chain liquid crystalline oligomers (**PLC$_1$** and **PLC$_2$**)[a]

| Compound | R | $T$ (°C) $\Delta H$ (kJ mol$^{-1}$) |
|---|---|---|
| **LC$_1$** [30] | $OC_6H_{13}$ | Cr 60.9 (35.3) SmA 118.5 (5.7) Iso |
| **PLC$_1$** | | Cr 48.4 (46.1) SmA 109.3 (8.9) Iso |
| **LC$_2$** [30] | $C_6H_{13}$ | Cr 37.3 (24.8) SmC 64.5 (1.2) SmA 89.5 (5.5) Iso |
| **PLC$_2$** | | Cr 25.4 (12.8) SmC 63.5 (16.1) SmA 77.9 (8.2) 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$^{-1}$).

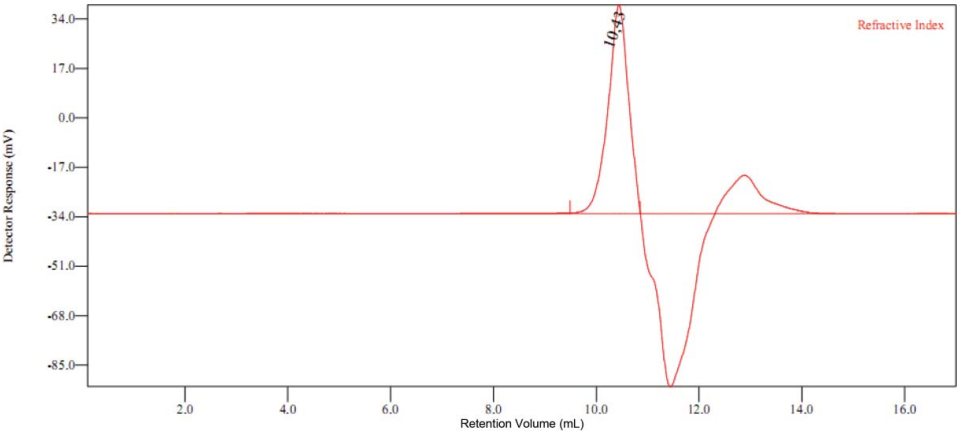



**Figure 3.** GPC curve of the **PLC$_2$**.

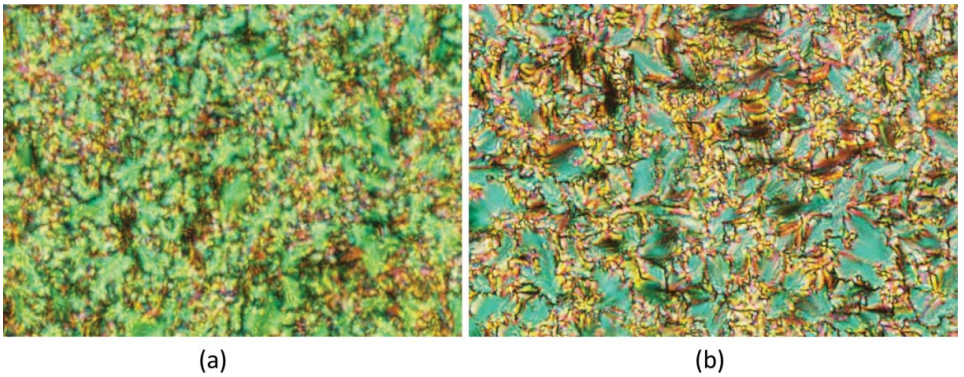



**Figure 4.** PM photomicrographs as observed on cooling for (a) the SmA mesophase of **PLC$_1$** at $T = 53$°C; (b) the SmC mesophase of **PLC$_2$** at $T = 62$°C.

chain in the mesogenic unit exhibits enantiotropic SmA and SmC mesophases in a similar way as has been previously reported for monomer **LC$_2$** [30]. An additional SmC mesophase occurs at 37°C and 25°C in the phase sequence of **LC$_2$** and **PLC$_2$**, respectively, that is not observed for the compounds containing a hexyloxy chain (**LC$_1$** and **PLC$_1$**). Additionally, the melting and clearing points are significantly decreased by the exchange of hexyloxy chain. The texture of the SmC mesophase of compound **PLC$_2$** is shown in Fig. 4(b).

