Thermodynamics of The Mixture of A Liquid Crystal and A Copolymer of Dimethylsiloxane

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5-dodecyloxy-2-[[[4-(S)-(2-methylbutoxy)phenyl]imino]methyl]phenol (BPIP) which represents liquid crystal transitions was synthesized by means of condensation reaction. On investigation by optical microscope, it was observed that BPIP maintained its chiral smectic mesophase of the fingerprint texture in its binary mixture with poly(methylhydrosiloxane-co-dimethylsiloxane) (HMS) in composition of 50% by weight. Liquid crystal-polymer interaction parameters of BPIP and HMS in the mixture were determined at temperatures between 90 and 105 in °C using trace amount solvents used as probes by inverse gas chromatography technique. The obtained small positive values of the liquid crystal-polymer interaction parameters being independent on solvent suggested that BPIP and HMS were immiscible but could not phase separate at studied temperature range.

Keywords: Chromatography, Thermodynamics, Miscibility, Mixture, Liquid Crystal, Poly(methylhydro siloxane-co-dimethylsiloxane)

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1. Introduction

Liquid crystals (LC) which exhibit extraordinary properties have a distinct relation with "order" and "dynamics" on molecular basis. They display numerous mesophases having various structural properties and spatial symmetries and exhibit unusual physical and physicochemical properties. These materials which are very sensitive to the different external effects have high application opportunities and are advantageous and perspective materials from technical, technological and economical points of view [1]. In some applications, the liquid crystal is dispersed in a polymeric matrix. In this case, it is desired that the dispersed phase should evenly spread in the mixture but in the same time it should maintain the liquid crystalline properties. In addition, the mixture should not undergo to the phase separation in the long term usage. This information is supplied by the magnitude of the liquid crystalpolymer interaction parameter, χ_{23} . Here, liquid crystal-polymer interaction term was preferred instead of common polymer-polymer interaction term. There are several techniques to determine the parameter χ_{23} in literature. Among them, inverse gas chromatography (IGC) is easier, faster and more economical [2,3] in determination the physicochemical properties and interaction parameters of polymers and their mixtures with other substances. In early works, it was seen that the parameter χ_{23} determined by IGC was slightly dependent on the solvent used as probe. Prolongo et al. [4] as well as Farooque and Deshpande [5] have individually suggested two distinct methods to remove the solvent effects on the parameter χ_{23} .

Recently, IGC has been successfully used to display the phase transitions and to determine the parameters χ_{23} of poly(dimethylsiloxane)- LC mixtures in a few studies [6-10]. However, the subject needs lots of experimental data to establish the basis of stable liquid crystal dispersion in a liquid polymer. A mixture of a synthesized LC with a liquid copolymer was studied by IGC in this study since there is no any data related to the mixtures of a LC with any other polymer or copolymer in literature, yet.

At first, 5-dodecyloxy-2-[[[4-(S)-(2-methylbutoxy)phenyl]imino]methyl]phenol (BPIP) being a liquid crystal was synthesized by means of condensation reaction. Then, BPIP and poly(methylhydrosiloxane-co-dimethylsiloxane) (HMS) and a mixture of them in composition of 50 % by weight were studied by IGC. Then, the parameters χ_{23} independent on solvent were determined by applying two distinct methods suggested by both Prolongo et al. and Farooque and Deshpande.

2. Experimental

2.1. Materials and Instrumentation

The characterization of the compound I (BPIP) synthesized here are based on various spectroscopic data, e.g., ¹H-, ¹³C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, respectively, in CDCl₃ solutions) with tetramethylsilane as internal standard, MS [AMD 402 (electron impact, 70 eV)], UV-VIS (Agilent 8453, CHCl₃ solutions), FT-IR (Perkin Elmer, CHCl₃ solutions). Microanalyse was performed using a Leco CHNS-932 elemental analyzer.

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, and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-6, heating and cooling rate: 5 K min⁻¹).

