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The effects of *para-*, *meta-* and *ortho-*monosubstituted azobenzene moiety in the side chain on phase behavior of mesogen-jacketed liquid crystalline polymers



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ABSTRACT

Three different mesogen-jacketed liquid crystalline polymers with monosubstituted azobenzene moiety in the side-chain have been studied. These are poly(2,5-bis{[para-(4'-methoxy-4-oxyhexyloxy azobenzene) benzyl] oxycarbonyl} styrene) (denoted as PPABCS), poly(2,5-bis{[meta-(4'-methoxy-4oxyhexyloxy azobenzene) benzyl] oxycarbonyl} styrene) (denoted as PMABCS) and poly(2, 5-bis {[ortho-(4'-methoxy-4-oxyhexyloxy azobenzene) benzyl] oxycarbonyl} styrene) (denoted as POABCS). The chemical structures of the monomers were confirmed by ¹H NMR, ¹³C NMR spectroscopy and elemental analysis. The structure characterization of the polymers was performed by ¹H NMR spectroscopy and gel permeation chromatography (GPC), and the phase structures and transitions of the polymers were studied using differential scanning calorimetry (DSC), polarized light microscopy (PLM), and one- and two-dimensional (1D, 2D) wide-angle X-ray diffraction. The effects of monosubstituted azobenzene moiety in different positions on the liquid crystalline behaviors of the polymers were also investigated. The results show that the phase transitional behaviors of mesogen-jacketed liquid crystalline polymers containing monosubstituted azobenzene moiety depend strongly on the position of the substituent on the azobenzene moiety. We identify that PPABCS can form a hierarchically ordered structure with double orderings on both the nanometer and subnanometer length scales. Most likely, the thick main-chains of PPABCS obtained by "jacketing" the central rigid portion of side-chain to the polyethylene backbone construct a 2D centered rectangular scaffold. The azobenzene-containing sidechains pack inside the main-chain scaffold form smecitc A (SmA)-like structure and are perpendicular to the main-chains. We compared PPABCS with PMABCS and POABCS, and found that the hierarchically ordered structure of PMABCS was similar to that of PPABCS. It is surprising that the main-chains of POABCS also construct a 2D centered rectangular scaffold, however, the packing of azobenzenecontaining side-chains inside the main-chain scaffold develops smecitc C (SmC)-like structure. Furthermore, the glass transition temperature (T_g), isotropic temperature (T_i) and liquid crystalline range $(\Delta T, \text{ from } T_g \text{ to } T_i)$ of the polymers decrease in the order, para > meta > ortho. It is very interesting phenomenon that the associated enthalpy changes of these polymers are also the same order, para > meta > ortho, which is different from those of MCLCPs and SCLCPs.

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1. Introduction

Liquid crystalline polymers have attracted much attention for their potential applications in many fields, including optical information storage, nonlinear optical material, holographic memories, and so on [1-11]. In the 1950s, Flory postulated that the lattice model was a highly versatile approach for various problems in

liquid crystalline systems, and he revealed that the formation of liquid crystalline depended on the chain rigidity, aspect ratio, chemical structure, conformation and configuration, and other factors [12–14].

In recent years, the effect of the position of the substituent in the mesogenic moiety on the properties of the polymers has been widely studied. Most of the research works has focused on the effect of its substituent position on photochemical behaviors [15–17], photoelectron properties of polymers [18,19], non-linear optical properties [20], liquid crystalline behavior [21–28]. Owing to the very high melting point (T_m) and low solubility of main-chain liquid



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crystalline polymers (MCLCPs), many studies have been devoted to decreasing the $T_{\rm m}$ and $T_{\rm g}$, in addition to improving the solubility by incorporating ortho- or meta-linkages into the side chain. Moreover, the effects of para-, meta-, or ortho-linkages on the formation of liquid crystalline have also been investigated [22,28]. The Chung's result has been shown that the formation of liquid crvstallinity of MCLCPs is found strongly dependent on the configuration of the para-, meta-, or ortho-linkages in the monomeric moieties; of these, the para-linkage is most favorable for generating liquid crystallinity, and the ortho-linkage has a greater tendency to form liquid crystallinity than the meta-linkage [22]. Recently, our results have been demonstrated that the transitional behavior of SCLCPs 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 smectic A phase. Furthermore, the glass transition temperature (T_g) of the polymers decreases in the order, *para* > *meta* > *ortho*. For the *para* and *meta*-monosubstituted polymers, the isotropic temperature (T_i) and liquid crystalline range (ΔT , from T_g to T_i) are found to be in the order, *para* > *meta*, and the associated enthalpy changes in these polymers is the opposite order, meta > para [28].

