

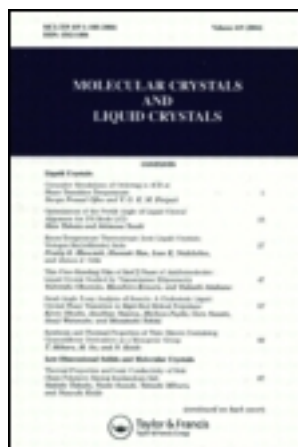
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### Synthesis and Mesomorphic Properties of 2-(4-Alkyloxyphenyl)benzothiazoles

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## Synthesis and Mesomorphic Properties of 2-(4-Alkyloxyphenyl)benzothiazoles

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*A homologous series of 2-(4-alkyloxyphenyl)benzothiazoles with an even number of carbons in the terminal alkoxy chain was synthesized and characterized. The structure of the compounds was postulated using elemental analyses, FT-IR, NMR, and mass spectrometry techniques. Their liquid crystalline properties have been investigated by optical polarizing microscopy, DSC, and X-ray diffraction (XRD) techniques. Whilst the n-octyloxy to n-hexadecyloxy derivatives exhibited a monotropic smectic A phase, the n-ethoxy to n-hexyloxy and the n-octadecyloxy derivatives were not mesogenic. The mesomorphic properties of the present series were compared with other structurally related series to establish the chemical structure-mesomorphic properties relationship.*

**Keywords:** 2-(4-alkyloxyphenyl)benzothiazole; heterocycles; Smectic A; structure-property relationship

## INTRODUCTION

Conventional thermotropic liquid crystals consist of anisotropic molecules that are either rod-shaped (calamitic) or disc-shaped (discotic) [1]. The 1,4-disubstituted phenyl rings forms the linear core in majority of the low molar mass calamitic mesogen systems. Over the

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past few decades, liquid crystals comprising heterocycles as core units have received overwhelming attention due to their unique properties [2–4]. Earlier report has shown that the introduction of heterocycles as the central core has greatly influenced the mesomorphic properties of the calamitic molecules owing to their unsaturation and/or their more polarizable nature [5]. It has also been claimed that the inclusion of the heteroatom considerably changes the polarity, polarizability, and to a certain extent the geometry of the molecule, thereby influencing the type of mesophase, the phase transition temperatures, dielectric constants, and other properties of the mesogens [6,7].

The slightly bent structure of mesogen possessing a single heterocyclic ring such as thiophene has led to unique physical properties such as reduced packing ability, medium to strong lateral dipole, high anisotropy of polarizability and low viscosity. Materials consisting of thiophene, 1,3-thiazole, or 1,3,4-thiadiazole as the core unit have significant lateral dipole moments which would contribute to physical parameters such as increased dielectric anisotropy and dielectric biaxiality [2]. Other examples of single heterocyclic ring liquid crystals include those with furyl [8], pyridine [8–10], substituted pyrimidine carboxylic acid [11], thiazole [12], thiadiazole [13], and oxadiazole [14] moieties.

Benzothiazole, another type of heterocycle, has emerged in its usage as a core unit in calamitic liquid crystals. It has been reported that liquid crystalline compounds incorporating a benzothiazole-fused ring exhibit good hole-transporting properties with a low ionization potential, making them of potential interest as hole-transporting materials in organic light-emitting devices (OLEDs) [15–17]. Pavluchenko *et al.* [18] reported on mesogens comprising benzothiazole and benzoxazole with central linkages and lateral substituents at different positions so as to evaluate the effect of structural changes on mesomorphic properties. Substitution at the sixth position of the benzothiazole ring was found to be thermally more stable as compared to that of the fifth position. Belmar *et al.* [19] studied the influence of central linking groups on the mesomorphic properties of 6-*n*-decyloxy-2-(4-alkoxybenzylidene-amino)benzothiazoles, *n*-[2-(6-*n*-decyloxybenzothiazolyl)]-4-*n*-alkoxybenzamides, and 6-*n*-decyloxy-2-(4-*n*-alkoxyphenylazo)benzothiazoles. Results indicated that the imine and azo derivatives both exhibited smectic and nematic phases while only the smectic phase was observed for the amide derivatives. This observation can be ascribed to the hydrogen bonding between the molecules of the amide derivatives, which prevent the formation of nematic phase [19].

