OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 2, No. 6, June 2008, p. 374 - 378

Synthesis, characterization and retention behavior of 4-(tetradecyloxy)-N-(4-hexyloxyphenyl)-2-hydroxybenzalimine

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A liquid crystalline compound, 4-(tetradecyloxy)-N-(4-hexyloxyphenyl)-2-hydroxybenzalimine (THPHBI) has been synthesized and characterised. Phase transition temperatures of 4-(tetradecyloxy)-N-(4-hexyloxyphenyl)-2-hydroxybenzalimine were determined by polarizing microscopy, differential scanning calorimetry and inverse gas chromatography technique (IGC).
The retention diagrams of n-butyl acetate (nBA), iso-butyl acetate (IBA), benzene (B), toluene (T) and ethylbenzene (EB) were plotted between 40 and 160 °C by IGC. Specific retention volume, V_g^0, weight fraction activity coefficient, Ω_1^∞, Flory Huggins polymer-solvent interaction parameter, χ_{12}^∞, equation of state polymer-solvent interaction parameter, χ_{12}^* and effective exchange energy parameter, X_{eff} were determined for studied solvents. Then, the exchange enthalpy parameter, X_{12} and entropy parameter Q_{12} were determined by using a relation for the enthalpy interaction parameter, χ_h^* of the equation of state theory, which was arranged for the IGC.

(Received April 16, 2008; accepted June 4, 2008)

Keywords: Inverse gas chromatography, Phase transition temperature, Liquid crystal, Interaction parameter, Equation of state parameters

1. Introduction

The natural progress of development of liquid crystals (LC) in physics and chemistry gave rise to the production of new mesogenic materials, which have unusual structural and physical properties. Mesogenic salicylaldimine compounds are very interesting materials for the physical investigations. Depending on the carbon number of the terminal alkoxyl and/or alkyl groups in the salicylaldimine core, these materials display various mesomorphic properties [1, 2].

Some years ago, liquid crystalline materials were suggested as stationary phases for analytical gas chromatography where the molecular ordering of the liquid crystals should allow discrimination between closely related isomeric analytes [3]. For each of these applications, knowledge of the interactions between the components is important in designing and formulating new systems.

In this paper the synthesis, characterization and mesomorphic properties of a salicylaldimine compound 4-(tetradecyloxy)-N-(4-hexyloxyphenyl) -2-hydroxybenzalimine (THPHBI) are presented and the retention diagrams of some solvents on this liquid crystal compound were obtained by inverse gas chromatography (IGC). Although IGC has been widely used to investigate the interactions and phase transition temperatures of polymeric materials with various solvents [4-6], it is a new method determination of interactions and the phase transition temperatures of a liquid crystals with solvents and there is only a few study in the literature [7,8]. Then, some thermodynamic parameters in the Flory-Huggins theory and equation of state theory of the THPHBI were determined in the range of 40 °C and 160 °C. The exchange enthalpy parameters, X_{12}, and entropy parameters, Q_{12}, in the equation of state theory are assumed to be independent on temperature and composition of the mixture, but this situation is not confirmed yet. It was the first time, we have determined exchange enthalpy and entropy parameters of poly(dimethylsiloxane) and methylhydrosiloxane-dimethylsiloxane copolymer with some solvents directly from IGC measurements earlier [9-13]. The parameters X_{12} and Q_{12} of these polymer-solvent systems were comparable with those determined earlier by other techniques at lower polymer concentrations. There is no any other data in the literature related to the determination of parameters X_{12} and Q_{12} of THPHBI. In this study, it is the first time it is determined the parameters X_{12} and Q_{12} by IGC measurements, also investigated the dependence of X_{12} and Q_{12} parameters on temperature for THPHBI at temperature range in between 125 and 160 °C.

2. Experimental

2.1. Materials and instrumentation

The characterization of the liquid crystalline compound THPHBI synthesized here are based on various spectroscopic data, e.g., ^{1}H-, ^{13}C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions) with tetramethylsilane as internal standard, MS [AMD 402 (electron impact, 70 eV)].

