## Liquid Crystals

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# Synthesis and characterisation of polymethacrylates containing *para*-, *meta*- and *ortho*-monosubstituted azobenzene moieties in the side chain

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Three sets of novel side-chain liquid crystalline polymers with monosubstituted azobenzene moieties in the side-chain have been studied. These are poly(*p*-(4′-methoxy-4-oxyhexyloxy azobenzene) benzyl methacrylate) (PPHABM), poly(*m*-(4′-methoxy-4-oxyhexyloxy azobenzene) benzyl methacrylate) (PMHABM) and poly(*o*-(4′-methoxy-4-oxyhexyloxy azobenzene) benzyl methacrylate) (POHABM). The chemical structure of the monomers was confirmed by $^{1}$H NMR, $^{13}$C NMR spectroscopy and elemental analysis. The structural characterisation of the polymers was performed by $^{1}$H NMR spectroscopy and gel permeation chromatography, and their phase behaviour and liquid crystalline properties were studied using differential scanning calorimetry, polarised optical microscopy and wide-angle X-ray diffraction. The results show that the transitional behaviour of side-chain liquid crystalline polymers containing monosubstituted azobenzene moieties depends strongly on the position of the substituent on the azobenzene moiety; for example, the *ortho*-monosubstituted polymers do not form liquid crystalline phases, but all the *para*- and *meta*-monosubstituted polymers exhibit a smectic A phase. Furthermore, the glass transition temperature ($T_g$) of the polymers decreases in the order, *para* > *meta* > *ortho*. For the PPHABM and PMHABM polymers the isotropic temperature ($T_i$) and liquid crystalline range ($\Delta T$, from $T_g$ to $T_i$) are found to be in the order, *para* > *meta*, although it is surprising that the associated enthalpy changes in these polymers is the opposite order, *meta* > *para*.

**Keywords:** side-chain liquid crystalline polymer; azobenzene mesogen; monosubstituted position; liquid crystalline behaviour

## 1. Introduction

Liquid crystalline polymers containing azobenzene side-chains (Azo-SCLCPs) have attracted considerable attention on account of their wide range of potential applications, including optical data storage [1, 2], non-linear optics [3], photomechanical systems [4–9], liquid crystal displays [10] and holographic memories, photo-switches and wave-guide switches [11–20]. In principle, Azo-SCLCPs comprise three elements: a polymer backbone, an azobenzene mesogenic unit, and flexible spacer groups connecting the backbone and the mesogenic unit. In side-chain liquid crystalline polymers the characteristic properties depend on their chemical structure, for example their backbone rigidity, the aspect ratio of the mesogenic groups, and their conformation, configuration, molar mass, polydispersity and tacticity [21–42].

The effect of the position of the substituent in the mesogenic unit on the properties of the polymer has received considerable attention recently. Much of the research has focused on the effect of its position on photochemical behaviour [43–45], photoelectronic properties [46, 47], non-linear optical properties [48] and liquid crystalline behaviour [49–55]. Due to the very high melting point ($T_m$) and low solubility of main-chain thermotropic liquid crystalline polymers (MCLCPs), many studies have been devoted to decreasing the glass transition temperature ($T_g$) and $T_m$, in addition to improving their solubility by incorporating *ortho*- or *meta*-substituents into the side-chain.

The effect of *para*-, *meta*-, or *ortho*-linkages on the production of liquid crystallinity has also been investigated [50, 53]. It has been shown that for main-chain liquid crystalline polymers, the formation of liquid crystallinity is strongly dependent on the configuration of the *ortho*-, *meta*- and *para*-linkages in the monomeric units; of these, the *para*-linkage is the most favourable for generating liquid crystallinity, and the *ortho*-linkage has a greater effect than the *meta*-linkage [50]. However, there have been few publications devoted to the effect of the position of the substituent on the properties of SCLCPs. We have assumed that the presence of mesogenic *para*-, *meta*- or *ortho*-substituents will not only influence the glass transition and isotropic temperatures of SCLCPs, but also their liquid crystalline behaviour. In the present study we have compared the effect of *para*-, *meta*- and *ortho*-substituents on liquid crystalline behaviour.

Three different polymethacrylates containing *para*-, *meta*- and *ortho*-monosubstituted azobenzene moieties, respectively, were synthesised using the