Prajapati and Bonde reported two mesogenic homologous series comprising 6-substituted-benzothiazole ring systems with an azo

centre linkage [20]. The study revealed that the methoxyl substituent at the sixth position of the benzothiazole ring favored the formation of the nematic phase. As part of our studies on heterocyclic mesogens, we report in this article the synthesis and the mesomorphic properties of a homologous series of 2-(4-alkyloxyphenyl)benzothiazoles without central linking groups and lateral substituents. In addition, they were compared to structurally related compounds to establish the chemical structure-mesomorphic properties relationship.

## EXPERIMENTAL

2-Aminothiophenol, 1-bromoalkane ( $C_nH_{2n+1}Br$  where  $n = 2, 4, 6, 8, 10, 12, 14, 16, 18$ ), and potassium iodide were obtained from Merck (Germany). 4-Hydroxybenzaldehyde was purchased from Acros Organics (USA). Potassium hydroxide was obtained from R&M Chemicals (U.K.).

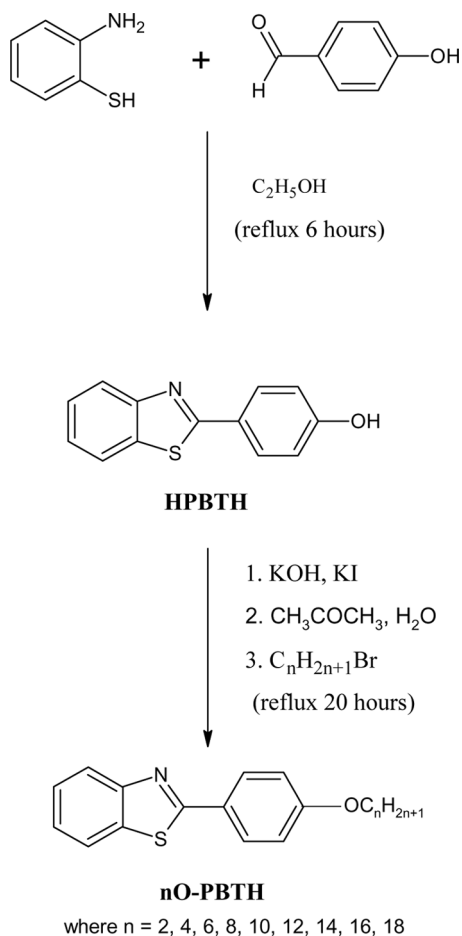
IR spectra were recorded using a Perkin-Elmer System 2000 FT-IR Spectrometer via KBr disc procedure. The range of measurement was from  $4000\text{--}400\text{ cm}^{-1}$ .  $^1H$  NMR (400 MHz) and  $^{13}C$  NMR (100 MHz) spectra were recorded in  $CDCl_3$  using a Bruker Avance 400 MHz Spectrometer with TMS as the internal standard. EI-MS (70 eV) were measured with a Mass Spectrometer Finnigan MAT95XL-T at a source temperature of  $200^\circ C$ . The sample was introduced using direct inlet probe. Microanalyses were carried out on Perkin Elmer 2400 LS Series CHNS/O analyzer. Melting points of the synthesized compounds were determined using a Barnstead Electrothermal Melting Point Apparatus. Thin Layer Chromatography (TLC) was carried out on aluminium-backed silica-gel plates (Merck 60 F<sub>254</sub>) and visualized under short-wave UV light.

Phase-transition temperatures and enthalpy changes were measured using a Differential Scanning Calorimeter Mettler Toledo DSC823<sup>e</sup> at heating and cooling rates of  $10^\circ C/min$  and  $-10^\circ C/min$ , respectively. A polarizing optical microscope (Carl Zeiss) equipped with a Linkam heating stage was used for temperature dependent studies of the liquid crystal textures. A video camera (Video Master coomo20P) installed on the polarizing microscope was coupled to a video capture card (Video Master coomo600), allowing real-time video capture and image saving. Textures exhibited by the compounds were observed using polarized light with crossed polarizers. Samples were prepared as thin films sandwiched between a glass slide and a cover slip. Phase identification was made by comparing the observed textures with those reported in the literature [21,22].

Synchrotron powder X-ray diffraction (XRD) measurements were performed at beamline BL17A of the National Synchrotron Radiation

Research Center (NSRRC) in Taiwan, where the X-ray wavelength used was 1.32633 Å. XRD data were collected using imaging plates (IP, of an area =  $20 \times 40 \text{ cm}^2$  and a pixel resolution of 100) curved with a radius equivalent to the sample-to-image plate distance of 280 mm, and the diffraction signals were accumulated for 3 min. The powder samples were packed into a capillary tube and heated by a heat gun, where the temperature controller is programmable by a PC with a PID feedback system. The scattering angle theta was calibrated by a mixture of silver behenate and silicon.

