

# Synthesis and thermodynamical interactions of (S)-5-(2-methylbutoxy)-2-[[[4-hexyloxyphenyl]Imino]methyl]-Phenol liquid crystal with some solvents

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Liquid crystalline compound (S)-5-(2-methylbutoxy)-2-[[[4-hexyloxyphenyl]imino]methyl]-phenol (MBHOPIMP) has been prepared and characterized. Phase transition temperatures of MBHOPIMP were determined by polarizing microscopy, differential scanning calorimetry. The retention diagrams of octane, nonane, cyclopentane, cyclohexane, ethyl acetate, butyl acetate, iso-butyl acetate, benzene, toluene, ethylbenzene and chlorobenzene on MBHOPIMP were plotted at temperatures between 110 and 130 °C by inverse gas chromatography technique. Then, specific retention volume,  $V_g^0$ , Flory-Huggins polymer-solvent interaction parameter,  $\chi_{12}^\infty$ , hard-core polymer-solvent interaction parameter,  $\chi_{12}^*$  and effective exchange energy parameter,  $X_{\text{eff}}$  were determined.

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## 1. Introduction

Liquid crystals show various mesophases which occur depending on molecular structure under special conditions of temperature or concentration. To understand the relationship between molecular structure and mesogenic properties exhibited, several molecular designs have been made and many types of desirable materials have been synthesized. Liquid crystal molecules with rod-like molecular shape are composed of a rigid core with two flexible terminal alkyl or alkoxy chains. The rod-like molecules with the salicylaldimine core has attracted much interest due to their various mesogenic properties exhibited depending on the modification of terminal chains which can strongly affect the mesomorphism [1]. In addition, the synthesis of chiral liquid crystals has increased considerably over the last few years due to a chiral moiety in the structure of the molecules which can give rise to unusual electrooptical properties. The presence of a chiral moiety within mesogenic molecules is significant for obtaining chiral mesophases [2-3].

Recently, there are some reports about determination of thermal properties and solubility behaviour of liquid crystal materials by inverse gas chromatography method [4]. Special attention can be paid for these applications due to investigation of interactions of liquid crystal molecules with solvents. Although inverse gas chromatography method (IGC) has been widely used to investigate the interactions of polymeric materials with various solvents [5-7], it is a novel technique for the determination of the interactions of liquid crystals with various solvents [8-10].

Here, we present the synthesis, characterization and mesomorphism of a salicylaldimine compound (S)-5-(2-methylbutoxy)-2-[[[4-hexyloxyphenyl]

imino]methyl]phenol (MBHOPIMP) with a chiral moiety and alkoxy chain at the terminus. Then, specific retention volume and thermodynamical interaction parameters such as Flory-Huggins polymer-solvent interaction parameter, equation-of-state polymer solvent interaction parameter and effective exchange energy parameter were calculated at the temperatures between 110 and 130 °C by IGC because thermodynamical equilibrium occurred at this temperature range. In our previous study, (S)-5-(2-methylbutoxy)-2-[[[4-hexylphenyl] imino]methyl]phenol was characterized by polarizing microscopy (PM), differential scanning calorimetry (DSC) and IGC [8]. We also compared the phase transitions and thermodynamical data of MBHOPIMP with those of an analog containing the corresponding alkyl chain (n-hexyl-) instead of alkoxy chain (n-hexyloxy-) attached to one of the side chains.

## 2. Experimental

### 2.1. Materials and instrumentation

The characterization of the MBHOPIMP presented here are based on various spectroscopic data, e.g.  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in  $\text{CDCl}_3$  solutions) with tetramethylsilane as internal standard, UV-VIS (Agilent 8453,  $\text{CHCl}_3$  solutions), FT-IR (Perkin Elmer,  $\text{CHCl}_3$  solutions), MS (AMD 402 (electron impact, 70 eV)). Microanalyses were performed using a Leco CHNS-932 elemental analyzer.

The liquid crystalline properties were investigated using polarized light optical microscopy and DSC. Microscopy was performed on a Leitz Laborlux 12 Pol polarizing microscope, equipped with a Linkam THMS

600 hot stage and a Linkam TMS93 temperature controller. DSC-termograms were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 K min<sup>-1</sup>.

Octane (O), nonane (N), cyclopentane (CP), cyclohexane (CH), ethyl acetate (EA), butyl acetate (NBA), iso-butyl acetate (IBA), benzene (B), toluene (T), ethylbenzene (EB) and chlorobenzene (CB) were Merck AG. Inc. products. Support material being Chromosorb-W (AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG Inc. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc.