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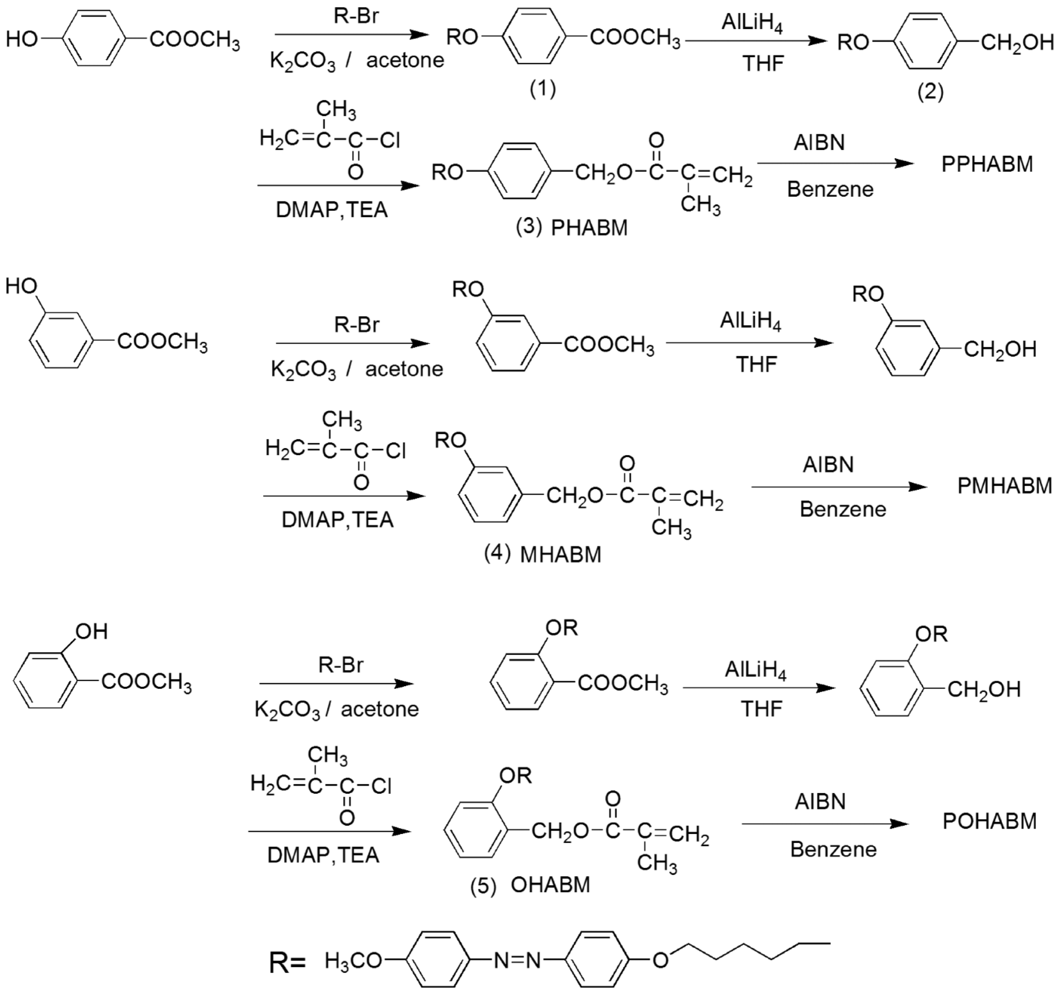

Scheme 1. Synthetic route to the monomers, PHABM, MHABM and OHABM, and the corresponding polymers, PPHABM, PMHABM and POHABM.

route shown in Scheme 1. The phase behaviour and thermal properties of these polymers were investigated using differential scanning calorimetry (DSC), polarised optical microscopy (POM) and wide-angle X-ray diffraction (WAXD).

## 2. Experimental

### *2.1 Instrumental measurements*

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker ARX400 spectrometer at room temperature, using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane as internal standard. Elemental analysis was carried out on an Elementar Vario EL. Thermo-gravimetric analysis (TGA) was performed on a TA–SDT 2960 at a heating rate of 20°C min$^{-1}$ under nitrogen.

Gel permeation chromatography (GPC) measurements were carried out at 35°C on a Waters 1515 instrument with a set of HT3, HT4 and HT5. The $\mu$-Styragel columns used THF as an eluent at a flow rate of 1.0 mL min$^{-1}$. Calibration was conducted using polystyrene standards.

DSC measurements were carried out under nitrogen on a TA DSC Q100 calorimeter with a programmed heating procedure. The temperature and heat flow were calibrated using indium and zinc standards at cooling and heating rates of 10°C min$^{-1}$. Samples typically of 3–10 mg mass were encapsulated in sealed aluminium pans.

To observe the liquid crystalline (LC) texture of the samples, POM experiments were carried out on a Leica DM–LM–P coupled with a Mettler–Toledo hot stage (FP82HT). Samples for POM were obtained by melt-pressing small amounts of polymer between two cover glasses.

One-dimensional wide-angle X-ray diffraction (1D–WAXD) experiments were conducted on a

Philips X'Pert PRO diffractometer with a 3 kW ceramic tube as X-ray source (Cu K$\alpha$), and an X'Celerator detector. The reflection peak positions were calibrated against silicon powder ($2\theta > 15°$) and silver behenate ($2\theta < 10°$). The sample stage was set horizontally, and a temperature control unit (Paar Physica TCU 100) was employed in conjunction with the diffractometer to study the structure evolution as a function of temperature. The heating and cooling rates in the WAXD experiments were 10°C min$^{-1}$.