The synthetic route of 2-(4-alkyloxyphenyl)benzothiazoles, **nO-PBTH** is illustrated in Scheme 1.



**SCHEME 1** Synthetic route of **nO-PBTH**.

## Synthesis

### Synthesis of 2-(4-Hydroxyphenyl)benzothiazole, HPBTH

The compound was synthesized according to the method described by Toba *et al.* [23]. Five mmol (0.6260 g) of 2-aminothiophenol and 5 mmol (0.6106 g) of 4-hydroxybenzaldehyde were refluxed upon stirring for 6 hours in 40 mL of ethanol. The reaction mixture was subsequently cooled to room temperature following which to it 60 mL of distilled water was added slowly until the mixture turned cloudy. It was refrigerated overnight at about 20°C, and the solid formed was filtered and washed with cold ethanol:water (1:1.5) and dichloromethane. Yield 75%. IR (KBr)  $\nu_{\max}$  cm<sup>-1</sup> 3417 (O-H), 3053, 2996 (C-H aromatic), 1606 (C=N, thiazole), 1483, 1455 (C=C aromatic), 1074 (C-S-C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm 5.3 (1 H, s, OH), 6.9 (2 H, d, Ar-H), 7.3 (1 H, t, Ar-H), 7.4 (1 H, t, Ar-H), 7.9 (1 H, d, Ar-H), 8.0 (3 H, m, Ar-H).

### Synthesis of 2-(4-Alkyloxyphenyl)benzothiazoles, nO-PBTH

2-(4-Alkyloxyphenyl)benzothiazoles were synthesized via modification of the method described by Prajapati *et al.* [24]; 0.9 mmoles (0.2046 g) of **HPBTH** in 35 ml of acetone and 0.9 mmoles (0.0505 g) of KOH in 5 ml of distilled water were mixed in a round bottom flask to which a small amount of KI was added as a catalyst. The mixture was refluxed upon stirring for 1 hour following which 1.35 mmoles of the appropriate 1-bromoalkane (C<sub>n</sub>H<sub>2n+1</sub>Br, n = 2, 4, 6, 8, 10, 12, 14, 16, 18) was added and was further refluxed for another 20 hours. The mixture was cooled to room temperature, and the white precipitate formed was separated by filtration. The solid obtained was recrystallized several times with absolute ethanol whereupon the pure compound was isolated. The percentage yields and analytical data of the title compounds are tabulated in Table 1. The IR, NMR (<sup>1</sup>H and <sup>13</sup>C), and mass spectral data for the representative compound, **16O-PBTH**, are summarized as follows.

**16O-PBTH**: Yield 63%. IR (KBr)  $\nu_{\max}$  cm<sup>-1</sup> 3057, 3030 (C-H aromatic), 2955, 2849 (C-H aliphatic), 1608 (C=N, thiazole), 1487, 1465 (C=C aromatic), 1261 (Ar-O-R ether), 1073 (C-S-C, thiazole). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm 0.9 (t, 3 H, CH<sub>3</sub>-), 1.3–1.5 (m, 26 H, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>13</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-), 1.8–1.9 (m, 2 H, -CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.1 (t, 2H, -CH<sub>2</sub>-O-), 7.0 (d, 2 H, Ar-H), 7.4 (t, 1 H, Ar-H), 7.5 (t, 1 H, Ar-H), 7.9 (d, 1 H, Ar-H), 8.0 (m, 3 H, Ar-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm 168.44 (C=N), 161.96, 154.59, 135.21, 129.49, 126.62, 126.50, 125.18, 123.17, 121.93, 115.24 for aromatic carbons, 68.64 (-O-CH<sub>2</sub>-), 32.38, 30.16, 30.14, 30.12, 30.05, 30.02, 29.83, 29.60, 26.44, 23.15 for methylene carbons [-(CH<sub>2</sub>)<sub>14</sub>CH<sub>2</sub>O-], 14.61 (-CH<sub>3</sub>). EI-MS m/z (rel. int. %): 451(42) (M)<sup>+</sup>, 227(100).