Poly (methylhydrosiloxane-co-dimethyl siloxane) (HMS) was a product of ABCR. Methyl acetate (MA), ethyl acetate (EA), tert-butyl acetate (tBA), cyclo pentane (c-P), cyclohexane (c-H), n-hexane (Hx), n-heptane (Hp), benzene (B) 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 BPIP

5 mmol of 4-dodecyloxy-2-hydroxybenzaldehyde [11], 6 mmol of (S)-4-(2methylbutyloxy)aniline [12] 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 6 h under reflux. After cooling, a yellow precipitate was obtained. The precipitate was extracted with diethyl ether (3 x 100 ml). The combined organic layers were washed with NaHCO₃ and NaCl and dried with anhydrous Na₂SO₄ before the diethyl ether was removed under reduced pressure. The crude products were purified by crystallization from acetone/methanol.

The BPIP was characterized by various spectroscopic methods, e.g., ¹H, ¹³C NMR (CDCl₃), UV-VIS, IR and mass and given below.

Compound I (BPIP): Yield: 1.73 g (74%), yellow crystals. — ¹H NMR: δ (ppm)= 13.90 (s; OH), 8.48 (s; HC=N), 7.22-7.19 (m; 3 arom. H), 6.90 (d, J \approx 8.7 Hz; 2 arom. H) 6.47-6.44 (m; 2 arom. H), 3.97 (t, J \approx 6.6 Hz; OCH₂), 3.82, 3.73 (2 dd, J \approx 6.0 Hz and J \approx 8.9 Hz, respectively; OCH₂ of the chiral alkyl chain), 1.88-1.84 (m; CH), 1.80-1.75 (m; CH₂), 1.59-1.24 (m; 10 CH₂), 1.01 (d, J \approx 6.7 Hz; CH₃), 0.94, 0.87 (2 t, J \approx 7.4 Hz and J \approx 6.8 Hz, respectively; 2 CH₃). — ¹³C NMR: δ (ppm) = 163.73, 163.21, 158.17, 141.20, 113.10 (5 s; 5 arom. C), 159.42 (d, HC=N), 73.22, 68.20 (2 t; 2 OCH₂), 34.74 (d; CH), 31.91, 29.69, 29.65, 29.58, 29.55, 29.36, 29.34, 29.09, 26.14, 25.98, 22.68 (11 t; 11 CH₂), 16.52, 14.01, 11.30 (3q, 3 CH₃). — MS: m/z (%) = 467 (100) [M⁺], 396 (13) [M⁺ - C₅H₁₁], 229 (38) [M⁺ - C₅H₁₁ - C₁₂H₂₅]. — UV-VIS: λ (nm) = 349.0. — IR: γ = 1625 cm⁻¹ (C=N). — C₃₀H₄₅NO₃ (467.7): calcd. C 77.04, H 9.69, N 2.99; found C 77.32, H 9.65, N 2.94.

The proposed molecular structure of BPIP presented in Fig. 1 is in full agreement with these spectroscopic data.



Figure 1. Molecular structure of compound I (BPIP).

3. Data Reduction on IGC

The specific retention volume, V_g^0 is determined experimentally from IGC measurements as follows [13-15]

$$V_{g}^{0} = Q(t_{R} - t_{A}) J 273.2 / (T_{r}w)$$
(1)

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

According to the theories of Flory-Huggins and equation-of-state, [16] the interaction parameters, χ_{12}^{∞} and χ_{12}^{*} between solvent and stationary phase are defined in Eq.2 and Eq.3, respectively:

$$\chi_{12}^{\infty} = \ln(273.2Rv_2 / p_1^0 V_g^0 V_1) - 1 - p_1^0 (B_{11} - V_1) / RT$$
⁽²⁾

$$\chi_{12}^* = \ln(273.2\text{Rv}_2^*/p_1^0\text{V}_g^0\text{V}_1^*) - 1 - p_1^0(\text{B}_{11} - \text{V}_1)/\text{RT}$$
(3)