Mesogen-jacketed liquid crystalline polymers (MILCPs) have been attracting increasing interests for its novelties in the structure and properties since the idea was first proposed by Zhou et al. in the 1987 [29]. Although the mesogen-jacketed liquidcrystalline polymers whose mesogenic units are laterally attached to the polymer backbone without or with very short spacers is a type of SCLCPs, which leads to the extended main chain conformation and some properties similar to main chain liquid crystalline polymers (MCLCPs) because of the spatial requirement of the bulky and rigid mesoenic units [30-32]. Presently, most of the studies are concentrated on the synthesis of MJLCPs and the investigation of the chemical structures of rigid or flexible side chain, for example, the type of the mesogen, the length or type of the terminal flexible substituents, nature of the polymer backbone, etc. effect on the phase structure [33–48]. However, there have been few publications devoted to the effect of the position of the substituent on the properties of MJLCPs. We have assumed that the presence of mesogenic para-, meta-, or ortho-monosubstituted will not only influence the glass transition and isotropic temperatures of MJLCPs, but also their liquid crystalline behaviors, which shall be different from those of MCLCPs and SCLCPs. In the present study, we have compared the effects of para-, meta-, or ortho-monosubstituent on the liquid crystalline behavior of MJLCPs.

Azobenzene mesogen is one of the typical functional units, which can undergo photon-driven reversible cis-trans isomerization [49]. Liquid crystalline polymers containing azobenzene mesogens have been widely studied for potential applications in specific areas, such as reversible optical data storage, optical switching, polarization holography, and so forth [50]. Moreover, their liquid crystalline behaviors have been investigated and they may form low-ordered LC phase, i.e. nematic (N), smectic A (SmA) and smectic C (SmC) phases [51].

Three different mesogen-jacketed liquid crystalline polymers containing *para-*, *meta-*, or *ortho*-monosubstituted azobenzene moiety in the side-chains, respectively, were synthesised using route shown in Scheme 1. The chemical structures of the monomers were confirmed by ¹H NMR, ¹³C NMR spectroscopy and elemental analysis. The structure characterization of the polymers was performed by ¹H NMR spectroscopy and gel permeation chromatography (GPC), and the phase structures and transitions of the polymers were studied using differential scanning calorimetry

(DSC), polarized light microscopy (PLM), and one- and twodimensional (1D, 2D) wide-angle X-ray diffraction.

2. Experimental section

2.1. Materials

The compound of vinylterephthalic acid was synthesized using the method previously reported [52]. Azobisisbutyronitrile (AIBN) was purified by recrystallization from ethanol. Chlorobenzene was washed with H₂SO₄, NaHCO₃, and distilled water separately and was distilled from calcium hydride. THF (AR; Beijing Chemical Co.) and Triethylamine (Acros, 99%) were heated under reflux over calcium hydride for at least 8 h and distilled before use. All other reagents were used as received from commercial sources.

2.2. Synthesis of monomers

The synthetic route of the monomers, 2, 5-bis{[*para*-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzyl] oxycarbonyl} styrene) (denoted as PABCS), 2, 5-bis{[*meta*-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzyl] oxycarbonyl} styrene) (denoted as MABCS) and 2, 5-bis{[*ortho*-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzyl] oxycarbonyl} styrene) (denoted as OABCS), and their corresponding polymers were illustrated in Scheme 1. The experimental details of the monomers synthesis and characterization are described below using PABCS as an example.

2.2.1. Synthesis of 4-(6-bromohexyloxy)-4'-methoxy azobenzene (1)

4-(6-Bromohexyloxy)-4'-methoxy azobenzene was prepared by the method quoted in the literature [53]. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.89–7.86 (m, 4H, Ar–H), 7.01–6.97 (m, 4H, Ar–H), 4.06– 4.02 (m, 2H, –CH₂–), 3.89 (s, 3H, –OCH₃), 3.45–3.42 (m, 2H, – CH₂Br), 1.93–1.82 (m, 4H, –CH₂–), 1.55–1.51 (m, 4H, –CH₂–).

2.2.2. Synthesis of methyl 4-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzoate (2)

Compound 2 was obtained by the etherification of methyl 4hydroxybenzoate with 4-(6-Bromohexyloxy)-4'-methoxy azobenzene (compound 1). In a 1000 mL three-neck round bottom flask equipped with a condenser, N₂ inlet-outlet and mechanical stirrer, a mixture of K₂CO₃ (16.56 g, 120 mmol), acetone (400 mL) was thoroughly degassed with N2. Then, methyl 4-hydroxybenzoate (6.08 g, 40 mmol) and compound 1 (15.64 g, 40 mmol) were added, and the mixture was heated to 60 °C. After 48 h, the reaction was found to be complete by thin-layer chromatography (TLC) and ¹H NMR analyses. The reaction mixture was filtrated and washed with acetone to remove excessive compound 1. The precipitate was dissolved in CH₂C1₂, then, the potassium salt was filtered off. The solvent was evaporated under reduced pressure to obtain yellow solid. Afterwards, the crude product dissolved in CH₂C1₂ was purified by column chromatography (silica gel, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.02–7.99 (m, 2H, Ar– H), 7.92–7.89 (m, 4H, Ar–H), 7.04–7.00 (m, 4H, Ar–H), 6.94–6.92 (m, 2H, Ar-H), 4.10-4.04 (m, 4H, -OCH₂-), 3.91 (s, 3H, -OCH₃), 3.90 (s, 3H, -OCH₃), 1.88–1.85 (m, 4H, -CH₂-), 1.61–1.59 (m, 4H, $-CH_2-$).