## 2.2 Materials

Azo-bis-isobutyronitrile (AIBN) was purified by recrystallisation from ethanol. Benzene, for use in the polymerisation reaction, was washed successively with concentrated sulphuric acid and deionised water, dried over anhydrous calcium chloride and distilled from calcium hydride. Tetrahydrofuran (THF; AR grade, Beijing Chemical Co.) and triethylamine (99%, Acros) were heated under reflux over calcium hydride for at least 8 h and distilled before use. 4-Dimethylaminopyridine (DMAP) was purchased from Aldrich Chemical Co. Anhydrous magnesium sulphate ($MgSO_4$) was used for drying all organic extracts. All other reagents were used as received from commercial sources.

## 2.3 Synthesis of the monomers

### 2.3.1 4-(6-bromohexyloxy)-4′-methoxy azobenzene

This monomer was prepared by the method quoted in the literature [56].

$^1$H NMR (400 MHz, $CDCl_3$, $\delta$ ppm): 1.55–1.51 (m, 4H, –$CH_2$–), 1.93–1.82 (m, 4H, –$CH_2$–), 3.45–3.42 (m, 2H, –$CH_2Br$), 3.89 (s, 3H, –$OCH_3$), 4.06–4.02 (m, 2H, –$OCH_2$–), 7.01–6.97 (m, 4H, Ar–H), 7.89–7.86 (m, 4H, Ar–H).

### 2.3.2 p-(4′-Methoxy-4-oxyhexyloxy azobenzene) benzyl formate (1)

Compound **1** was obtained by the etherification of methyl 4-hydroxybenzoate with 4-(6-bromohexyloxy)-4′-methoxy azobenzene. In a 500 mL three-necked round-bottom flask, methyl 4-hydroxybenzoate (11.40 g, 75 mmol), 4-(6-bromohexyloxy)-4′-methoxy azobenzene (R–Br; 29.33 g, 75 mmol) and potassium carbonate (13.8 g, 100 mmol) were dissolved in acetone (180 ml) and the mixture refluxed under nitrogen. After 24 h the reaction was confirmed to be complete by thin-layer chromatography (TLC) and $^1$H NMR. After cooling to room temperature, the reaction mixture was filtered and washed with hot acetone to remove residual R–Br. The resulting precipitate was dissolved in $CH_2Cl_2$ and the potassium salt removed by filtration. The solution was concentrated under reduced pressure and the crude product dissolved in dichloromethane and purified by column chromatography (silica gel, $CH_2Cl_2$).

$^1$H NMR (400 MHz, $CDCl_3$, $\delta$ ppm): 1.60–1.88 (m, 8H, –$CH_2$–), 3.91 (s, 6H, –$OCH_3$), 4.08–4.10 (m, 4H, –$OCH_2$–), 6.92–6.94 (m, 2H, Ar–H), 7.00–7.04 (m, 4H, Ar–H), 7.89–7.92 (m, 4H, Ar–H), 7.99–8.02 (m, 2H, Ar–H).

### 2.3.3 p-(4′-Methoxy-4-oxyhexyloxy azobenzene) benzyl methanol (2)

Compound **2** was prepared by the reduction of *p*-(4′-methoxy-4-oxyhexyloxy azobenzene) benzyl formate by means of lithium aluminium hydride ($LiAlH_4$). In a 500 mL three-neck round-bottom flask equipped with condenser, an ice bath, nitrogen supply and magnetic stirrer, $LiAlH_4$ (0.82 g, 21.6 mmol) was suspended in dry THF (20 mL), and a solution of compound **1** (10.0 g, 21.6 mmol) in dry THF (200 mL) added very slowly drop-wise. After the addition was complete, the mixture was allowed to react a further 2 h at room temperature. The reaction was confirmed to be complete using TLC and $^1$H NMR analysis. Water was then added slowly under vigorous stirring to terminate the reaction, and dilute hydrochloric acid added to dissolve the precipitate. The product was extracted with $CH_2Cl_2$, the extract dried over magnesium sulphate ($MgSO_4$), and concentrated to give a yellow solid. The crude product was purified by column chromatography (silica gel, $CH_2Cl_2$) and the solvent removed under vacuum, giving compound **2**.

$^1$H NMR (400 MHz, $CDCl_3$, $\delta$ ppm): 1.57–1.85 (m, 8H, –$CH_2$–), 3.88 (s, 3H, –$OCH_3$), 3.98–4.06 (m, 4H, –$OCH_2$–), 4.66 (s, 2H, –$CH_2OH$), 6.87–6.89 (m, 2H, Ar–H), 6.96–7.01 (m, 4H, Ar–H), 7.27–7.29 (m, 2H, Ar–H), 7.84–7.88 (m, 4H, Ar–H).