Transition temperatures were measured using a Linkam THMS 600 hot stage and a Linkam TMS 93 temperature control unit in conjunction with a Leitz Laborlux 12 Pol polarizing microscope (PM), and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 (DSC), heating and cooling rate: 10 K min^{-1}).

The solvents butyl acetate (nBA), iso-butyl acetate (IBA), benzene (B), toluene (T), ethylbenzene (EB) and 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 5890 Model, series II gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents. Data acquisition and analysis were performed by means of HP-3365 software. The column was stainless steel tubing with 3.2 mm o.d. and 1m in length.

2.2. Synthesis of the NBAM

The THPHBI were prepared in the usual way [14] by a *p*-toluensulfonic acid (40 mg) catalyzed condensation of 4-tetradecyloxy-2 hydrobenzaldehyde (5 mmol) with 4-hexyloxyaniline (6 mmol) in toluene (25 mL) and purified by crystallization from acetone/ethanol.

The THPHBI was characterized by various spectroscopic methods. The spectroscopic data are given below.

Yield: 1.91 g (75%) of yellow crystals. **^{1}H-NMR**: δ (ppm) = 13.84 (s; OH), 8.48 (s; HC=N), 7.22, 7.20, 6.90 (3d, *J* ≈ 8.5 Hz each; 1, 2 and 2 arom. H, respectively), 6.45-6.30 (m; 2 arom. H), 3.97, 3.95 (2t, *J* ≈ 6.5 Hz; 2 x OCH_2 groups). **^{13}C-NMR**: δ (ppm) = 164.18, 163.15, 158.01, 141.10, 119.03 (5s; 5 arom. C), 159.33 (d; HC=N), 133.15, 121.99, 115.16, 107.53, 101.37 (5d: 1, 2, 2, 1 and 1 arom. CH, respectively), 68.34, 68.22 (2t; 2 x OCH_2 groups). $C_{33}H_{51}NO_3$ (509.77); **MS (EI)**: *m/z (%)* = 509 (100) $[M]^+$, 313 (36) [509-$C_{14}H_{28}$].

2.3. Inverse Gas Chromatography Theory

The specific retention volume, V_g^0 is determined experimentally from inverse gas chromatography measurements as follows [15,16].

$$V_g^0 = Q\,(t_R - t_A)\,J\,273.2/(T_r w) \tag{1}$$

where Q is carrier gas flow rate measured at the room temperature T_r; t_R and t_A are retention times of the solvent and air, respectively; J is pressure correction factor, w is weight of liquid crystal in the column.

Ω_1^∞ is the weight fraction activity coefficient of solvent at infinite dilution, defined by the following equation,

$$\ln\Omega_1^\infty = \ln\,(273.2\,R / V_g^0 p_1^0 M_1) - p_1^0 (B_{11} - V_1^0)/RT \tag{2}$$

where R is the universal gas constant; p_1^0, B_{11} and V_1^0 are saturated vapor pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature T; M_1 is the molecular weight of solvent, respectively.

According to the theories of Flory-Huggins and equation-of-state interaction parameters, χ_{12}^∞ and χ_{12}^* are defined in the Eq.(3) and Eq.(4), respectively:

$$\chi_{12}^\infty = \ln\left(\frac{273.2\,Rv_2}{p_1^0 V_g^0 V_1^0}\right) - \left(1 - \frac{V_1^0}{M_2 v_2}\right) - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \tag{3}$$

$$\chi_{12}^* = \ln\left(\frac{273.2\,Rv_2^*}{p_1^0 V_g^0 V_1^*}\right) - \left(1 - \frac{V_1^*}{M_2 v_2^*}\right) - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \tag{4}$$

where v_2 and v_2^* are specific volume and specific hard-core volume of the liquid crystal respectively.
V_1^* is molar hard-core volume of the solvent.

The effective exchange energy parameter, X_{eff} in the equation of state theory is defined as follows,

$$\begin{aligned} RT\chi_{12}^* &= p_1^* V_1^* \{3T_{1r} \ln[(v_{1r}^{1/3} - 1)/(v_{2r}^{1/3} - 1)] \\ &\quad + v_{1r}^{-1} - v_{2r}^{-1} + X_{eff}/P_1^* v_{2r}\} \end{aligned} \tag{5}$$

where p_1^* is characteristic pressure, v_{1r} and v_{2r} are reduced volume of the solvent and liquid crystal, respectively. T_{1r} is reduced temperature of the solvent.