**TABLE 1** Percentage Yields and Analytical Data of **nO-PBTH**

Compound	Yield (%)	Formula	% Found (% Calcd.)		
			C	H	N
<b>2O-PBTH</b>	37	C <sub>15</sub> H <sub>31</sub> NOS	70.50 (70.56)	5.19 (5.13)	5.43 (5.49)
<b>4O-PBTH</b>	49	C <sub>17</sub> H <sub>17</sub> NOS	72.09 (72.05)	6.11 (6.05)	4.89 (4.94)
<b>6O-PBTH</b>	43	C <sub>19</sub> H <sub>21</sub> NOS	73.29 (73.31)	6.80 (6.75)	4.45 (4.50)
<b>8O-PBTH</b>	43	C <sub>21</sub> H <sub>25</sub> NOS	74.36 (74.34)	7.51 (7.37)	3.95 (4.13)
<b>10O-PBTH</b>	47	C <sub>23</sub> H <sub>29</sub> NOS	75.22 (75.20)	8.08 (7.90)	3.70 (3.81)
<b>12O-PBTH</b>	44	C <sub>25</sub> H <sub>33</sub> NOS	75.90 (75.95)	8.43 (8.35)	3.63 (3.54)
<b>14O-PBTH</b>	52	C <sub>27</sub> H <sub>37</sub> NOS	76.58 (76.60)	8.87 (8.75)	3.17 (3.31)
<b>16O-PBTH</b>	63	C <sub>29</sub> H <sub>41</sub> NOS	77.13 (77.16)	9.18 (9.09)	3.18 (3.10)
<b>18O-PBTH</b>	71	C <sub>31</sub> H <sub>45</sub> NOS	77.53 (77.66)	9.52 (9.39)	2.83 (2.92)

## RESULTS AND DISCUSSION

Structural identification of the title compounds was carried out by employing a combination of elemental analysis and spectroscopic techniques (FT-IR, NMR, and EI-MS). The percentages of C, H, and N from the elemental analysis conform with the calculated values for compounds **nO-PBTH** (where  $n = 2, 4, 6, 8, 10, 12, 14, 16, 18$ ) and are presented in Table 1. The prominent molecular ion peak at  $m/z$  451 in the mass spectrum of **16O-PBTH**, establishing a molecular formula of C<sub>29</sub>H<sub>41</sub>ONS, which supports the proposed structure.

### FTIR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR Spectral Studies

The diagnostic absorption bands at 2849 and 2955 cm<sup>-1</sup> in the FTIR spectrum of **16O-PBTH** provides evidence for the alkoxy chain. The presence of the aromatic rings was inferred from the absorption bands at 3030, 3057, 1487, and 1465 cm<sup>-1</sup>. The absorption bands assignable to the stretching of the C=N and C-S-C bonds of benzothiazole were observed at 1608 and 1073 cm<sup>-1</sup>, respectively. These values conform with those reported in the IR spectra for various substituted benzothiazoles [20,25]. The absorption band at 1261 cm<sup>-1</sup> was indicative of the C-O stretching of the aromatic ether (Ar-O-R). Compounds **nO-PBTH** ( $n = 2, 4, 6, 8, 10, 12, 14, 18$ ) exhibited similar characteristic absorptions as discussed for **16O-PBTH**.

The triplets at  $\delta = 0.9$  and 4.1 ppm in the <sup>1</sup>H NMR spectrum of **16O-PBTH** were assigned to methyl protons and methylene protons (Ar-O-CH<sub>2</sub>-) that bonded directly to aromatic ether group, respectively. The multiplets between  $\delta = 1.3$ –1.9 ppm were attributed to the remaining methylene protons [CH<sub>3</sub>-(CH<sub>2</sub>)<sub>14</sub>-] of the alkoxy chain.



The  $^1\text{H}$  NMR spectrum of **16O-PBTH** also suggests the presence of eight aromatic protons.

The  $^{13}\text{C}$  NMR spectrum of **16O-PBTH** suggests the presence of 29 carbons. The peak at  $\delta = 168.44$  ppm owing to the presence of the imine carbon ( $-\text{C}=\text{N}-$ , thiazole), was in agreement with that reported in literature [19]. The signals within the range of  $\delta = 115.24$ – $161.96$  ppm were assigned to the carbons of the benzothiazole and aromatic moieties. The carbon resonances between  $\delta = 14.61$ – $68.64$  ppm were indicative of the methylene and methyl carbons of the alkoxy chain. The results as inferred from the IR and NMR spectral data of the title compounds were consistent with the proposed structure.