2.2.3. Synthesis of 4-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzyl alcohol (**3**)

Compound **3** was prepared by the reduction of methyl 4-(4'methoxy- 4-oxyhexyloxy azobenzene) benzoate (compound **2**) with LiAlH₄. Into a three-neck round-bottom flask, equipped with a condenser, ice bath, N₂ inlet-outlet, and magnetic stirrer, LiAlH₄ (0.76 g, 20 mmol) was suspended in dry THF (20 mL), and the



Scheme 1. Synthetic Route of the Monomers and Polymers.

solution of compound **2** (9.24 g, 20 mmol) in dry THF (200 mL) was added dropwise very slowly. After the addition was complete, the mixture was reacted for further 2 h at room temperature. The reaction was found to be complete by TLC and ¹H NMR analyses. Water was then added slowly with vigorous stirring to terminate the reaction, and then diluted HCl was added to dissolve the precipitate. The product was extracted with CH₂Cl₂. The extracts were dried over MgSO₄, and condensed to give a yellow solid. Afterward, the crude product dissolved in dichloromethane was purified by column chromatography (silica gel, CH₂Cl₂/acetone, 50/1). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.89–7.85 (m, 4H, Ar–H), 7.29–7.27 (m, 2H, Ar–H), 7.01–6.97 (m, 4H, Ar–H), 6.89–6.88 (m, 2H, Ar–H), 4.62 (s, 2H, –OCH₂–), 4.07–3.97 (m, 4H, –OCH₂–), 3.79 (s, 3H, –OCH₃), 1.86–1.83 (m, 4H, –CH₂–), 1.58–1.55 (m, 4H, –CH₂–).

2.2.4. 2,5-Bis{[para-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzyl] oxycarbonyl} styrene (4, PABCS)

An amount of vinyl terephthalic acid (1.92 g, 10 mmol) was mixed with thionyl chloride (40 mL), and the mixture was stirred for about 4 h at 50 $^{\circ}$ C till get a clear solution. The excess thionyl

chloride was removed by evaporation under reduced pressure. The residue was washed twice by petroleum ether, then, dissolved in dried THF (20 mL). Compound 3 (8.68 g, 20 mmol), DMAP (3.67 g, 30 mmol) and triethylamine (4 mL) were dissolved in dried THF (100 mL). Under intense stirring at the temperature of the ice bath, the solution of vinylterephthal chloride was slowly dropped into the solution over a 0.5 h time period. The mixture was further stirred at room temperature for 24 h, and then most of the THF was evaporated under reduced pressure. Then, water and dilute HCl was added to dissolve the precipitate, the product was extracted with CH₂Cl₂. The extracts were dried over anhydrous MgSO₄, and condensed to give a solid. Afterward, the raw product dissolved in dichloromethane was purified first by column chromatography (silica gel, CH₂Cl₂/acetone, 100/1), and recrystallised from THF/diethyl ether to give the monomer (PABCS, 4).

¹H NMR (400 MHz, CDCl₃, δ ppm): 8.22–7.87 (m, 3H, Ar–H); 7.86–7.84 (m, 8H, Ar–H); 7.40–7.38 (q, 1H, =CH–); 7.38–7.37 (m, 4H, Ar–H); 7.01–6.97 (m, 8H, Ar–H); 6.91–6.89 (m, 4H, Ar–H); 5.74–5.69 (dd, 1H, =CH₂); 5.40–5.37 (dd, 1H, =CH₂); 5.30, 5.28 (s, 4H, -OCH₂-); 4.05-3.96 (m, 8H, -OCH₂-); 3.87 (s, 6H, -OCH₃); 1.84-1.83 (m, 8H, -CH₂-); 1.56-1.55 (m, 8H, -CH₂-).

¹³C NMR (δ , ppm, CDCl₃): 25.84, 25.86, 29.16, 29.30 (–CH₂–), 55.52 (–OCH₃); 67.01, 67.04, 67.94, 68.15 (–OCH₂–); 114.18, 114.63, 114.70, 124.31, 124.33, 127.62, 127.73, 128.13, 130.15, 130.19, 130.33, 132.52, 133.29, 139.59, 147.03, 147.17, 159.34, 161.15, 161.57 (Ar); 117.66 (CH₂=); 134.87 (=C–); 165.66, 166.63 (C=O).

Calc. for $C_{62}H_{64}N_4O_{10}$ (Mol. Wt. 1024): C, 72.64; H, 6.29; N, 5.47; Found: C, 72.85; H, 6.32; N, 5.55.