where R is the universal gas constant; p_1^0 , B_{11} and V_1 are saturated vapour pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature T. v is specific volume and superscript asterisk indicates hard-core volume of the corresponding solvent (1) and substance used as stationary phase (2). The infinity sign used as superscript in the interaction parameter indicates that the amount of stationary phase (usually a polymer) in the mixture approaches to infinity as compared with the amount of solvent in the IGC conditions since trace amount solvent is injected into the column carrying the stationary phase. In the equation-of-state theory, the state parameters are reduced by dividing to the corresponding characteristic parameters such as $V^r = V/V^*$, $T^r = T/T^*$ and $p^r = p/p^*$.

Solvent (1) - liquid crystal (2) - polymer (3) - interaction parameter $\chi^{\infty}_{1(23)}$ of ternary mixtures is obtained experimentally from the V_g^0 data of the columns containing the mixture by means of the equation:

$$\chi_{1(23)}^{\infty} = \ln(273.2R(w_2v_2 + w_3v_3) / V_g^0 p_1^0 V_1) - (1 - V_1 / V_2)\phi_2$$

$$- (1 - V_1 / V_3)\phi_3 - p_1^0 (B_{11} - V_1) / RT$$
(4)

and it is related to the other interaction parameters by means of the additive relation

$$\chi_{1(23)}^{\infty} = \varphi_2 \chi_{12}^{\infty} + \varphi_3 \chi_{13}^{\infty} - \varphi_2 \varphi_3 \chi_{23} (V_1 / V_2)$$
(5)

where w and ϕ are weight and volume fractions of liquid crystal (2) and polymer (3) in the blend, respectively.

It was seen that the magnitude of χ_{23} depends on the solvent used in the experiments. In order to minimize the solvent effect on the parameter χ_{23} , Prolongo et al.[4] have proposed a method based on the equation-of-state theory. In order to proceed by equation-of-state theory, it is necessary to substitute the volume fraction φ_i in the Flory-Huggins theory by segment fraction, ϕ_i :

$$\phi_i = \mathbf{w}_i \mathbf{v}_i^* / \Sigma(\mathbf{w}_i \mathbf{v}_i^*) \tag{6}$$

where w_i is weight fraction of the component *i*. In the equation of state theory, the additive relation is written in segment fractions

$$\chi_{1(23)}^{*} = \chi_{12}^{*} \phi_{2} + \chi_{13}^{*} \phi_{3} - \phi_{2} \phi_{3} \chi_{23}^{A} (V_{1}^{*} / V_{2}^{*})$$
⁽⁷⁾

and the residual chemical potential of the solvent in a ternary mixture, $\chi^*_{1(23)}$ is written in the IGC conditions, i.e. $\phi_1 \rightarrow 0$,

$$\chi_{1(23)}^{*} = \chi_{12}^{*} V_{2}^{r} \theta_{2} / V_{23}^{r} + \chi_{13}^{*} V_{3}^{r} \theta_{3} / V_{23}^{r} - \chi_{23}^{T} (V_{1}^{*} / V_{2}^{*}) (s_{1} / s_{3}) \phi_{2} \phi_{3} + \Gamma$$
(8)

where Γ is a free volume term, V^r is reduced volume of the binary systems and θ_i is the molecular surface fraction defined as

$$\theta_{i} = w_{i}v_{i}^{*}s_{i} / \Sigma(w_{i}v_{i}^{*}s_{i})$$
⁽⁹⁾

with s_i the molecular surface to volume ratio of the component *i*. The values of s_1, s_2 and s_3 can be estimated using a spherical model for the solvents and liquid crystal whereas cylinder model for the polymer units with volume v^* .