### **Phase-Transition Behavior and Liquid Crystallinity of nO-PBTH**

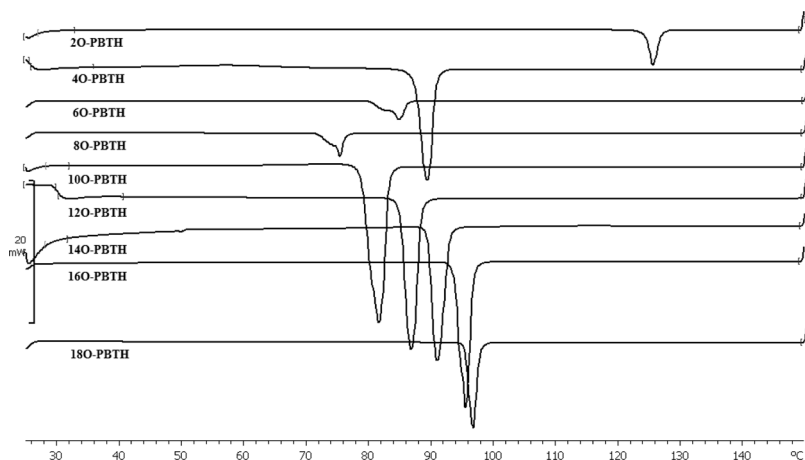
The transition temperatures and associated enthalpy changes of **nO-PBTH** obtained from the DSC measurements are summarized in Table 2. The DSC thermograms of all the members during the heating and cooling cycles are depicted in Figures 1 and 2, respectively. The representative optical photomicrographs are shown in Figure 3. A plot of the transition temperatures against the number of carbons

**TABLE 2** Transition Temperatures and Associated Enthalpy Changes of **nO-PBTH** Upon Heating and Cooling

Compound	Transition temperatures, °C ( $\Delta H$ , kJ mol $^{-1}$ )
<b>2O-PBTH</b>	Cr 125.7 (18.18) I <i>Cr 95.7 (16.16) I</i>
<b>4O-PBTH</b>	Cr 89.5 (36.16) I <i>Cr 78.0 (34.71) I</i>
<b>6O-PBTH</b>	Cr 85.1 (20.87) I <i>Cr 73.0 (20.12) I</i>
<b>8O-PBTH</b>	Cr 75.5 (27.86) I <i>Cr 48.8 (17.12) SmA 74.8 (6.97) I</i>
<b>10O-PBTH</b>	Cr 81.7 (44.42) I <i>Cr 63.1 (32.03) SmA 79.3 (8.80) I</i>
<b>12O-PBTH</b>	Cr 86.9 (55.61) I <i>Cr 63.8 (42.11) SmA 81.2 (10.41) I</i>
<b>14O-PBTH</b>	Cr 91.7 (59.52) I <i>Cr 70.7 (47.00) SmA 81.2 (9.79) I</i>
<b>16O-PBTH</b>	Cr 95.7 (70.41) I <i>Cr 77.3 (57.37) SmA 79.8 (11.20) I</i>
<b>18O-PBTH</b>	Cr 96.8 (58.49) I <i>Cr 85.2 (56.27) I</i>

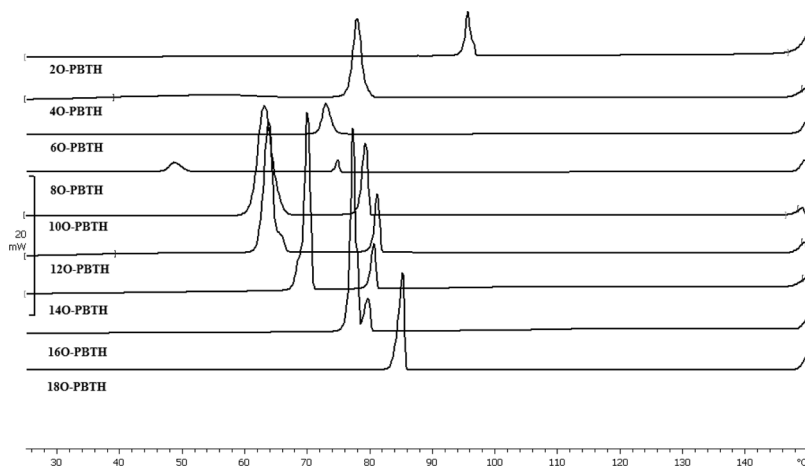
The values in *italics* were taken during cooling cycle.

Cr = Crystal; SmA = Smectic A; I = Isotropic liquid.