A Hewlett-Packard 6890 N gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents. The column was stainless steel tubing with 3.2 mm o.d. and 1m in length. The flow rate of the carrier gas was kept below 6 cm<sup>3</sup>/minute. The polymer was coated on the support by slowly evaporation of chloroform as stirring the Chromosorb W in the polymer solution. The loading of the coated polymer on the support was determined as 10.23 % by calcination.

## 2.2. Synthesis of the MBHOPIMP

(S)-4-(2-methylbutoxy)-2-hydroxybenzaldehyde [11] (2.5 mmol), 3 mmol of 4-hexyloxyaniline and *p*-toluenesulfonic acid (40 mg) were dissolved in 25 mL toluene. A Dean-Stark trap was adapted to the flask and the solution was boiled for 5 h under reflux. After cooling, a yellow precipitate was obtained. The precipitate was extracted with diethylether (3 x 100 mL). The combined organic layers were washed with NaHCO<sub>3</sub> and NaCl and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> before the diethyl ether was removed under reduced pressure. The crude product was purified by crystallization from acetone/methanol.

**(S)-5-(2-methylbutoxy)-2-[[[4-hexyloxyphenyl]imino]methyl]phenol (MBHOPIMP):**  
 Yield: 0.75 g (78 %), yellow crystals. — <sup>1</sup>H NMR: δ (ppm) = 13.88 (s; OH), 8.47 (s; HC=N), 7.24-7.18 (m; 3 arom. H), 6.90 (d, J ≈ 8.9 Hz; 2 aromatic H), 6.47-6.44 (m; 2 aromatic H), 3.95 (t, J ≈ 6.5 Hz; OCH<sub>2</sub>), 3.84, 3.75 (2dd, J ≈ 9.1 Hz and J ≈ 6.5 Hz each; OCH<sub>2</sub> of the chiral alkyl chain), 1.90-1.82 (m; chiral CH), 1.81-1.74 (m; CH<sub>2</sub>), 1.60-1.21 (m; 4 CH<sub>2</sub>), 1.00 (d, J ≈ 6.9 Hz; CH<sub>3</sub>), 0.94, 0.90 (2t, J ≈ 7.5 Hz and J ≈ 6.9 Hz, respectively; 2 CH<sub>3</sub>). — <sup>13</sup>C NMR: δ (ppm) = 163.57, 163.25, 157.84, 141.16, 113.04 (5s; 5 arom. C), 159.29 (d, HC=N), 132.96, 121.84, 115.12, 107.31, 101.62 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 73.02, 68.39 (2t; 2 OCH<sub>2</sub>), 34.67 (d; CH), 31.66, 29.34, 26.21, 25.80, 22.68 (5t; 5 CH<sub>2</sub>), 16.58, 14.11, 11.37 (3q; 3 CH<sub>3</sub>). — MS: m/z (%) = 383 (100) [M<sup>+</sup>], 313 (42) [M<sup>+</sup> - C<sub>5</sub>H<sub>11</sub>], 229 (50) [M<sup>+</sup> - C<sub>5</sub>H<sub>11</sub> - C<sub>6</sub>H<sub>13</sub>] — UV-VIS: λ (nm) = 352.0. — IR: γ = 1625 cm<sup>-1</sup> (C=N). — C<sub>24</sub>H<sub>33</sub>NO<sub>3</sub> (383.5): calcd. C 75.16, H 8.67, N 3.65; found C 75.06, H 8.59, N 3.82.

## 2.3. Inverse Gas Chromatography Theory

The specific retention volume, V<sub>g</sub><sup>0</sup> is determined experimentally from IGC measurements as follows [12-14]

$$V_g^0 = \frac{Q(t_R - t_A)J273.2}{(T_r w)} \quad (1)$$

where Q is carrier gas flow rate measured at the room temperature T<sub>r</sub>; t<sub>R</sub> and t<sub>A</sub> are retention times of the solvent and air, respectively; J is pressure correction factor, w is weight of liquid crystal in the column.