### 2.3.4 p-(4′-methoxy-4-oxyhexyloxy azobenzene) benzyl methacrylate (PHABM; 3)

Compound **2** (4.35 g, 10 mmol), triethyl nitrogen ($NEt_3$; 3.03 g, 30 mmol) and DMAP (3.69 g, 30 mmol) were dissolved in dry THF (50 mL), and methacryloyl chloride (5.2 g, 50 mmol) added very slowly drop-wise at 0–5°C. The mixture was allowed to react a further 12 h at room temperature and the reaction confirmed to be complete by TLC and $^1$H NMR analysis. A few drops of water were added to terminate the reaction. The mixture was partitioned between $CH_2Cl_2$ and water. The organic layer was washed in succession with dilute hydrochloric acid, aqueous sodium bicarbonate solution and brine, then dried over $MgSO_4$ and evaporated under reduced pressure to obtain a yellow solid. The crude product was purified by column chromatography (silica gel,

$CH_2Cl_2$), and recrystallised from THF/diethyl ether to give the monomer (PHABM, **3**).

$^1$H NMR (400 MHz, $CDCl_3$, $\delta$ ppm): 1.55–1.84 (m, 8H, –$CH_2$–), 1.95 (s, 3H, –$C(CH_3)=CH_2$), 3.89 (s, 3H, –$OCH_3$), 3.96–4.07 (m, 4H, –$OCH_2$–), 5.12 (s, 2H, –$CH_2O$–), 5.55 (s, 1H, –$C(CH_3)=CHH$), 6.12 (s, 1H, –$C(CH_3)=CH$), 6.87–6.89 (m, 2H, Ar–H), 6.97–7.01 (m, 4H, Ar–H), 7.29–7.31 (m, 2H, Ar–H), 7.86–7.89 (m, 4H, Ar–H).

$^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$ ppm): 18.48 (–$CH_3$), 26.00, 26.01, 29.30, 29.32 (–$CH_2$–), 55.66 (–$OCH_3$), 66.40 (–$OCH_2$–), 67.96, 68.27 (–$OCH_2$–), 114.31, 114.63, 114.81, 124.47, 124.49, 124.78, 128.25, 130.03, 147.02, 147.25, 159.25, 161.30, 161.69 (Ar), 125.73 ($CH_2$=), 136.51 (=C–), 167.44 (C=O).

Calc. for $C_{30}H_{34}O_5N_2$ (Mol. wt. 502.2): C, 71.65; N, 5.63; H, 6.74; Found: C, 71.69; N, 5.57; H, 6.82.

The other monomers were prepared in a similar manner. The spectral data were as follows.

#### 2.3.5 m-*(4′-methoxy-4-oxyhexyloxy azobenzene (benzyl methacrylate (MHABM, **4**)*

$^1$H NMR (400 MHz, $CDCl_3$, $\delta$ ppm): 1.57–1.84 (m, 8H, –$CH_2$–), 1.97 (s, 3H, –$C(CH_3)=CH_2$), 3.88 (s, 3H, –$OCH_3$), 3.97–4.07 (m, 4H, –$OCH_2$–), 5.16 (s, 2H, –$CH_2O$–), 5.59 (s, 1H, –$C(CH_3)=CHH=$), 6.16 (s, 1H, –$C(CH_3)=CHH$), 6.85–6.95 (m, 4H, Ar–H), 6.98–7.01 (m, 4H, Ar–H), 7.86–7.89 (m, 4H, Ar–H).

$^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$ ppm): 18.49 (–$CH_3$), 26.00, 26.03, 29.30, 29.34 (–$CH_2$–), 55.66 (–$OCH_3$), 66.40 (–$OCH_2$–), 67.92, 68.27 (–$OCH_2$–), 114.25, 114.27, 114.30, 114.80, 120.19, 124.46, 124.48, 129.71, 137.77, 147.10, 147.25, 159.39 161.28, 161.68 (Ar), 125.95 ($CH_2$=), 136.37 (=C–), 167.32 (C=O).

Calc. for $C_{30}H_{34}O_5N_2$ (Mol. wt. 502.2): C, 71.65; N, 5.63; H, 6.74; Found: C, 71.62; N, 5.59; H, 6.76.

#### 2.3.6 o-*(4′-methoxy-4-oxyhexyloxy azobenzene) benzyl methacrylate (OHABM, **5**)*

$^1$H NMR (400 MHz, $CDCl_3$, $\delta$ ppm): 1.55–1.85 (m, 8H, –$CH_2$–), 1.95 (s, 3H, –$C(CH_3)=CH_2$), 3.70 (s, 3H, –$OCH_3$), 3.88–4.06 (m, 4H, –$OCH_2$–), 5.12 (s, 2H, –$CH_2O$–), 5.55 (s, 1H, –$C(CH_3)=CHH$), 6.12 (s, 1H, –$C(CH_3)=CHH$), 6.87–6.89 (m, 2H, Ar–H), 6.97–7.01 (m, 4H, Ar–H), 7.30–7.32 (m, 2H, Ar–H),7.86–7.89 (m, 4H, Ar–H).