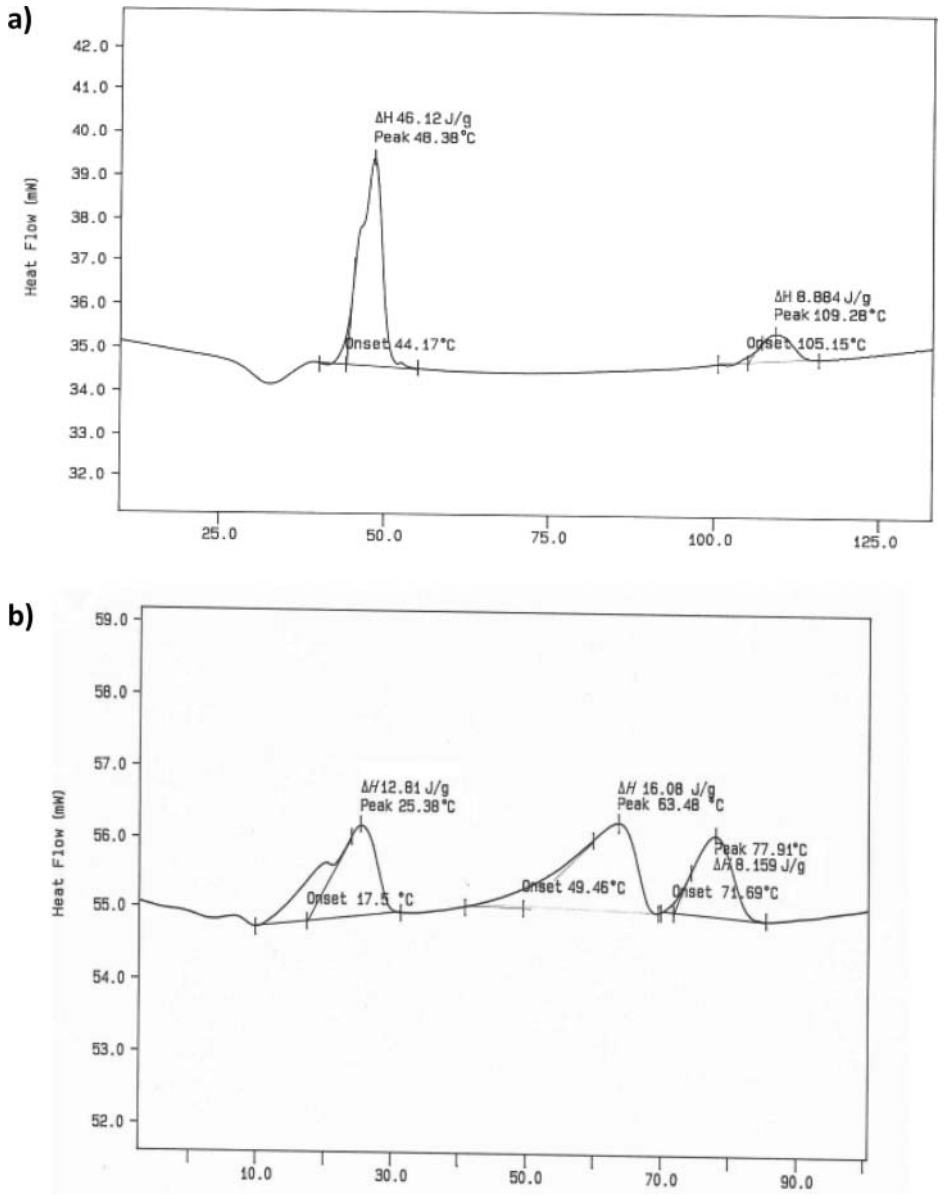



**Figure 5.** DSC thermograms during the second heating process for (a) **PLC$_1$** and (b) **PLC$_2$** (10 K·min$^{-1}$).