According to the theories of Flory-Huggins and equation-of-state interaction parameters, χ<sub>12</sub><sup>∞</sup> and χ<sub>12</sub><sup>\*</sup> are defined in the Eq.(2) and Eq.(3), respectively:

$$\chi_{12}^{\infty} = \ln \left( \frac{273.2 R v_2}{p_1^0 v_g^0 v_1^0} \right) - \left( 1 - \frac{V_1^0}{M_2 v_2} \right) - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \quad (2)$$

where R is the universal gas constant; p<sub>1</sub><sup>0</sup>, B<sub>11</sub> and V<sub>1</sub><sup>0</sup> are saturated vapor pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature T, v<sub>2</sub> is specific volume of the liquid crystal, M<sub>2</sub> is molecular weight of the liquid crystal, respectively.

$$\chi_{12}^* = \ln \left( \frac{273.2 R v_2^*}{p_1^* v_g^* v_1^*} \right) - \left( 1 - \frac{V_1^*}{M_2 v_2^*} \right) - \frac{p_1^* (B_{11} - V_1^0)}{RT} \quad (3)$$

where v<sub>2</sub><sup>\*</sup> is specific hard-core volume of the liquid crystal and V<sub>1</sub><sup>\*</sup> is molar hard-core volume of the solvent.

The effective exchange energy parameter, X<sub>eff</sub> in the equation of state theory is defined as follows,

$$RT \chi_{12}^* = p_1^* V_1^* \{ 3 T_{1r} \ln[(v_{1r}^{1/3} - 1)/(v_{2r}^{1/3} - 1)] + v_{1r}^{-1} - v_{2r}^{-1} + X_{eff}/p_1^* v_{2r} \} \quad (4)$$

where p<sub>1</sub><sup>\*</sup> is characteristic pressure, v<sub>1r</sub> and v<sub>2r</sub> are reduced volume of the solvent and liquid crystal, respectively. T<sub>1r</sub> is reduced temperature of the solvent.

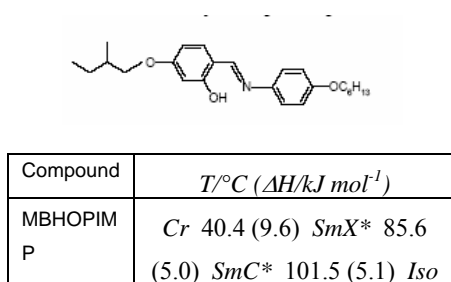
## 3. Results and discussion

The synthesis and mesogenic behaviour of a salicylaldehyde compound (S)-5-(2-methylbutoxy)-2-[[[4-hexyloxyphenyl]imino]methyl]phenol (MBHOPIMP) are reported. The mesogenic salicylaldehyde compound including a chiral moiety which is attached in the terminal position was obtained in a three-step process as described in literature [11]. (S)-2-methylbutyl tosylate was prepared by the reaction of (S)-2-methylbutanol with *p*-toluenesulfonyl chloride. The synthesis of (S)-4-(2-methylbutoxy)-2-hydroxybenzaldehyde was carried out by etherification of 2,4-dihydroxybenzaldehyde with the (S)-2-methylbutyltosylate in DMF [11]. The target Schiff base MBHOPIMP [15] was synthesized by a *p*-toluenesulfonic acid catalyzed condensation of 4-hexyloxyaniline with (S)-4-(2-methylbutoxy)-2-

hydroxybenzaldehyde in toluene and purified by crystallization from acetone/methanol.

The structure of MBHOPIMP was characterized using various spectroscopic methods ( $^1\text{H}$ -,  $^{13}\text{C}$ -NMR, UV-VIS, IR and mass) and elemental analysis. The proposed structures are in full agreement with these spectroscopic data (see Experimental Section).

The mesomorphic properties of the obtained salicylaldehyde compound were investigated using PM and DSC. The investigation shows that it exhibits chiral smectic mesophases. The transition temperatures, corresponding enthalpy values and mesophase types observed for this compound are given in Fig.1.



<sup>a</sup>Perkin-Elmer DSC-7; heating rates 10 K min<sup>-1</sup> for the melting and clearing process; the enthalpies are in

Fig. 1. Phase transition temperatures<sup>a</sup>  $T$  ( $^\circ\text{C}$ ) and transition enthalpies<sup>a</sup>  $\Delta H$  ( $\text{kJ mol}^{-1}$ ) of compound MBHOPIMP. Cr: crystalline, Sm: smectic and Iso: isotropic phase.