$^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$ ppm): 18.55 (–$CH_3$), 26.00, 26.06, 29.31, 29.36 (–$CH_2$–), 55.66 (–$OCH_3$), 62.19 (–$OCH_2$–), 68.02, 68.27 (–$OCH_2$–), 111.41, 114.31, 114.83, 114.80, 120.56, 123.90, 124.17, 124.79, 129.34, 129.46, 147.10, 147.27, 157.06, 161.33, 161.69 (Ar), 125.62 ($CH_2$=), 136.62 (=C–), 167.44 (C=O).

Calc. for $C_{30}H_{34}O_5N_2$ (Mol. wt. 502.2): C, 71.65; N, 5.63; H, 6.74; Found: C, 71.49; N, 5.51; H, 6.78.

### 2.4 *Synthesis of the polymers*

The polymers were each obtained by conventional solution radical polymerisation, typically carried out as described in the following example.

The monomer PHABM (**3**; 0.50 g, 1.0 mmol), 0.01 M of AIBN (500 $\mu$L) in chlorobenzene solution, and dry benzene (1.5 mL), were placed in a 25 mL reaction tube containing a magnetic stirrer bar. After three freeze–pump–thaw cycles, the tube was sealed under vacuum. Polymerisation was carried out at 60°C over 24 h. The sample was diluted with THF and precipitated into a large volume of hot acetone. The sample was purified by similarly re-precipitating three times from THF into hot acetone, and dried overnight at room temperature *in vacuo*.

## 3. Results and discussion

### 3.1 *Synthesis and characterisation of the monomers and polymers*

As shown in Scheme 1, each of the monomers (PHABM, MHABM and OHABM) was synthesised in three steps. The monomer PHABM will be taken as a representative example.

The preparation and characterisation of 4-(6-bromohexyloxy)-4′-methoxy azobenzene, has been described elsewhere [56]. First, methyl *p*-(4′-methoxy-4-oxyhexyloxy azobenzene) benzoate was prepared by etherification of methyl 4-hydroxybenzoate as the potassium salt in hot acetone solution. Then, *p*-(4′-methoxy-4-oxy-hexyloxy azobenzene) benzyl alcohol was synthesised by reduction of methyl *p*-(4′-methoxy-4-oxy hexyloxy azobenzene) benzoate with $LiAlH_4$. Finally, the monomer PHABM was obtained by the esterification of methacryloyl chloride and *p*-(4′-methoxy-4-oxyhexyloxy azobenzene) benzyl alcohol. The crude product was purified by column chromatography on silica gel using $CH_2Cl_2$ as eluent, followed by recrystallisation from THF/diethyl ether to obtain the monomer, PHABM.

The structure of the monomers was confirmed by $^1$H NMR, $^{13}$C NMR spectroscopy and elemental analysis. It proved difficult to polymerise the monomers, PHABM, MHABM and OHABM, to obtain high molecular weight materials by atom transfer radical polymerisation, due to chain transfer reactions with the multi-benzylic protons in the side-groups, but we were able to obtain polymers of a variety of molecular weights by free radical polymerisation.

As an example, Figures 1(a) and (b) show the $^1$H NMR spectra of the monomer, PHABM, and the corresponding polymer, PPHABM, respectively. The

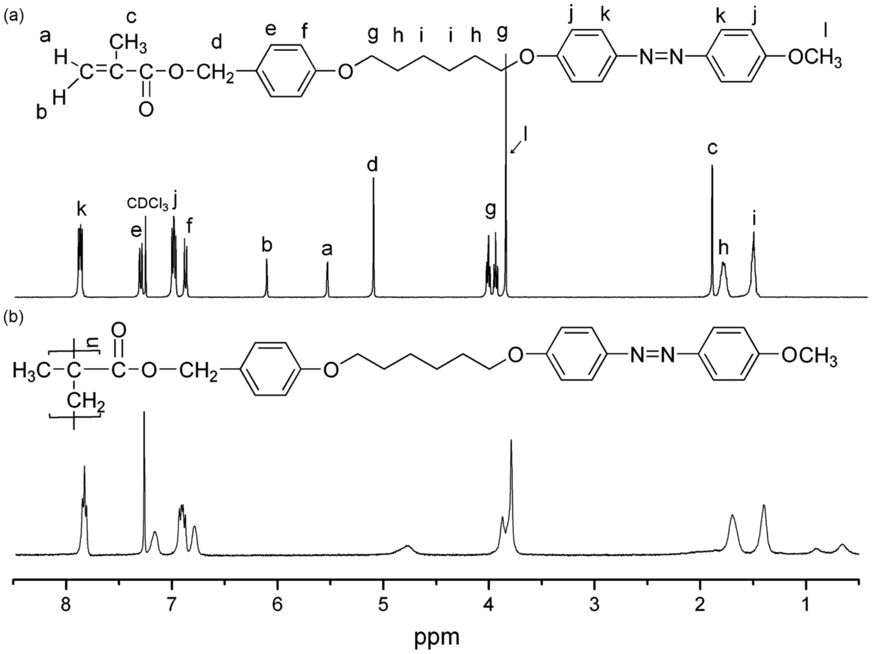

Figure 1. $^1$H NMR spectra of PHABM (a) and PPHABM (b).