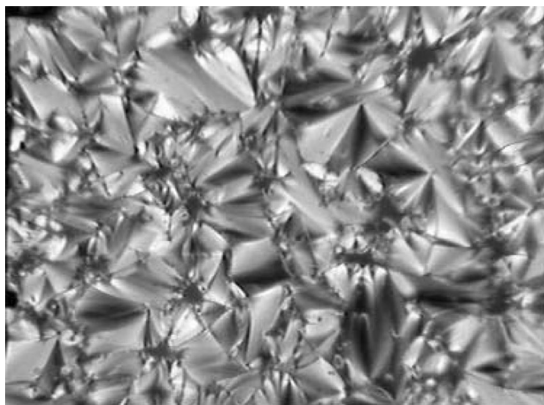


**FIGURE 1** DSC thermograms of **nO-PBTH** during heating cycle.

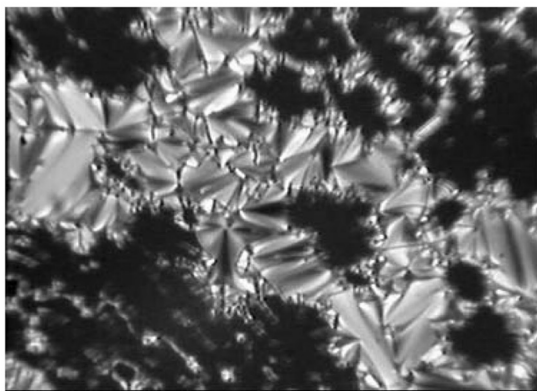
in the alkoxy chain during the heating and cooling cycles are shown in Figures 4 and 5. Based on the plot, it can be deduced that the meso-phase behaviors were greatly influenced by the length of the terminal chains. The crystal-isotropic transition (melting) temperatures exhibited a descending trend as the length of the terminal alkoxy chain of the derivatives increased from C2 to C8. However, the lengthening of carbon chain from the n-octyloxy to the n-octadecyloxy derivatives led to ascending trend of melting temperatures. This phenomenon can be



**FIGURE 2** DSC thermograms of **nO-PBTH** during cooling cycle.



(a)

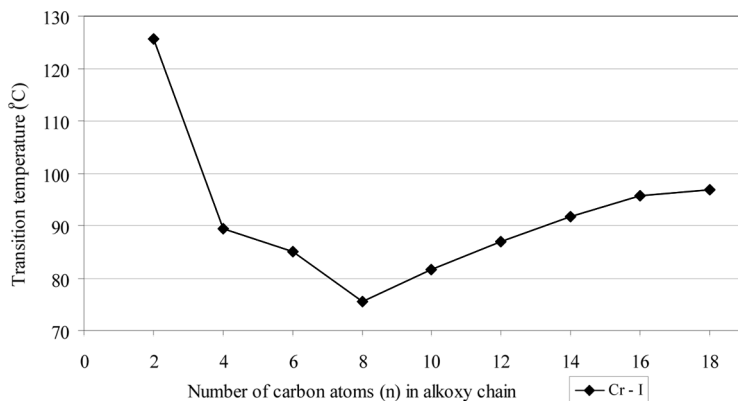


(b)

**FIGURE 3** (a) Optical photomicrograph of **100-PBTH** exhibiting homogeneously aligned smectic A phase with fan-shaped textures; (b) optical photomicrograph of **120-PBTH** exhibiting smectic A phase with fan-shaped and homeotropic (dark area) textures.

attributed to the the increased intermolecular Van der Waals attraction as the length of the alkoxy chain increased [26].

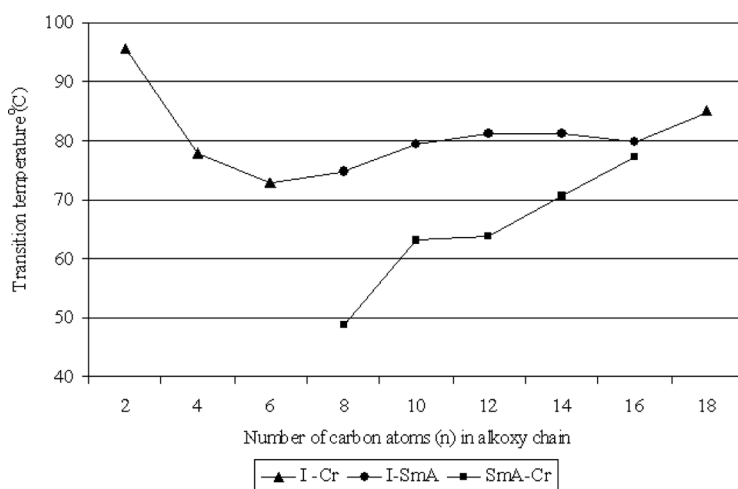
Under the polarizing microscope, the n-octyloxy to the n-hexadecyloxy derivatives exhibited monotropic smectic A phase. In the monotropic mesogens, the melting points were always equal to or higher than the clearing points, hence exhibiting supercooling properties [27]. As a representative illustration, the optical photomicrographs of compounds **100-PBTH** and **120-PBTH** are illustrated in Fig. 3. **100-PBTH** exhibited homogeneously aligned fan-shaped



**FIGURE 4** Plot of transition temperatures versus the number of carbons ( $n$ ) in the alkoxy chain of **nO-PBTH** during heating cycle.

textures whereas the co-existence of homogenous and homeotropic (dark region) smectic A with fan-shaped textures were observed for **12O-PBTH**. The assignments of the mesophases were made on the basis of the textures observed from POM as the mesophases displayed the typical fan-shaped textures for a smectic A phase [21,22].