The enthalpic interaction parameter χ_h^* can be obtained from the slope of the plot χ_h^* versus 1/T from IGC measurements according to its definition [9-13]

$$\chi_h^* = [\partial \chi_{12}^* / \partial (1/T)]/T \tag{6}$$

According to the equation of state theory, χ_h^* is approximated as under the gas chromatographic conditions.

$$\chi_h^* = (p_1^* V_1^*/RT)[(v_{1r}^{-1} - v_{2r}^{-1}) + (\alpha_2 T/v_{2r})(T_{1r} - T_{2r})/T_{2r}] + V_1^*(1+\alpha_2 T)X_{12}/(v_{2r}RT) \quad (7)$$

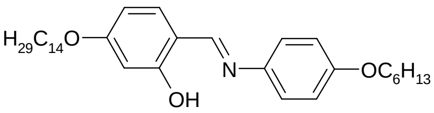
where X_{12} is the exchange enthalpy parameter. X_{eff} combines the parameters of exchange enthalpy X_{12} and entropy Q_{12} as follows:

$$X_{eff} = X_{12} - T\, v_{2r}\, Q_{12} \quad (8)$$

3. Results and discussion

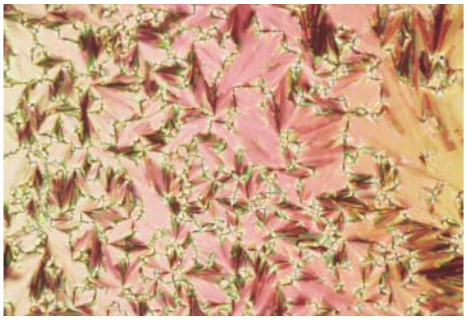
The THPHBI was prepared under a nitrogen atmosphere and in two step process. It has been purified by several recrystallization from acetone/methanol. The pure product obtained as yellow crystals was characterized by various spectroscopic methods, e.g., ^1H, ^{13}C NMR ($CDCl_3$) and mass. The proposed molecular structure of

THPHBI presented in Fig. 1 is in full agreement with these spectroscopic data (see Experimental Section).



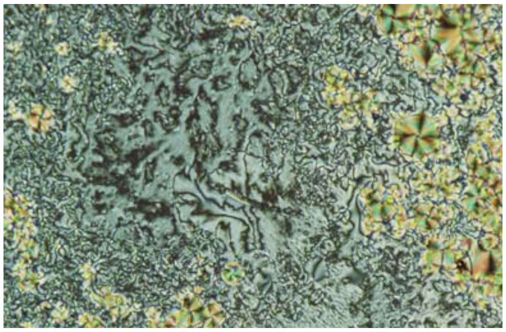
Compound I

This new compound THPHBI exhibits liquid crystalline properties and shows thermotropic enantiotropic mesophase. The investigations by PM and DSC show that it exhibits *smectic C* (*SmC*) mesophase. On cooling of THPHBI from isotropic phase, smectic phase with broken fan-shaped and schlieren textures can be observed (see Fig. 2a and 2b, respectively).



(a)

Fig. 1. Molecular structure of the THPHBI.



(b)

Fig. 2. Optical texture of SmC phase of THPHBI observed at (a) 107 °C (b) 125 °C on cooling from isotropic phase.

THPHBI shows similar mesomorphic properties with the previously synthesized analogs [2,14]. During heating, the crystal (*Cr*)-*SmC* phase transition occurs at 79.5 °C and the *SmC – isotropic liquid (Iso)* phase transition occurs at 121.3 °C, in this case, the *SmC* mesophase exists in the temperature interval as 41.8 °C. During cooling, *Iso-SmC* phase transition occurs at 117.5 °C and *SmC–Cr* phase transition occurs at 47.1 °C; in this case, the *SmC* mesophase exists in the temperature interval as 70.4 °C degree. In Fig. 3, DSC scan can be seen in during heating process.