characteristic resonance peaks of the vinyl substituent of the monomer can be seen at 5.55 and 6.12 ppm, denoted a and b, respectively. After polymerisation these signals had disappeared completely, and the chemical shifts of the polymers were quite broad on account of the lower mobility of the protons, consistent with the expected polymer structure.

The monomers and polymers were completely soluble in common organic solvents such as chloroform, THF, chlorobenzene and 1,2-dichlorobenzene. GPC analysis was carried out to determine the apparent molecular weight distribution of the polymers, and the molecular characterisation of the polymers is summarised in Table 1.

### 3.2 *Phase transitions and phase structures*

Before investigating the liquid crystalline behaviour of the polymers (PPHABM, PMHABM and POHABM), we first examined their thermal stabilities by TGA in a nitrogen atmosphere. The results in Table 1 demonstrate that all the polymers were quite stable, 5% weight loss occurring only above 370°C. The phase transitions of the three polymers were studied by DSC, and the transition temperatures and corresponding enthalpy changes are also summarised in Table 1. To eliminate the effect of thermal history, all the samples were initially heated from 30°C to 230°C at a rate of 20°C min$^{-1}$ and held at 230°C for 5 min. The DSC thermal diagrams were recorded at 10°C min$^{-1}$ during a second heating, and the DSC traces are shown in Figure 2.

Table 1. GPC, DSC and TGA results.

| Polymer | $M_n$[a] ($\times 10^{-4}$) | $M_w$/ $M_n$[a] | $T_g$(°C)[b] | Phase transitions (°C) and corresponding enthalpy changes (J mol$^{-1}$)[b] | $T_{d,N2}$[c] (°C) |
|---|---|---|---|---|---|
| POHABM-1 | 4.27 | 1.76 | 61 | —[d] | 374 |
| POHABM-2 | 7.62 | 1.84 | 62 | — | 374 |
| POHABM-3 | 14.24 | 2.06 | 62 | — | 375 |
| PMHABM-1 | 2.39 | 2.05 | 78 | S 135 (16.15) I | 387 |
| PMHABM-2 | 5.80 | 2.79 | 78 | S 136 (15.95) I | 387 |
| PMHABM-3 | 14.11 | 2.86 | 79 | S 136 (15.81) I | 388 |
| PPHABM-1 | 1.44 | 1.71 | 87 | S 178 (13.45) I | 386 |
| PPHABM-2 | 4.65 | 1.63 | 91 | S 183 (12.21) I | 388 |
| PPHABM-3 | 16.52 | 2.74 | 94 | S 185 (10.90) I | 393 |

Notes: [a]Obtained from Waters 1515 instrument, linear PS as standard.
[b]Phase transitions and corresponding enthalpy changes were evaluated by DSC at a rate of 10°C min$^{-1}$ during the second heating (S: smectic A phase; I: isotropic phase).
[c]Temperature at which the weight loss of the polymers reached 5%.
[d]No liquid crystal phase transition detected by DSC.

Each of the polymers, PPHABM, PMHABM and POHABM, exhibited clear glass transitions, at temperatures ($T_g$) of ~62°C, ~78°C and ~90°C, respectively, thus decreasing in the order *para* > *meta* > *ortho*. This trend was similar to that observed for MCLCPs [43–47]. All the POHABMs exhibited glass transitions only during heating and cooling, whereas each of the PMHABMs and PPHABMs had two phase transitions, attributed to the isotropic–liquid crystalline phase transition and the glass transition.

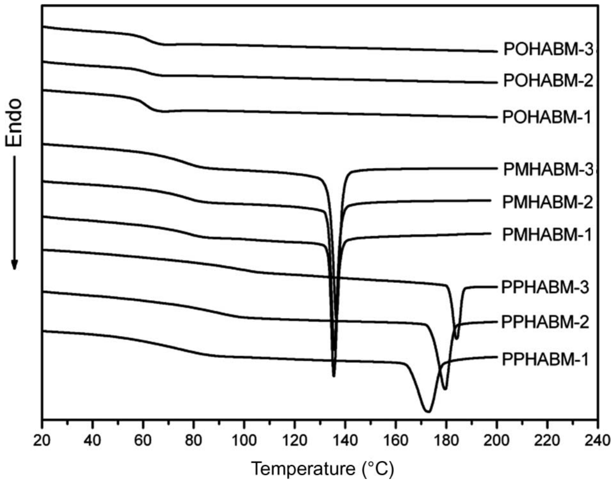

Figure 2. DSC curves of the polymers during the second heating at a rate 10°C $\mathrm{min}^{-1}$.