The rest of the members ( $n=2, 4, 6,$  and  $18$ ) did not exhibit liquid crystal phases. **2O-PBTH**, **4O-PBTH**, and **6O-PBTH** were



**FIGURE 5** Plot of transition temperatures versus the number of carbons ( $n$ ) in the alkoxy chain of **nO-PBTH** during cooling cycle.

non-mesomorphic perhaps due to the shorter terminal alkoxy chains, resulting in higher melting points, thus suppressing the liquid crystal phase. The high flexibility owing to the long terminal chain (C<sub>18</sub>H<sub>36</sub>O-) in **180-PBTH** also depressed the formation of liquid crystal phase [28].

### **XRD Studies of *nO*-PBTH**

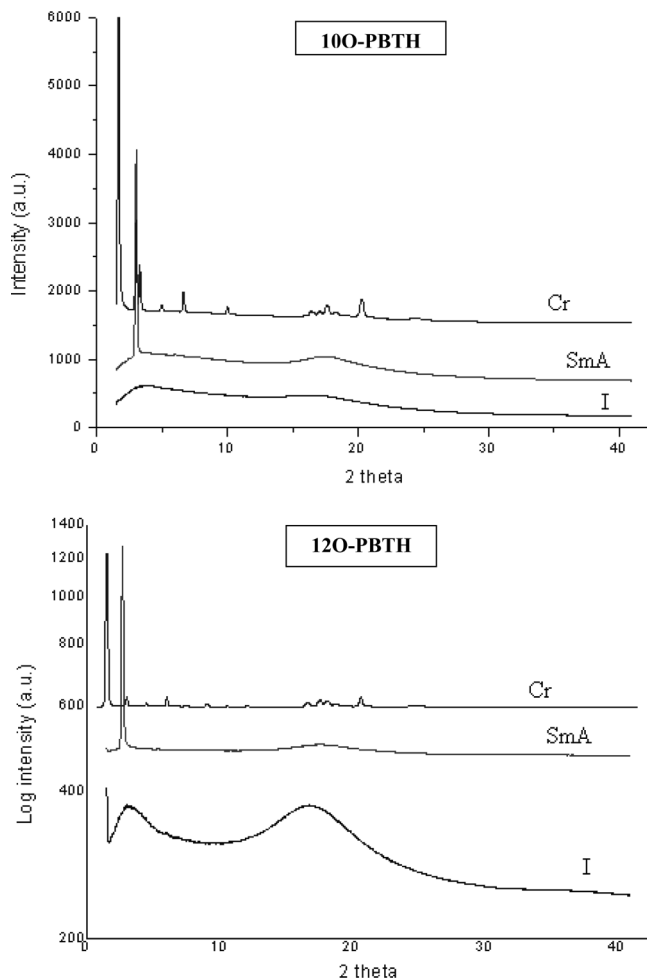
Although the liquid crystal phase type of the title compound can be concluded preliminary by DSC and POM, it is necessary to measure them by XRD analysis and give additional information about their structure parameters. XRD patterns of representative compounds **100-PBTH** and **120-PBTH** are shown in Fig. 6.

In general, a smectic, nematic, cholesteric structure has a broad peak associated with lateral packing at  $2\theta \approx 16\text{--}21^\circ$  in a wide-angle XRD curve. A sharp and strong peak at a low angle ( $1^\circ < 2\theta < 6^\circ$ ) in a small angle X-ray scattering curve can be observed for smectic structures, but it cannot be seen for nematic and cholesteric structures [29–31]. An XRD pattern of **100-PBTH** and **120-PBTH** showed sharp reflection peaks at  $2\theta$  of 2.99 and 2.65 ( $d = 25.56$  and  $28.84 \text{ \AA}$ ), which were corresponding to the smectic layer spacing. Combining the polarized microscopy with XRD measurements confirmed that these compounds were smectogenic A.