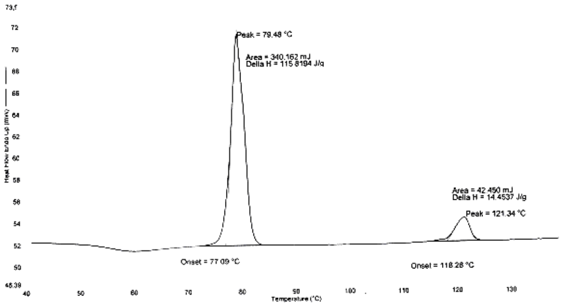


Fig. 3. DSC scan of THPHBI during the second heating process

The phase transition between *SmC* mesophase and *Iso* phase by cooling of the THPHBI takes place at lower temperatures than the temperatures by heating, i.e., the thermic hysterezis takes place for the phase transitions between *SmC* and *Iso* phase. The thermic hysterezis has been also observed by number of researchers, which used different experimental methods, for the first order phase transitions between liquid crystalline mesophase and isotropic liquid in various liquid crystals [17-19].

The specific retention volume, V_g^0 of the studied solvents on the THPHBI was obtained from IGC measurements between 40 and 160 °C using Eq.1. According to retention diagram in Fig. 4., *Cr-SmC* and *SmC-Iso* transitions for THPHBI were found to be 73 °C and 118

°C, respectively, as the point from which the deviation from linearity was first seen. The *Cr-SmC* and *SmC-Iso* transition temperatures obtained by inverse gas chromatography technique are in good agreement with the ones obtained by DSC.

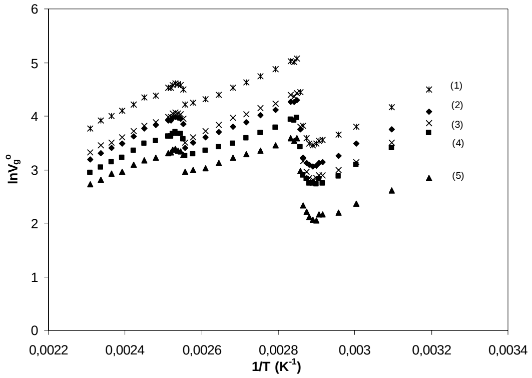


Fig. 4. The retention diagrams of EB(1), nBA(2), T(3), IBA(4) and B(5) on THPHBI.

According to Guillet [4], the solvent is good if Ω_1^∞ is lower than 5 and poor if it is higher than 10. The values between 5 and 10 indicate moderately solubility. The values of Ω_1^∞ suggest that all studied solvents given in Table 1 are good for the THPHBI at the studied temperatures.

Table 1. The weight fraction activity coefficient at infinite dilution of the solvents, Ω_1^∞ of THPHBI with studied solvents at various column temperatures.

t(°C)	nBA	IBA	B	T	EB
125	4.15	4.41	3.48	2.80	3.24
130	3.96	4.21	3.35	2.72	3.25
135	3.53	3.91	3.19	2.57	2.97
140	3.74	3.93	3.22	2.54	2.96
145	3.75	3.97	3.23	2.59	2.96
150	3.63	3.82	3.60	2.54	2.88
155	3.60	3.78	3.10	2.44	2.80
160	3.58	3.77	3.10	2.50	2.87

The polymer-solvent interaction parameters, χ_{12}^∞ and χ_{12}^* were determined from Eq.(3) and Eq.(4) and their values were given in Table 2 and Table 3, respectively. The values of χ_{12}^∞ greater than 0.5 represent unfavourable liquid crystal-solvent interactions while the values lower than 0.5 indicate favourable interactions in dilute liquid crystal solutions. The values of the parameters in Table 2 and 3 suggest that all solvents are good for THPHBI. The trends of all sets of data are similar, showing a decrease of the interaction parameter as the temperature is increased. This indicates that the solvent quality increases with temperature.