From Figure 2 and Table 1 it will be seen that the isotropic temperatures ($T_i$) and the liquid crystalline range ($\Delta T$, from $T_g$ to $T_i$) of the PMHABMs were ~136°C and ~58°C, respectively, while those of the PPHABMs were ~83°C and ~92°C. The trend in both $T_i$ and $\Delta T$ for PPHABM and PMHABM decreased in the order *para* > *meta*. It was surprising, however, that the associated enthalpy changes in polymers PPHABM and PMHABM decreased in the reverse order, *meta* (~16.0 J $\mathrm{mol}^{-1}$) > *para* (~12.0 J $\mathrm{mol}^{-1}$), which is different from the results for MCLCPs [50]. This suggests that the enthalpy changes may be dependent on the shape of the side-chains and the flexibility of the polymers [57, 58]. The mechanism for this surprising result will be separately studied in detail in the near future.

The optical textures shown by polymers PPHABM, PMHABM and POHABM were observed using POM. In the case of POHABMs, the appearance of birefringence was not observed either during heating or on cooling. Combining the results of POM and DSC, it was concluded that POHABMs do not exhibit liquid crystalline behaviour. In the case of PMHABM, however, similar liquid crystalline textures were observed during both heating and cooling.

Taking PMHABM-1 as a representative example, when the sample was heated above $T_g$ a typical focal–conic fan texture appeared (Figure 3(a)), indicating that the smectic phase had been formed. Further heating above 135°C caused the texture to disappear, indicating that the isotropic phase was formed. With PPHABMs, similar fan textures appeared during heating and cooling (Figure 3(b)), again suggesting that the liquid crystalline phase was smectic in character. When the samples were heated above $T_i$, the isotropic phase was observed.

To establish the phase structures and transitions more clearly, WAXD experiments were performed at different temperatures, and the samples, PPHABM-1, PMHABM-1 and POHABM-1, were selected as representative. For POHABM-1, no low-angle diffraction peaks in the low $2\theta$ region (2–15°) were observed in the WAXD patterns during heating and cooling, indicating that an ordered structure had not developed. PMHABM-1 and PPHABM-1 behaved similarly, although the temperature of measurement was different.

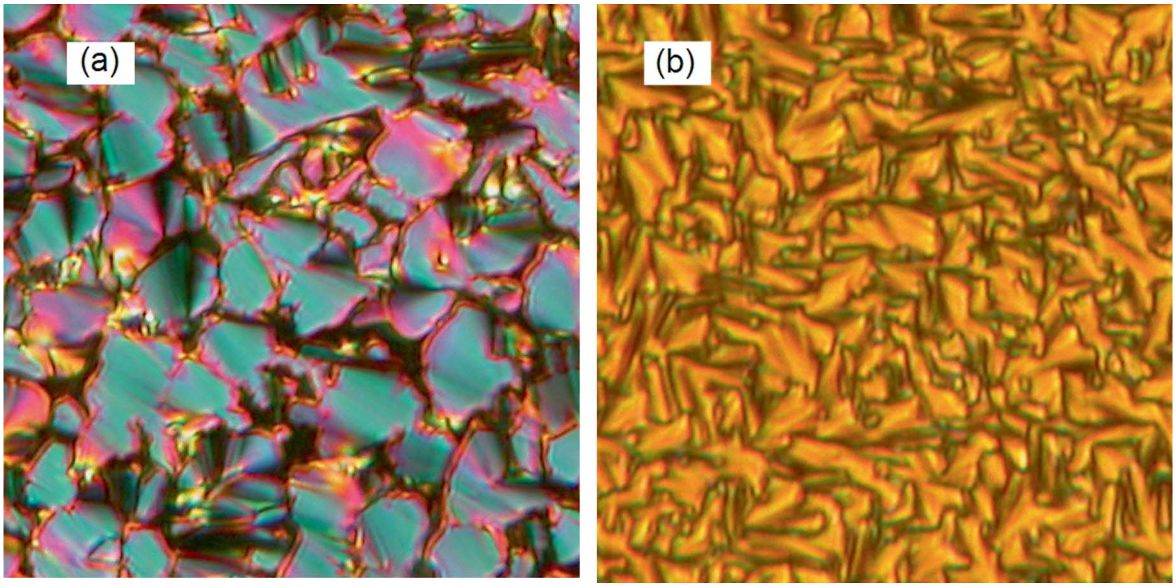

Figure 3. POM images of (a) PMHABM-1 at 130°C, and (b) PPHABM-1 at 160°C (magnification × 200).