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

2.2.5. 2,5-Bis{[meta-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzyl] oxycarbonyl} styrene (**MABCS**, **5**)

¹H NMR (400 MHz, CDCl₃, δ ppm): 8.26–7.92 (m, 3H, Ar–H); 7.88–7.85 (m, 8H, Ar–H); 7.45–7.38 (q, 1H, =CH–); 7.31–7.29 (m, 4H, Ar–H); 7.00–6.96 (m, 8H, Ar–H); 6.88–6.86 (m, 4H, Ar–H); 5.76–5.71 (dd, 1H, =CH₂); 5.42–5.39 (dd, 1H, =CH₂); 5.34, 5.31 (s, 4H, $-OCH_2-$); 4.04–3.96 (m, 8H, $-OCH_2-$); 3.87 (s, 6H, $-OCH_3$); 1.84–1.82 (m, 8H, $-CH_2-$); 1.56–1.55 (m, 8H, $-CH_2-$).

¹³C NMR (δ, ppm, CDCl₃): 25.81, 25.91, 29.11, 29.21 (–CH₂–), 55.54 (–OCH₃); 62.92, 63.00, 67.97, 68.09 (–OCH₂–); 111.33, 111.37, 114.19, 114.68, 114.70, 120.34, 124.03, 124.19, 124.35, 128.20, 128.31, 129.69, 129.72, 129.87, 130.45, 132.64, 133.39, 139.55, 146.95, 147.18, 151.17, 161.18, 161.55 (Ar); 117.63 (CH₂=); 134.93 (=C–); 165.65, 166.69 (C=O).

2.2.6. 2,5-Bis{[ortho-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzyl] oxycarbonyl} styrene (**OABCS**, **6**)

¹H NMR (400 MHz, CDCl₃, δ ppm): 8.26–7.92 (m, 3H, Ar–H); 7.89–7.84 (m, 8H, Ar–H); 7.48–7.40 (q, 1H, =CH–); 7.41–7.28 (m, 4H, Ar–H); 7.00–6.93 (m, 8H, Ar–H); 6.93–6.87 (m, 4H, Ar–H); 5.75–5.71 (dd, 1H, =CH₂); 5.42, 5.40 (s, 4H, $-OCH_2-$); 5.439–5.36 (dd, 1H, =CH₂); 4.02–3.94 (m, 8H, OCH_2-); 3.87 (s, 6H, $-OCH_3$); 1.84–1.74 (m, 8H, $-CH_2-$); 1.51–1.50 (m, 8H, $-CH_2-$).

¹³C NMR (δ , ppm, CDCl₃): 25.86, 25.89, 29.17, 29.21 (–CH₂–), 55.54 (–OCH₃); 67.04, 67.09, 67.84, 68.13 (–OCH₂–); 114.17, 114.39, 114.44, 114.67, 120.31, 120.36, 124.33, 124.34, 128.22, 128.48, 129.72, 130.47, 132.36, 133.20, 137.19, 137.06, 139.74, 146.97, 147.12, 159.34, 161.14, 161.54 (Ar); 117.85 (CH₂=); 134.85 (=C–); 165.55, 166.49 (C=O).

2.3. Polymerization

The polymers were each obtained by conventional solution radical polymerization (see Scheme 1), typically carried out as described in the following example.

The monomer PABCS (**4**; 0.5 g, 0.5 mmol), 0.01 M of AIBN (300 μ L) in chlorobenzene solution, and dry chlorobenzene (2 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. Polymerization was carried out at 60 °C for 24 h. The sample was diluted with THF and precipitated into a large volume of hot acetone. The sample was purified by similarly reprecipitating three times from THF into hot acetone, and dried overnight at room temperature in vacuo.

2.4. Instruments and measurements

Elemental analysis was carried out with an Elementar Vario EL instrument.

 1 H and 13 C NMR spectra were recorded on a Bruker ARX400 spectrometer at room temperature, using deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the internal standard.

The TGA was performed on a TA SDT 2960 instrument at a heating rate of 20 $^{\circ}$ C/min in nitrogen atmosphere.

The apparent number-average MW (M_n) and MW distribution (M_w/M_n) were measured on a GPC (Waters 1515) instrument with a set of HT3, HT4 and HT5. The μ -Styragel columns used THF as an eluent, and its flow rate was 1.0 mL/min at 35 °C. Calibration was made with polystyrene standards (PS).

DSC examination was carried out on a TA DSC Q100 calorimeter with a programed heating procedure in nitrogen. The sample size was about 5 mg and encapsulated in hermetically sealed aluminum pans, whose weights were kept constant. The temperature and heat flow scale at different cooling and heating rates were calibrated using standard materials such as indium and benzoic acid.

LC texture of the polymers was examined under PLM (Leica DM-LM-P) coupled with a Mettler-Toledo hot stage (FP82HT). The films with thickness of $\sim 10 \ \mu m$ were casted from THF solution and slowly dried at room temperature.