Table 2. Flory-Huggins liquid crystal l- solvent interaction parameters, χ_{12}^∞ of THPHBI with studied solvents at various column temperatures

t(°C)	nBA	IBA	B	T	EB
125	0.52	0.53	0.24	0.06	0.25
130	0.47	0.48	0.20	0.03	0.25
135	0.36	0.40	0.15	-0.03	0.16
140	0.41	0.40	0.12	-0.04	0.15
145	0.41	0.41	0.15	-0.03	0.15
150	0.37	0.40	0.09	-0.05	0.12
155	0.36	0.35	0.10	-0.10	0.09
160	0.35	0.34	0.10	-0.08	0.11

Table 3. Equation of state liquid crystal- solvent interaction parameters, χ_{12}^* of THPHBI with studied solvents at various column temperatures.

t(°C)	nBA	IBA	B	T	EB
125	0.66	0.67	0.41	0.19	0.35
130	0.61	0.62	0.36	0.15	0.35
135	0.50	0.55	0.31	0.10	0.26
140	0.55	0.55	0.28	0.08	0.25
145	0.56	0.56	0.31	0.11	0.26
150	0.52	0.52	0.24	0.08	0.23
155	0.51	0.51	0.25	0.05	0.20
160	0.52	0.51	0.25	0.07	0.22

The effective exchange energy parameters, X_{eff} in the equation of state theory were obtained from Eq.(5) and results were given in Table 4. It was determined that X_{eff} of THPHBI in all solvents is changeable depending on temperature.

Table 4. The effective exchange energy parameters, X_{eff} (J/cm^3) of THPHBI with studied solvents at various column temperatures

t(°C)	nBA	IBA	B	T	EB
125	6.89	5.02	-0.62	-7.99	3.35
130	5.99	3.10	-1.89	-7.19	2.56
135	-0.15	0.18	-3.95	-10.94	-0.67
140	4.01	0.29	-4.59	-11.13	-0.42
145	2.63	1.60	-1.81	-12.82	-1.39
150	1.03	-0.80	-2.96	-11.82	-3.44
155	0.64	-1.05	-1.57	-14.72	-4.17
160	0.83	-1.69	-2.36	-14.37	-2.70

The parameters X_{12} were obtained by means of the Eq.(7) using the values of χ_h^* found from slopes of the plots according to Eq.(6). Then, parameters Q_{12} were calculated from Eq. (8). Results were given in Table 5 and Table 6, respectively. Although the parameters X_{12} and Q_{12} have very slightly changed for studied solvents, the temperature dependences of X_{12} and Q_{12} are negligible.

Table 5. The exchange enthalpy parameters, X_{12} (J/cm^3) of THPHBI with studied solvents at various column temperatures

t(^{o}C)	nBA	IBA	B	T	EB
125	53.06	61.87	100.91	61.58	59.52
130	52.27	62.43	99.48	59.19	60.58
135	54.37	62.93	98.45	60.41	60.07
140	52.37	63.18	97.20	59.81	59.78
145	54.36	62.22	96.21	62.79	60.77
150	54.90	63.60	92.85	60.36	61.79
155	55.23	63.69	91.65	61.49	61.22
160	55.70	64.71	92.98	62.37	60.63

Table 6. The exchange entropy parameters, $Q_{12}.10^2$ (J/cm^{3}K^{-1}) of THPHBI with studied solvents at various column temperatures

t(^{o}C)	nBA	IBA	B	T	EB
125	0.096	0.12	0.21	0.14	0.18
130	0.095	0.12	0.21	0.14	0.12
135	0.11	0.13	0.21	0.14	0.12
140	0.096	0.12	0.20	0.14	0.12
145	0.10	0.12	0.19	0.15	0.12
150	0.10	0.12	0.19	0.14	0.13
155	0.10	0.12	0.18	0.15	0.12
160	0.10	0.12	0.18	0.14	0.12

4. Conclusions

The liquid crystal THPHBI has been synthesized and characterized. Phase transition temperatures of THPHBI were determined by PM, DSC, and IGC. The transition temperatures of THPHBI obtained by IGC are in good agreement with the ones obtained by DSC and PM. The values of interaction parameters found in this study suggest that studied solvents are good for THPHBI. It was seen that the temperature dependences of X_{12} and Q_{12} are negligible.

Acknowledgement

This research has been supported by Yildiz Technical University Scientific Research Projects Coordination Department.

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