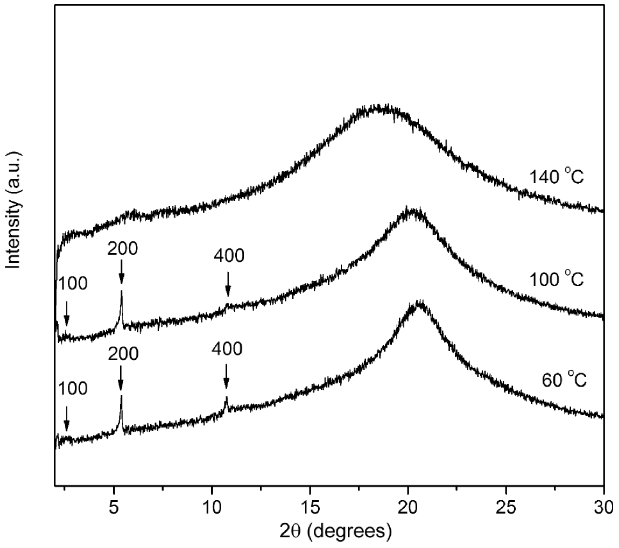

Figure 4. 1D–WAXD patterns of the sample PMHABM-1 during the first heating.

Taking PMHABM-1 as typical, Figure 4 shows WAXD patterns for PMHABM-1 during heating from 60°C to 140°C. As indicated by the arrows in Figure 4, at 100°C three low-angle diffraction peaks were observed, at 2.66° (*d* spacing, 3.32 nm), 5.35° (*d* spacing, 1.65 nm) and 10.70° (*d* spacing, 0.83 nm). The scattering vectors of the three peaks were found to be in the ratio 1 : 2 : 4. The three low-angle diffraction peaks were therefore in good agreement with the (100), (200) and (400) reflections of a smectic A structure. In the high $2\theta$ region (15–30°), an intense scattering band corresponding to a *d* spacing of 0.44 nm was seen, arising from the average lateral distance between neighbouring side-chain azobenzene mesogenic units (Figure 4). Above 140°C, the two low-angle diffraction peaks disappeared, and scattering could be seen in the low $2\theta$ region (2–15°), indicating that the sample had become isotropic (Figure 4). This result is consistent with observations made by POM.

### *3.3 The effect of* **para, meta** *and* **ortho** *mesogen monosubstitution*

The results indicate that POHABMs do not form liquid crystalline phases either on heating or cooling, whereas PPHABMs and PMHABMs each exhibit a smectic A phase during both heating and cooling. It has been noted from Figure 2 and Table 1 that the $T_g$ of the polymers PPHABMs, PMHABMs and POHABMs decreased in the order, *para* > *meta* > *ortho*, and that both $T_i$ and $\Delta T$ are seen to decrease in the order *para* > *meta*. In comparison, the bond angle between the methoxy-substituent on the azobenzene moiety and the first benzene ring linked to the main chain of the polymer increased in the order *ortho* < *meta* < *para*. In the case of the *ortho*-polymers (POHABMs), the kinetic mobility of the azobenzene mesogen is very limited, due the small bond angle, which reduces the ability of the azobenzene mesogens to align. The POHABMs do not therefore exhibit liquid crystalline behaviour.

Moreover, we suggest that the flexible spacer groups connecting the first benzene ring and the monosubstituted azobenzene mesogenic unit are also very important in the ordering process. When the length of the flexible spacer is increased, the *ortho*-monosubstituted polymer may provide a wider range of chain conformations to align the azobenzene mesogens effectively. However, in the polymers PMHABM and PPHABM, the azobenzene mesogens are able to achieve the required alignment, since the bond angle is sufficiently large and the length of the flexible spacers connecting the first benzene ring and the monosubstituted azobenzene moiety is now sufficient. The polymers PMHABM and PPHABM therefore do in fact exhibit a smectic A phase.

We propose that mesophase formation in side-chain liquid crystalline polymers with monosubstituted azobenzene moieties is strongly dependent on the position of the substituent on the azobenzene moiety. Moreover, side-chain liquid crystalline polymers containing *para*-monosubstituted azobenzene moieties have an enhanced shape anisotropy compared with those with in the *meta*-position, and thus show greater stabilisation of the mesophases.

## 4. Conclusions

This investigation has revealed that the formation of liquid crystalline phases depends strongly on the position of the monosubstituent on the azobenzene moiety; for example, *ortho*-monosubstituted polymers (POHABMs) do not form liquid crystalline phases either on heating or cooling, whereas the *para*- and *meta*-monosubstituted polymers (PPHABMs and PMHABMs) exhibit a smectic A phase. Furthermore, the glass transition temperature is decreased by incorporating *ortho*- and *meta*-monosubstituted units into the polymer side-chain, and the general trend is that the $T_g$ of the three types of polymer decreases in the order, *para* > *meta* > *ortho*. For the polymers PPHABM and PMHABM, the isotropic temperature and the liquid crystalline range are seen to decrease in the order *para* > *meta*. By contrast, the enthalpy changes decreased in the reverse order, *meta* > *para*.

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