### **Chemical Structure–Mesomorphic Property Relationship**

There is a close relationship between the mesomorphic properties and molecular structure of organic compounds. Thus, transition temperatures, mesophase range, and types of mesophases can be correlated with the molecular structure of the compounds. In Table 3, the transition temperatures, types of mesophases, mesophase range, and molecular structure of **80-PBTH** are compared with other structurally related compounds **A** [20], **B** [32], and **C** [19].

Whilst **80-PBTH** exhibited a smectic A phase, compound **A** was nematogenic. The difference could be resulted from the additional methoxyl group at the sixth position of the benzothiazole ring along with the additional azo linkage between the two aromatic rings in compound **A**. Hence, the nematic phase in compound **A** could be due to the methoxyl substituent which diminished the formation of the smectic A [9]. The azo linkage between the two aromatic core units in compound **A** conferred stepped core structure leading to the broadening effect, thus disrupting the lamellar packing, and therefore generating the nematic phase [1]. Similar structure–property relationship was also inferred from compound **C** whereby this structurally related compound exhibited a nematic phase owing to the presence of an azo linkage.

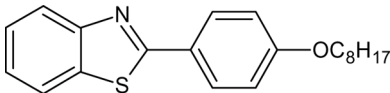
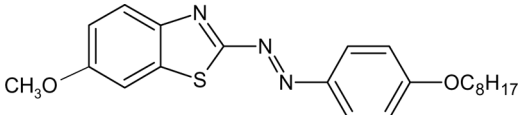
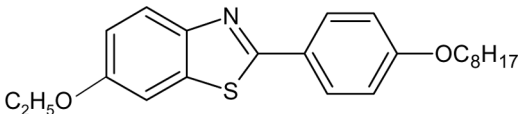
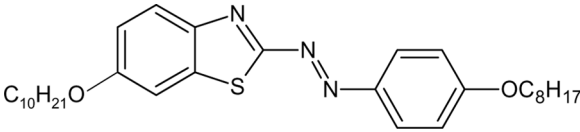


**FIGURE 6** XRD patterns of **100-PBTH** and **120-PBTH** at different temperatures upon cooling from the isotropic phase.

Meanwhile, the additional azo linkage also tends to increase the transition temperatures and mesophase range of compound **A** when compared to **80-PBTH**. The increase in the mesophase range of compound **A** could have originated from (i) an increase in the length-to-breadth ratio of the molecule and (ii) an increase in the polarizability due to the extension of  $\pi$ -conjugation [33].

Structurally related compound **B** exhibited a smectic C phase instead of a nematic or smectic A phase. Upon comparison to **80-PBTH**,

**TABLE 3** Transition Temperatures, Mesophase Range, and Molecular Structures of **80-PBTH**, **A**, **B**, and **C**

	<b>80-PBTH</b>		
	<b>Compound A</b>		
	<b>Compound B</b>		
	<b>Compound C</b>		
		Mesophase range (°C)	
Compound	Transition temperatures (°C)	Sm	N
<b>80-PBTH</b>	Cr (SmA 74.8)* 75.5 I	–	–
<b>A</b>	Cr 94 N 136 I	–	42
<b>B</b>	Cr 106 SmC 134 I	28	–
<b>C</b>	Cr 70.7 SmC 95.0 N 123.8 I	24.3	28.8

(\*) Monotropic value.

it can be rationalized that the presence of the ethoxyl substituent at the sixth position of the benzothiazole ring promoted the formation of the smectic C phase in compound **B**. The ethoxyl group in compound **B** favoured the intermolecular interaction that gave rise to a tilted arrangement of the molecules in the smectic layers. The similar pattern can also be inferred by comparing the molecular structures of compound **A** and **C**. It is clearly observed that as the length of the alkoxy chain at the sixth position of the benzothiazole ring increases, the molecules favour the tilted SmC phase.

## CONCLUSION

In this article, we have reported the synthesis and mesomorphic properties of a homologues series of 2-(4-alkyloxyphenyl)benzothiazoles.

The n-octyloxy to n-hexadecyloxy derivatives exhibited a monotropic smectic A phase. The remaining members were non-mesomorphic. Comparison of the present series with other structurally related compounds revealed that transition temperatures and mesophase stability were greatly affected by the linking (terminal and centre) groups. The presence of the azo linkage disrupts the lamellar packing hence generating the nematic phase. The study also revealed that the methoxyl group at the sixth position of the benzothiazole ring stabilized the nematic phase whereas the ethoxyl group or a longer alkoxy chain at the sixth position of the benzothiazole ring will stabilize the smectic C phase.

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