One-dimensional (1D) wide-angle X-ray diffraction (WAXD) experiments were performed on a Philips X' Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu K_α) and an X' celerator detector. The reflection peak positions were calibrated with silicon powder ($2\theta > 15^{\circ}$) and silver behenate ($2\theta < 10^{\circ}$). The sample stage is set horizontally, and a temperature control unit (Paar Physica TCU 100) in conjunction with the diffractometer was utilized to study the structure evolutions as a function of temperature. The heating and cooling rates in the WAXD experiments were 10 °C/min.

Two-dimensional wide-angle X-ray diffraction (2D WAXD) fiber patterns were recorded on a Bruker D8 Discover diffractometer equipped with a general area detector diffraction system (GADDS) as a 2D detector, in a transmission mode at room temperature. Again, calibrations were made against silicon powder and silver behenate. Samples were mounted on the sample stage, and the point-focused X-ray beam was aligned either perpendicular or parallel to the mechanical shearing direction.

3. Results and discussion

3.1. Synthesis and characterization of the monomers and polymers

As shown in Scheme 1, each of the monomers (PABCS, MABCS and OABCS) was synthesized in the similar manner. The monomer PABCS will be taken as a representative example.

The preparation and characterization of 4-(6-bromohexyloxy)-4'-methoxy azobenzene, has been described elsewhere [53]. First, methyl *para*-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzoate was prepared by etherification of methyl 4-hydroxybenzoate with 4-(6-bromohexyloxy)-4'-methoxy azobenzene. Then, *para*-(4'methoxy-4-oxy-hexyloxy azobenzene) benzyl alcohol was synthesized by reduction of methyl *para*-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzoate with LiAlH₄. Finally, the monomer PABCS was obtained by esterification of vinyl terephthalic chloride and *para*-(4'-methoxy-4-oxy-hexyloxy azobenzene) benzyl alcohol. The rude product was purified by column chromatography (silica gel, CH₂Cl₂/acetone, 100/1), followed by recrystallization from THF/ diethyl ether to obtain the monomer, PABCS.

The structure of the monomers was confirmed by ¹H NMR, ¹³C NMR spectroscopy and elemental analysis. In order to study the influence of Mw on the phase behavior, we attempted to synthesize the polymers with different molecular weights via ATRP. The result showed that the high MW polymer couldn't be prepared, but we were able to obtain polymers of high molecular weight by free radical polymerization.

As an example, Fig. 1a and b show the ¹H NMR spectra of the monomer, PABCS, and the corresponding polymer, PPABCS,



Fig. 1. ¹H NMR spectra of PABCS (a) and PPABCS (b) in CDCl₃-d.

respectively. The characteristic resonance peaks of the vinyl substituent of monomer PABCS can be seen at 5.40–5.37, 5.74–5.69 and 7.40–7.38 ppm, denoted m, n and o, respectively. After polymerization, these signals had disappeared completely, and the chemical shifts of the polymers were quite broad, consistent with the expected polymer structure.

The monomers and polymers were completely soluble in common organic solvents such as THF, benzene and chlorobenzene. GPC analysis was carried out to determine the apparent MW and molecular weight distributions of the polymers, and the molecular characterization of the polymers is summarized in Table 1.

3.2. Phase transitions and phase structures

TGA was employed to characterize the thermal stabilities of the polymers (PPABCS, PMABCS and POABCS). As could be seen from

 Table 1

 GPC, DSC and TGA results and thermotropic properties of the polymers.

Sample	M_{n}^{a} (×10 ⁻⁴)	$\frac{M_{ m w}}{M_{ m n}{}^{ m a}}$	Tg (°C) ^b	T _{LC−I} (°C) ^b	ΔH_{LC-I} (J/g) ^b	Liquid crystalline range $\Delta T (^{\circ}C)^{b}$	<i>T</i> _d (N ₂) (°C) ^c
PPABCS	7.75	1.65	80	219	9.69	139	337
PMABCS	7.01	1.72	66	188	9.24	122	353
POABCS	8.31	1.62	64	157	2.80	93	354

^a Obtained from Waters 1515 instrument, linear PS as standards.

^b The glass transition temperature ($T_{\rm g}$), the liquid crystal transition temperature ($T_{\rm LC-I}$) and corresponding enthalpy changes ($\Delta H_{\rm LC-I}$) were evaluated by DSC at a rate of 10 °C/min under the second heating.

^c Temperature at which the weight loss of the polymers reached 5% was obtained from TGA under nitrogen [$T_d(N_2)$] by TGA heating experiments at a rate of 20 °C/min.