By combining the Equation 7 with the Equation 8, the following equation was obtained by Prolongo et al.

$$\frac{(\chi_{23}^{A} + \kappa) / V_{2}^{*} s_{1}}{\chi_{23}^{T} / V_{2}^{*} s_{3}} = \frac{[(s_{3} - s_{2})(\chi_{12}^{*} - \chi_{13}^{*})] / [(\phi_{2} s_{2} + \phi_{3} s_{3}) V_{1}^{*} s_{1}]}{(10)}$$

where

$$\kappa = (V_2^* / V_1^*) \begin{cases} \Gamma / \phi_2 \phi_3 + \chi_{12} [(V_2^r / V_{23}^r) - 1] [\phi_3^{-1} + (s_2 - s_3) / (\phi_2 s_2 + \phi_3 s_3)] \\ + \chi_{13} (V_3^r / V_{23}^r - 1) [\phi_2^{-1} - (s_2 - s_3) / (\phi_2 s_2 + \phi_3 s_3)] \end{cases}$$
(11)

and

$$\Gamma = P_{1}^{*}V_{1}^{*} / RT[\Gamma_{1p} - (V_{2}^{r}\theta_{2}\Gamma_{12}) / V_{23}^{r}) - (V_{3}^{r}\theta_{3}\Gamma_{13} / V_{23}^{r})] + P_{2}^{*}V_{1}^{*}s_{1}\theta_{2}\Gamma_{23} / RTs_{2}\theta_{3}$$
(12)

where

$$\Gamma_{ij} = V_i^{r-1} - V_{ij}^{r-1} - 3T_i^r \ln[(V_{ij}^{r1/3} - 1)/(V_i^{r1/3} - 1)]$$

Where χ_{23}^{A} and χ_{23}^{T} are liquid crystal-polymer interaction parameter and liquid crystal-polymer interaction parameter being independent on solvent, respectively.

Although the binary Flory-Huggins interaction parameters are used in the original method, it was preferred to use equation-of-state interaction parameters, χ_{12}^* in the above equations in this study.

It was proposed that a plot of the left hand side of Eq.10 versus $(\chi_{12}^* - \chi_{13}^*)$ yields a linear straight line of which χ_{23}^T can be found from the intercept. All of the equation-of-state-parameters of the components and their mixtures must be known in this method however the reduced parameters of binary systems can only be calculated approximately because of the absence of their experimental data. Therefore, its use becomes complicated and uncertain. The authors stated that κ was small quantity and might be ignored.

Later, Farooque and Deshpande suggested a simpler method to eliminate the solvent dependence of the parameter, χ_{23}^{D} of a blend. According to this method, solvent-independent interaction parameter, χ_{23}^{D} was given as follow [5]

$$\left(\chi_{1(23)}^{\infty} - \chi_{13}^{\infty}\right) / V_1 = \varphi_2\left(\chi_{12}^{\infty} - \chi_{13}^{\infty}\right) / V_1 - \left(\varphi_2\varphi_3 / V_2\right)\chi_{23}^{D}$$
(13)

Eq. 11 suggests that the $(\chi_{1(23)}^{\infty} - \chi_{13}^{\infty})/V_1$ versus $(\chi_{12}^{\infty} - \chi_{13}^{\infty})/V_1$ plot must give a straight line of which χ_{23}^{D} can be found from the intercept.

4. Results and discussion

The synthesized BPIP exhibits liquid crystalline properties and shows thermotropic enantiotropic mesophase. The investigations by polarizing microscopy (PM) show that it exhibits *smectic* C^* (*SmC*^{*}) mesophase (Fig. 2).



Figure 2. Optical texture of smectic C* phase of BPIP observed at 80°C on cooling from isotropic phase.

The BPIP shows similar mesomorphic properties with the previously synthesized analogs [17]. During heating, the *crystal* (*Cr*) – *SmC** phase transition occurs at 76 °C and the *SmC**– *isotropic liquid* (*I*) phase transition occurs at 87 °C, in this case, the *SmC** mesophase exists in the temperature interval as 11 °C. During cooling, *I-SmC** phase transition occurs at 85 °C and *SmC**–*Cr* phase transition occurs at 66 °C; in this case, the *SmC** mesophase exists in the temperature interval as 19 °C degree. On cooling from *I* phase, *SmC** mesophase with fingerprint texture can be observed in the Fig. 2. It means that the BPIP has a low clearing point (*SmC**-*I*) and has a narrow *SmC** range as can be seen in its DSC scan (Fig. 3).