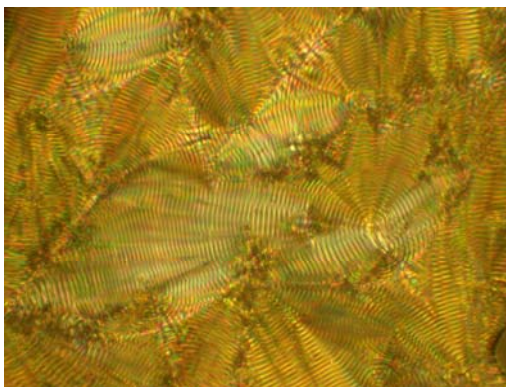


Fig. 2. Polarised optical photomicrograph of the mesophase of the MBHOPIMP as observed on cooling (smectic C\* phase at 92  $^\circ\text{C}$ ).

The MBHOPIMP shows similar mesomorphic properties with the previously synthesized analogs [15]. For the compound MBHOPIMP, a fingerprint texture of the chiral smectic C\* phase is observed by investigation by means of polarizing optical microscopy when the sample is cooled from the isotropic phase (see Fig. 2). An additional mesophase (SmX\*) appears below this smectic C\* phase. The crystal phase melting and the chiral smectic C\* phase clearing are determined at around 40.4  $^\circ\text{C}$  and 101.5  $^\circ\text{C}$ , respectively (see Fig. 3).

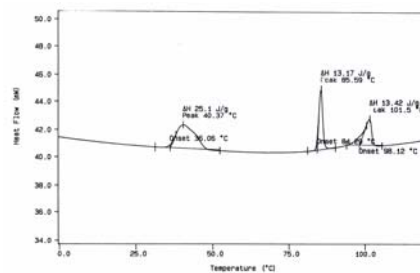


Fig. 3. DSC scans of the compound MBHOPIMP during the second heating process.

A comparison of the phase transition data of MBHOPIMP with an analog containing the corresponding alkyl chain (n-hexyl-) instead of alkoxy chain (n-hexyloxy-) attached to one of the side chains, shows that the kind of side chain in this case effects mesophase ranges. Both mesogens show a fingerprint texture of the chiral smectic C\* phase. For compound MBHOPIMP, the clearing point is significantly higher than observed for the analog with a n-hexyl alkyl chain (phase sequence: Cr 43.9 SmC\* 50.4 Iso) [8, 15]. In addition, SmX\* mesophase occurs below this smectic C\* phase.

The specific retention volume,  $V_R^0$  of the studied solvents on the MBHOPIMP was obtained from IGC measurements at temperatures in  $^\circ\text{C}$  between 110 and 130 using Eq.1. Results were given in Fig.4.

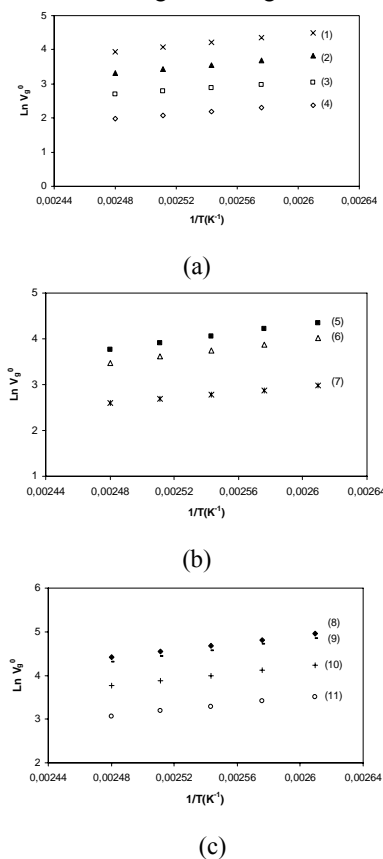


Fig. 4. The retention diagram of N (1), O (2) CH (3), CP(4), nBA (5), IBA(6), EA (7), CB (8), EB (9), T (10) and B (11) on MBHOPIMP

The liquid crystal-solvent interaction parameters,  $\chi_{12}^{\infty}$  and  $\chi_{12}^*$  were determined from Eq.(2) and Eq.(3) and the values found in this study were given in Table 1 and 2, respectively. They were compared with the values obtained previously at 95°C of analog containing alkyl chain (n-hexyl-) instead of alkoxy chain (n-hexyloxy-) attached to one of the side chains [8]. It was seen that there is no any significant difference of the values of the parameters  $\chi_{12}^{\infty}$  and  $\chi_{12}^*$ . The values of  $\chi_{12}^{\infty}$  greater than 0.5 represent unfavorable liquid crystal-solvent interactions while the values lower than 0.5 indicate favorable interactions in dilute liquid crystal solutions. The values of the parameters suggest that studied alkanes and acetates are poor while aromatic solvents are good for MBHOPIMP. The solvent quality slightly increased in the case of O, N, CH, EA, IBA, T, EB, CB, however it did not change with temperature in the case of CP, NBA and B.