Table 1, all the polymers were quite stable, 5% weight loss occurring only above 330 °C in nitrogen atmosphere. The phase transitions of the polymers were studied by DSC, and the transition temperatures and corresponding enthalpy changes were also summarized in Table 1. To eliminate the effect of thermal history, all the samples were initially heated from 30 °C to 240 °C at a rate of 20 °C min⁻¹ and held at 240 °C for 5 min. The DSC thermal diagrams were recorded at 10 $^{\circ}$ C min⁻¹ during the first cooling and second heating process, of which the DSC traces are shown in Fig. 2. Each of the polymers had two phase transitions, attributed to the glass transition and the isotropic-liquid crystalline phase transition. From Fig. 2 and Table 1, it will be seen that the glass transition temperatures (T_g) of the polymers (PPABCS, PMABCS and POABCS) were ~80 °C, ~66 °C and ~64 °C, respectively; and that the isotropic temperatures (T_i) of three polymers were ~219 °C, ~188 °C and ~157 °C, respectively; and that the liquid crystalline range (ΔT , from T_g to T_i) were ~139 °C, ~122 °C and ~93 °C, respectively. The $T_{\rm g}$, $T_{\rm i}$ and ΔT for three polymers all decreased in the order of *para* > *meta* > *ortho*. This trend was similar to that observed for MCLCPs [22] and SCLCPs [28]. It was surprising, however, that the associated enthalpy changes in three polymers decreased in the same order, para (~9.69 $] g^{-1}$) > meta (~9.24 $] g^{-1}$) > ortho (~2.8 J g^{-1}), which is different from the results for MCLCPs and SCLCPs [22,28]. This suggests that the enthalpy changes may be dependent on the shape of the side-chains and the flexibility of the polymers [54,55]. The mechanism for this surprising result will be separately studied in detail in the near future.

The optical textures shown by the polymers (PPABCS, PMABCS and POABCS) were observed using PLM. At temperatures below T_i , three polymers all exhibited strong birefringence, and the PLM textures clearly indicted the existence of LC phases. Fig. 3 shows three typical PLM images recorded from PPABCS at 140 °C, PMABCS at 140 °C, and POABCS at 120 °C, respectively, corresponding to the three polymers. When three polymers were respectively heated above their T_i , the isotropic phases were observed.

To further elucidate the phase structures and transitions more clearly, WAXD experiments were performed at different temperatures. Fig. 4a represents a set of 1D WAXD patterns of the polymer PPABCS recorded during heating from 60 °C to 220 °C. As shown in Fig. 4a, the sample renders a diffuse scattering halo at 2θ of ~ 20° (*d* spacing of ~ 0.44 nm) in the high-angle region at lower temperatures, which turns into a typical amorphous halo when the temperature exceeds 219 °C, indicating that the sample has lose some



Fig. 2. DSC curves of the polymers (PPABCS, PMABCS and POABCS) during the first cooling and second heating at a rate of 10 $\,^{\circ}$ C min⁻¹.



Fig. 3. PLM images of (a) PPABCS at 140 °C, (b) PMABCS at 140 °C, and (c) POABCS at 120 °C during heating process (Magnification: ×200).



Fig. 4. 1D WAXD patterns of the samples (a) PPABCS, (b) PMABCS and (c) POABCS during the heating.

degrees of order on the subnanometer scale after the lowest transition at 80 °C. As indicated by the arrows in Fig. 4a, in the lowangle region, six diffraction peaks (indexed as peak 1, 2, 3, 4, 5 and 6 in Fig. 4a) at 2.57° (*d* spacing of 3.44 nm), 3.39° (*d* spacing of 2.61 nm), 4.44° (*d* spacing of 1.99 nm), 5.15° (*d* spacing of 1.72 nm), 5.79° (*d* spacing of 1.53 nm) and 7.71° (*d* spacing of 1.14 nm) can be identified, and the scattering vectors of the six peaks are found to be in the ratio 1:1.32:1.73:2:2.25:3. When temperature reaches 220 °C, all the low-angle diffractions disappear, indicating that the sample enters an isotropic state. The low- and high-angle diffractions at lower temperatures indicate that the polymer PPABCS possesses two ordered structures on different length scales of nanometer and sub-nanometer, respectively. We consider that the high-angle diffraction at 2θ of ~ 20° should be contributed from the packing of azobenzene containing side-chains, and the low-angle diffractions reflect the existence of an ordered structure formed by the main-chains composed of polyethylene backbone and the center rigid portion of side-chain.

To further investigate the effects of para-, meta-, or orthomonosubstituent on phase transition behaviors of the polymers, the phase transitions of the polymers PMABCS and POABCS could also be followed by 1D WAXD experiments. Table 2 lists the *d* spacings of the diffractions and smectic interlayer distances observed from the polymers PPABCS, PMABCS and POABCS, respectively. Fig. 4b depicts a set of 1D WAXD patterns of the polymer PMABCS at various temperatures. As shown in Fig. 4b, in the low-angle region, only three diffraction peaks (indexed as peak 1, 2, and 3 in Fig. 4b) can be observed at below 188 °C, and the scattering vectors of the three peaks are in the ratio 1.73:2:2.18. At below 66 °C, peak 2 is rather weak. With the increasing temperature, the intensity of the peak increases. Above 188 °C, all the lowangle diffraction peaks disappeared, and scattering could be seen in the low 2θ region, indicating that the sample had become isotropic. Moreover, a relatively sharp peak at 2θ of $\sim 20^{\circ}$ (*d* spacing of \sim 0.44 nm) could be seen in the high-angle region at lower temperatures, which is similar to that of the polymer PPABCS. For the polymer POABCS, four diffraction peaks (indexed as peak 1, 2, 3, and 4 in Fig. 4c) in the low-angle region can be observed from Fig. 4c and Table 2 at below 157 °C, and the scattering vectors of the four peaks are in the ratio 1:1.23:1.87:2, indicating that the ordered structure formed, which is also similar to those of PPABCS and

Table 2

WAXD date for the samples PPABCS, PMABCS and POABCS.