Figure 3. DSC scan of BPIP during the second heating process.

DSC scan and optical texture of BPIP/HMS mixture in composition of 50% by weight were given in Fig. 4 and Fig 5, respectively. Their investigations show that BPIP maintains the enantiotropic mesophase in the mixture. During heating of the mixture, the Cr- SmC^* phase transition occurs at 75 °C and the SmC^* -I phase transition occurs at 82 °C. During cooling, I- SmC^* phase transition occurs at 78 °C and the SmC^* -Cr phase transition occurs at 68 °C. This means that the BPIP/HMS mixture has lower clearing points and has a narrower SmC^* range than pure BPIP.



Figure 4. DSC scan of the BPIP/HMS mixture during the second heating process.



Figure 5. Optical texture of smectic C* phase of BPIP/HMS mixture observed at 76 °C on cooling from isotropic phase.

It was seen in Fig. 5 that BPIP/HMS mixture is almost homogenous and softer than pure liquid crystal because of HMS is amorphous. In the same time, the liquid crystal component in the mixture maintains its chiral smectic mesophase with fingerprint texture and somewhat closer transition points. These results suggest that the mixtures of BPIP and HMS can be used confidentially as a liquid crystalline dispersion.

The specific retention volume, V_g^0 of the studied solvents on the BPIP, HMS and their mixture were obtained experimentally from IGC measurements using Eq.1. At first, retention diagrams of EA on pure BPIP and on its mixture with HMS of 50 % by weight were plotted at temperatures between 40 °C and 105 °C as represented in Fig.6. In the retention diagram of BPIP, the *Cr-SmC** transition can be observed clearly at 77 °C however *SmC*-I* transition is not pronounced in spite of a small deviation from linearity around 78 °C. In the retention diagram of the mixture, *Cr-SmC** transition occurs at 76 °C with a narrow transition region. Since the *SmC*-I* transition occurred at 87 °C during PM observation, it was assumed that thermodynamic equilibrium has established at temperatures higher than 90 °C. Therefore, the values of V_g^0 of BPIP, HMS and their mixture were given at temperatures higher than 90 °C in Table 1, Table 2 and Table 3, respectively.



Figure 6. The retention diagrams of EA on BPIP (2) and BPIP/HMS (1) mixture at temperatures between 40 °C and 105 °C.

$t(^{\circ}C)$	MA	EA	tBA	В	c-P	c-H	Hx	Нр
90	20.	31.	48.	55.	19.	38.	21.	44.
	67	47	89	92	60	72	14	58
95	18.	28.	43.	50.	18.	35.	19.	39.
	98	14	48	11	04	26	10	63
100	17.	25.	39.	45.	16.	31.	17.	35.
	49	50	20	03	66	86	39	87
105	16.	22.	35.	41.	15.	29.	16.	32.
	20	99	35	61	69	12	00	89

Table 1. Specific retention volumes of the solvents, $V^0_{\sigma}(cm^3 g^{-1})$ on BPIP

<i>t</i> (°C)	MA	EA	tBA	В	c-P	c-H	Hx	Нр
90	15.85	26.49	49.36	39.52	22.37	41.93	26.85	52.52
95	14.02	23.86	43.14	36.84	20.80	37.65	25.10	46.14
100	12.94	22.10	39.39	33.38	19.24	33.72	21.93	43.18
105	11.40	19.46	34.61	29.37	17.28	29.71	19.64	37.24

Table 2. Specific retention volumes of the solvents, $V_g^0(cm^3 g^{-1})$ on HMS

Table 3. Specific retention volumes of the solvents, $V_g^0(cm^3 g^{-1})$ on the BPIP/HMS mixture in a composition of 50 % by weight