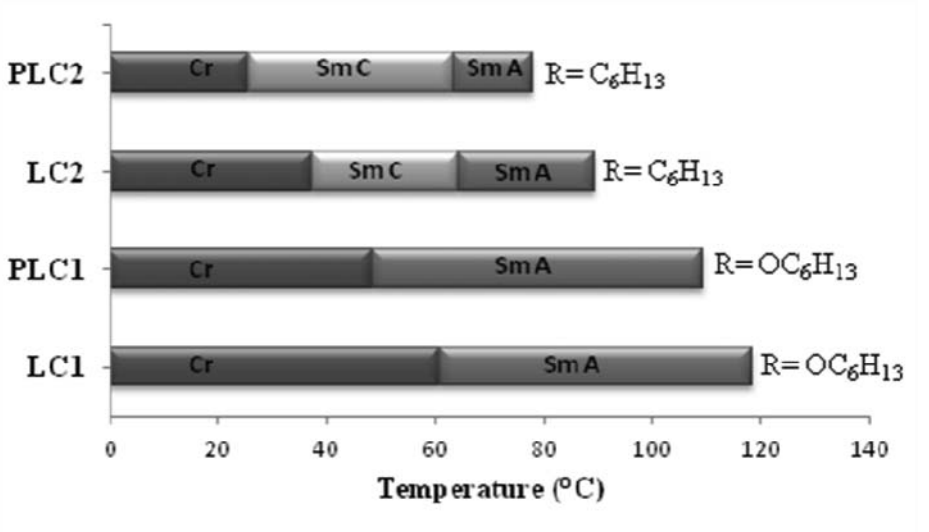



**Figure 6.** Comparison of the thermal behavior of monomers [30] and their corresponding oligomers **PLC$_1$** and **PLC$_2$**.

The DSC (second heating) thermograms for **PLC$_1$** and **PLC$_2$** are given in Fig. 5. **PLC$_1$** exhibits an endothermic peak at 109°C, which was assigned as an SmA-Iso transition and **PLC$_2$** exhibits two endothermic peaks at 63°C and 78°C, which were assigned as SmC-SmA and SmA-Iso transitions, respectively.

The transition temperatures, corresponding enthalpy values, and mesophase types observed for the **PLC$_1$** and **PLC$_2$** are summarized in Table 2.

As shown in Table 2, both oligomers show enantiotropic liquid crystalline behavior. DSC (second heating) thermograms for **PLC$_1$** and **PLC$_2$** are given in Fig. 5.

**PLC$_1$** exhibits an endothermic peak at 109°C, which was assigned as SmA-Iso transition and **PLC$_2$** exhibits two endothermic peaks at 63°C and 78°C, which were assigned as SmC-SmA and SmA-Iso transitions, respectively.

A comparison of the mesomorphic properties of the monomers **LC$_1$** and **LC$_2$** with their oligomers **PLC$_1$** and **PLC$_2$** shows that the melting point and clearing points are significantly reduced whereas the mesophases remain the same after oligomerization. Figure 6 gives a graphical overview of the behavior of the monomers and their corresponding oligomers.

## 3. Conclusions

We synthesized and characterized novel side chain liquid crystalline oligomers containing rod-like salicylaldimine mesogenic groups. To the best of our knowledge, the compounds reported here represent the first salicylaldimine-based side chain liquid crystalline oligomers.

According to our observations reported here, new side chain liquid crystalline oligomers behave very similarly to their vinyl-terminated salicylaldimine monomers (**LC$_1$** and **LC$_2$**). As a result of oligomerization, the melting and clearing points are significantly decreased whereas mesophases exhibited by monomers remain the same. The replacing

alkoxy chain by alkyl chain in the mesogenic unit leads an additional mesophase in the mesomorphic temperature range of both the monomer and homopolymer. Therefore, it can be concluded that the effect of homopolymerization on the mesomorphism of monomers such as vinyl-terminated salicylaldimine is relatively minor.

## Acknowledgments

The work has been supported by Yildiz Technical University Scientific Research Projects Coordination Department under Project Number: 24–01-02–03. We also acknowledge Mrs. N. Coskun for the synthesis of $PLC_1$ and $PLC_2$.



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