PPABCS (at 140 °C)		PMABCS (at	t 140 °C)	POABCS (at 120 °C)		
<i>d</i> (nm)	hkl ^a	<i>d</i> (nm)	hkl ^a	<i>d</i> (nm)	hkl ^a	
Low-angle r	egion ^b					
3.44	200	1.94	310	2.77	200	
2.61	210	1.68	400	2.25	110	
1.99	310	1.54	410	1.48	310	
1.72	400			1.39	400	
1.53	410					
1.14	600					
High-angle 1	region ^c					
~0.44 nm		∼0.44 nm		∼0.44 nm	~0.44 nm	
Smectic inte	erlayer distan	ces				
~6.88 nm		~6.72 nm		~5.54 nm		

^a Indices are based on the unit cells proposed.

^b Below the isotropic temperatures (T_i), the low-angle diffractions came from the centered rectangular scaffold of the main-chain. PPABCS at 140 °C, a = 6.88 nm, b = 4.00 nm and c = 0; PMABCS at 140 °C, a = 6.72 nm, b = 3.88 nm and c = 0; POABCS at 120 °C, a = 5.54 nm, b = 2.46 nm and c = 0.

^c Below the isotropic temperatures (*T*_i), the high-angle diffractions came from the packing of azobenzene-containing side-chains inside the main-chain scaffold. PPABCS, SmA-like structure; PMABCS, SmA-like structure; and POABCS, SmC-like structure.

PMABCS. However, the diffraction pattern of the polymer POABCS at 2θ of $\sim 20^{\circ}$ (*d* spacing of ~ 0.44 nm) in the high-angle region at low temperatures is obviously different from those observed from the polymers PPABCS and PMABCS, suggesting that the new ordered structure formed by the packing of azobenzene containing side-chains.

To further identify the supramolecular structures of the polymers PPABCS, PMABCS and POABCS, the 2D WAXD experiments were carried out. The samples were obtained by mechanical shear at temperature below the isotropic temperature. Fig. 5a schematically shows the sheared sample with x- (the shear direction) and z-direction (shear gradient), respectively. Fig. 5b shows a 2D WAXD pattern of the oriented PPABCS recorded at room temperature. In this figure, the X-ray incident beam is aligned parallel to y direction (See the schematic drawing of Fig. 5a, wherein x and z directions are the shear direction and shear gradient, respectively), where a pair of the high-angle diffractions, which is mainly resulted from the interference of side-chains which pack parallel to each other, is located on the meridian in Fig. 5b. Considering that the strong mechanical shearing can preferentially align the mainchain axis parallel to the shear direction (the meridian), this geometry of high angle diffraction signifies that side-chains are perpendicular to the main-chain axis. We conclude that the sidechains form a SmA-like packing at low temperatures. On the other hand, Three pairs of low-angle diffractions (spots 1, 3, and 5) at 2θ of 2.57°, 5.15° and 7.71° appear on the equator, respectively, and two pairs of low-angle diffractions (spots 2 and 4) at 2θ of 4.44° and 5.79° locate on guadrants, with an angle of 60° and 45° away from the equator, respectively. With the main-chain along the meridian, the low-angle diffractions located on the equator can be assigned as (*hk*0) of the main-chain ordered packing. We may assign 1, 3, and 5 to be (200), (400) and (600) diffraction, and 2 and 4 to be (310) and (410) diffraction, respectively. Combing the results shown in Fig. 5b, we may obtain a rectangular lattice, with a = 6.88 nm and b = 4.00 nm. Such a rectangular lattice has been observed in the self-assembly of dendrons [56,57], dendronized polymers [58,59], and MJLCPs [60-62]. The possible supramolecular structure of PPABCS at low temperatures is schematically drawn in Fig. 6a.