<i>t</i> (°C)	MA	EA	tBA	В	c-P	c-H	Hx	Нр
90	18.72	30.34	52.68	52.18	22.67	42.82	26.11	44.58
95	17.06	26.94	45.37	45.75	20.26	37.74	23.20	49.89
100	15.44	23.98	39.61	39.87	18.25	33.76	20.47	43.57
105	14.31	21.37	35.11	35.12	16.30	30.28	18.47	38.59

The liquid crystal–solvent and polymer-solvent interaction parameters, χ_{12}^{∞} and χ_{12}^{*} were determined from Eq.2 and Eq.3 and results were presented at Tables 4-7, respectively. In polymer solutions, the values of χ_{12}^{∞} greater than 0.5 represent unfavourable polymer-solvent interactions or *vice versa*. In the case of BPIP, the values of χ_{12}^{∞} suggest that all solvents studied are good, especially B are very good solvents at studied temperatures. In the case of HMS, it was seen that c-P, c-H, Hx, Hp are good while B and tBA are moderately good but MA and EA are poor solvents at studied temperatures. Solubility of the polymer and the liquid crystal in each of the studied solvents increases with temperature.

<i>t</i> (°C)	MA	EA	tBA	В	c-P	c-H	Hx	Нр
90	0.58	0.47	0.35	0.10	0.24	0.30	0.37	0.37
95	0.53	0.43	0.29	0.07	0.20	0.26	0.34	0.33
100	0.47	0.39	0.25	0.03	0.16	0.22	0.30	0.27
105	0.42	0.36	0.23	- 0.015	0.11	0.18	0.26	0.23

Table 4. Flory-Huggins polymer-solvent interaction parameters, χ_{12}^{∞} of BPIP with the solvents

t(°C)	MA	EA	tBA	B	c-P	c-H	Hx	Нр
90	0.87	0.75	0.45	0.56	0.22	0.33	0.24	0.31
95	0.85	0.71	0.41	0.48	0.17	0.30	0.17	0.29
100	0.80	0.64	0.35	0.45	0.13	0.27	0.18	0.21
105	0.80	0.63	0.36	0.44	0.12	0.27	0.16	0.21

Table 5. Flory-Huggins polymer-solvent interaction parameters, χ_{12}^{∞} of HMS with the solvents

Table 6. Equation-of-state polymer-solvent interaction parameters, χ^*_{12} of BPIP with the solvents

<i>t</i> (°C)	MA	EA	tBA	B	c-P	c-H	Hx	Нр
90	0.86	0.75	0.61	0.33	0.51	0.52	0.65	0.61
95	0.81	0.71	0.56	0.30	0.47	0.48	0.62	0.58
100	0.76	0.67	0.52	0.28	0.44	0.46	0.59	0.54
105	0.71	0.65	0.50	0.23	0.38	0.42	0.55	0.49

Table 7. Equation-of-state polymer-solvent interaction parameters, χ_{12}^* of HMS with the solvents

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	<i>t</i> (°C)	MA	EA	tBA	B	c-P	c-H	Hx	Нр
	90	1.07	0.95	0.63	0.70	0.40	0.47	0.44	0.50
	95	1.06	0.91	0.60	0.64	0.36	0.44	0.38	0.48
	100	1.02	0.85	0.55	0.61	0.32	0.43	0.39	0.40
	105	1.02	0.84	0.56	0.61	0.32	0.43	0.38	0.41

Ternary interaction parameters of the mixture according to Flory-Huggins and equation of state theories were obtained from Eq. 4. and Eq.5, respectively. The results were given in Table 8.