Table 1. Comparison of the Flory-Huggins liquid crystal- solvent interaction parameters,  $\chi_{12}^{\infty}$  of MBHOPIMP with solvents determined in this study with literature.

Solvents	110 °C	115 °C	120 °C	125 °C	130 °C
O	1.00	0.99	0.99	0.96	0.95
N	1.03	1.02	1.00	0.99	0.97
CP	0.75 0.71*	0.72	0.73	0.75	0.75
CH	0.80 0.68*	0.75	0.73	0.71	0.70
EA	0.79 0.79*	0.77	0.74	0.72	0.70
NBA	0.63	0.61	0.62	0.62	0.63
IBA	0.66	0.65	0.63	0.63	0.63
B	0.43	0.41	0.42	0.40	0.41
T	0.25	0.23	0.23	0.22	0.22
EB	0.45	0.43	0.42	0.42	0.41
CB	0.33	0.33	0.31	0.31	0.30

\*at 95°C, Ref [8]

Table 2. Comparison of the equation-of-state crystal-solvent interaction parameters,  $\chi_{12}^*$ , of MBHOPIMP with solvents determined in this study with literature

Solvents	110 °C	115 °C	120 °C	125 °C	130 °C
O	1.07	1.06	1.06	1.04	1.02
N	1.09	1.07	1.06	1.04	1.03
CP	0.89 0.85*	0.87	0.90	0.94	0.95
CH	0.91 0.78*	0.86	0.84	0.83	0.81
EA	0.94 0.94*	0.92	0.89	0.88	0.87
NBA	0.72	0.70	0.71	0.71	0.73
IBA	0.75	0.75	0.73	0.73	0.73
B	0.54	0.53	0.54	0.53	0.54
T	0.33	0.32	0.32	0.31	0.31
EB	0.51	0.49	0.49	0.48	0.48
CB	0.39	0.39	0.38	0.38	0.37

\*at 95°C, Ref [8]

The effective exchange energy parameters,  $X_{\text{eff}}$  in the equation of state theory were obtained from Eq.(4) and results were given in Table 3. It was determined that  $X_{\text{eff}}$  of MBHOPIMP in O, N, CP, CH, EA, IBA, T, EB and CB slightly decreased with temperature while those of NBA, and B did not change with temperature.

Table 3. Comparison of the effective exchange energy parameters,  $X_{\text{eff}}$  (J/cm<sup>3</sup>) of MBHOPIMP with solvents determined in this study with literature

Solvents	110 °C	115 °C	120 °C	125 °C	130 °C
O	16.8	16.5	16.5	15.7	15.4
N	15.5	15.1	14.9	14.4	14.2
CP	25.6 21.5*	21.7	20.6	20.3	19.6
CH	22.9 18.3*	20.4	19.7	19.1	18.7
EA	16.8 16.9*	15.4	13.9	13.0	12.3
NBA	7.6	6.6	6.8	6.8	7.2
IBA	5.2	4.9	3.9	3.9	3.9
B	8.6	7.4	8.0	6.9	7.3
T	-0.8	-2.0	-2.2	-2.8	-3.1
EB	8.8	7.9	7.4	6.9	6.7
CB	6.5	5.9	5.1	4.6	4.2

\*at 95°C, Ref [8]

#### 4. Conclusions

We have synthesized and characterized a new salicylaldehyde compound MBHOPIMP and investigated the mesomorphic properties of these materials. Phase transition temperatures of MBHOPIMP were determined by PM and DSC. The thermodynamic parameters obtained in this study at temperatures between 110 and 130 °C were compared with the ones obtained in our earlier study at 95 °C. It was seen that there was no any significant difference between thermodynamic parameters of the compounds with alkyl and alkoxy chain. This study suggested that studied alkanes and acetates were poor but aromatics were good solvents for MBHOPIMP between 110 and 130 °C. It was obtained that the temperature dependence of  $X_{\text{eff}}$  was negligible for all studied solvents.

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