Fig. 5c shows the 2D WAXD pattern of the oriented PMABCS at room temperature with the X-ray incident beam parallel to y direction. Three pairs of low-angle diffractions appear on the equator and are indexed as (200), (400), and (410), respectively, indicating that a rectangular lattice, with a = 6.72 nm and b = 3.88 nm, had formed. The pair of the high-angle diffractions is located on the meridian in Fig. 5c, indicating that the side-chains of PMABCS form a SmA-like packing and the diffraction behavior is similar to that of PPABCS. Fig. 5d depicts a 2D WAXD pattern of the oriented POABCS sample at room temperature. With the X-ray incident beam is aligned parallel to z direction, three pair of the low angle diffractions appeared on the equator, and were indexed as (200), (110), and (400), respectively, indicating that a rectangular lattice, with a = 5.54 nm and b = 2.46 nm, had formed. In the high-angle region, it is surprising, however, that four arcs of ~ 0.44 nm are in the quadrants and the tilting angle was $\pm 60^{\circ}$ (See Fig. 5d, $\alpha = 60^{\circ}$), which shall mainly come from the interference between the azobenzene-containing side-chains parallel to each other. Therefore, the 2D WXRD result indicates a SmC structure [63,64]. The side view of the packing model of POABCS at low temperatures deduced from the WAXD results is illustrated in Fig. 6b.

3.3. The effect of para, meta and ortho mesogen monosubstitution

The results indicate that the mesophase formation of the polymers PPABCS, PMABCS and POABCS is different from those of



Fig. 5. 2D-WAXD patterns of the sheared PPABCS (b), PMABCS (c) and POABCS (d) samples recorded at room temperature. (a) Schematic drawing of the sheared samples with x and z direction are the shear direction and shear gradient, respectively. The shear direction is on the meridian and the X-ray incident beam is along the (b) y-, (c) y-, and (d) z-direction, respectively.

MCLCPs and SCLCPs [22,28]. For MCLCPs, the formation of liquid crystallinity is found strongly dependent on the configuration of the *ortho-*, *meta-*, and *para-*linkages in monomeric units and that the *para-*linkage is most favorable to form liquid crystallinity and the *ortho-*linkage has a greater tendency to form liquid crystallinity than the *meta-*linkage. Moreover, for SCLCPs, the *ortho-*linkage does not form liquid crystallinity, the *para-* and *meta-*linkages all exhibit obvious liquid crystalline phase. However, for the polymers PPABCS, PMABCS and POABCS, the thick main-chains obtained by "jacketing" the central rigid portion of side-chain to the poly-ethylene backbone construct a 2D centered rectangular scaffold and can form a hierarchically ordered structure with double orderings on both the nanometer and subnanometer length scales, which are MJLCPs.

In comparison, the bond angle between the methoxysubstituent on the azobenzene moiety and the first benzene ring of the central rigid portion of side-chain increased in the order *ortho < meta < para.* In the case of the *ortho*-monosubstituted POABCS, the kinetic mobility of the azobenzene mesogen is very limited, due the small bond angle, which disturbs the order packaging of monosubstituted azobenzene moieties. The sidechains of the polymer POABCS only forms a SmC-like packing. 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 PPABCS and PMABCS, 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 side-chains of the polymers PPABCS and PMABCS therefore do in fact form SmA-like packing.

It has been noted from Fig. 2 and Table 1 that the glass transition temperature (T_g), isotropic temperature (T_i), liquid crystalline range (ΔT , from T_g to T_i) and enthalpy change of the polymers PPABCS, PMABCS and POABCS decrease in the order, *para* > *meta* > *ortho*. It is very interesting phenomenon that the associated enthalpy changes of these polymers are also the same order, *para* > *meta* > *ortho*, which is different from those of MCLCPs and SCLCPs. We propose that mesophase formation in mesogen-jacketed liquid crystalline polymers containing monosubstituted azobenzene moieties is strongly dependent on the position of the substituent on the azobenzene moieties have an enhanced shape anisotropy compared with those with in the *meta*- and *ortho*-position, and thus show greater stabilisation of the mesophases.



Fig. 6. Schematic drawing of the proposed supramolecular structure for PPABCS (a), view along the main-chain directions; for POABCS (b), side view of the model.

4. Conclusion

This investigation has revealed that the formation of liquid crystalline phases of mesogen-jacketed liquid crystalline polymers containing monosubstituted azobenzene moiety depends strongly on the position of the monosubstituent on the azobenzene moiety; for example, the main-chains of para-monosubstituted polymer PPABCS can form a hierarchically ordered structure with double orderings on both the nanometer and subnanometer length scales. The packing of side-chains inside the main-chain scaffold undergoes the transitions of smecitc A (SmA)-like \leftrightarrow isotropic. The hierarchically ordered structure of PPABCS renders a biaxial orientation with the side-chains perpendicular to the main-chains. We compared PPABCS with meta-monosubstituted polymer PMABCS and ortho-monosubstituted polymer POABCS, and found that the hierarchically ordered structure of PMABCS is similar to that of PPABCS. It is surprising that the main-chains of POABCS also constructed a 2D centered rectangular scaffold, however, the packing of side-chains inside the main-chain scaffold forms smecitc C (SmC)-like structure. Furthermore, the glass transition temperature (T_g), isotropic temperature (T_i) and liquid crystalline range (ΔT , from T_g to T_i) of the polymers decrease in the order, *para* > *meta* > *ortho*. It is very interesting phenomenon that the associated enthalpy changes of these polymers are also the same order, *para* > *meta* > *ortho*.

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