	90°C		95°C	
Solvent	$\chi_{1(23)}^{*}$	$\chi_{1(23)}^{\infty}$	$\chi_{1(23)}^{*}$	$\chi_{1(23)}^{\infty}$
MA	0.88	0.65	0.85	0.61
EA	0.80	0.56	0.77	0.53
tBA	0.55	0.33	0.53	0.30
В	0.41	0.23	0.41	0.22
c-P	0.38	0.15	0.37	0.14
c-H	0.43	0.24	0.42	0.23
Hx	0.46	0.22	0.44	0.20
Нр	0.53	0.31	0.52	0.29

Table 8. Ternary interaction parameters found from equation-of-state $\chi^*_{1(23)}$ and Flory–Huggins $\chi^{\infty}_{1(23)}$

	100°C		105°C	
Solvent	$\chi_{1(23)}^{*}$	$\chi_{1(23)}^{\infty}$	$\chi_{1(23)}^{*}$	$\chi_{1(23)}^{\infty}$
MA	0.82	0.58	0.78	0.52
EA	0.75	0.51	0.74	0.49
tBA	0.53	0.30	0.53	0.29
В	0.41	0.22	0.41	0.21
c-P	0.36	0.13	0.36	0.13
c-H	0.41	0.21	0.39	0.18
Hx	0.44	0.19	0.43	0.17
Нр	0.50	0.27	0.48	0.24

According to the method proposed by Prolongo et al., solvent independent liquid crystal-polymer interaction parameter χ_{23}^{T} was determined from the intercept of the linear lines plotted according to Eq. 10 by assuming κ equals to zero. According to the method proposed by Farooque and Deshpande., solvent independent liquid crystal-polymer interaction parameter. The solvent independent liquid crystal-polymer interaction parameter, χ_{23}^{D} was determined from the intercept of the linear lines plotted according to Eq. 13. The plots at 95 °C were given as an example in Fig. 7 and Fig. 8, respectively. The values of solvent independent parameters χ_{23}^{T} and χ_{23}^{D} were given at four different temperatures in Table 9.



Figure 7. Determination of χ_{23}^{T} according to Eq. 10 for BPIP/HMS mixture at 95 °C as proposed by Prolongo et al.



Figure 8. Determination of χ_{23}^{D} according to Eq. 13 for BPIP/HMS mixture at 95 °C as proposed by Deshpande and Farooque.

It was seen that both the parameters χ_{23}^{T} and χ_{23}^{D} are small positive although the values of former one are lower. This indicates that the liquid crystal and polymer are immiscible in the composition of 50% by weight at temperatures studied. Both methods can be used in determination of solvent independent interaction parameter between a liquid crystal and a polymer. The small positive values of the binary interaction parameters suggest that the liquid crystal dispersion does thermodynamically not tend to phase separation in long term use.

Table 9. The solvent independent interaction parameters of BPIP and HMS found from the methods of Prolongo et al, χ_{23}^{T} (Eq. 10) and Farooque and Desphande, χ_{23}^{D} (Eq. 13).

$t(^{\circ}C)$	χ_{23}^{T}	$\chi^{\rm D}_{23}$
90	0.223	0.873
95	0.160	0.525
100	0.064	0.175
105	0.032	0.089

5. Conclusions

We have prepared a new salicylaldimine compound BPIP containing a chiral side chain and investigated its mesomorphic properties. The BPIP displayed smectic phase as expected for rodlike molecules. The copolymer HMS did not considerably affect the liquid crystalline properties of BPIP in a mixture of 50% by weight.

This study suggests that hydrocarbons studied are good solvents for BPIP and HMS at temperatures between 90 °C and 105°C. It can be seen also that quality of the solvents studied increase with temperature for liquid crystal and copolymer. According to the solvent independent interaction parameters determined by methods proposed both Prolongo et al and Farooque and Deshpande, liquid crystal BPIP and copolymer HMS are immiscible for studied temperatures. The simpler method proposed by Farooque and Deshpande can be used successfully to determine solvent independent binary interaction parameter of a liquid-crystal and polymer. The small positive values of the interaction parameters suggest that BPIP dispersion in HMS should be stable in a long term use.

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