Polymer 51 (2010) 422-429



Contents lists available at ScienceDirect

# Polymer



journal homepage: www.elsevier.com/locate/polymer

# Structure–property relationship of a series of novel mesogen-jacketed liquid-crystalline polymers containing semirigid side chain with different numbers of alkoxy terminal groups

Chang-An Yang<sup>a</sup>, Qian Tan<sup>a</sup>, GuanQun Zhong<sup>a</sup>, HeLou Xie<sup>a</sup>, HaiLiang Zhang<sup>a,\*</sup>, Er-Qiang Chen<sup>b</sup>, Qi-Feng Zhou<sup>b</sup>

<sup>a</sup> Key Laboratory of Polymeric Materials & Application Technology of Hunan Province, Key Laboratory of Advanced Functional Polymer Materials of Colleges and Universities of Hunan Province, College of Chemistry, Xiangtan University, Xiangtan 411105, Hunan Province, PR China

<sup>b</sup> Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

#### ARTICLE INFO

Article history: Received 29 July 2009 Received in revised form 3 December 2009 Accepted 6 December 2009 Available online 16 December 2009

Keywords: Mesogen-jacketed liquid-crystalline polymer Mesogen Columnar nematic phase

# ABSTRACT

A series of vinyl monomers, 2, 5-bis [(4-methoxy benzyl) oxycarbonyl] styrene (MBCS); 2, 5-bis [(3, 5-dimethoxy benzyl) oxycarbonyl] styrene (DMBCS) and 2, 5-bis [(3, 4, 5-trimethoxy benzyl) oxycarbonyl] styrene (TMBCS) were synthesized and polymerized via free radical polymerization. The terminal groups of the semirigid side chain were systematically varied to investigate the effects of their numbers on the ability of mesophase formation of the resultant polymers. The chemical structures of the monomers were confirmed by elemental analysis, <sup>1</sup>H NMR and <sup>13</sup>C NMR. The characterization of the polymers was performed with <sup>1</sup>H NMR, gel permeation chromatography (GPC). The phase structures and transition behaviors were studied using differential scanning calorimetry (DSC), polarized light microscopy (PLM) and one- and two-dimensional wide-angle X-ray diffraction (WAXD). The experimental results suggested that the ability of mesophase formation of the polymers decreased as the rigidity of side-chain group decreased and increased as the number of the alkoxy terminal group increased, and that all the polymers with high molecular weight showed stable columnar nematic phase ( $\Phi_N$ ).

© 2009 Elsevier Ltd. All rights reserved.

# 1. Introduction

In recent years, liquid-crystalline polymers have attracted longstanding attention for their potential applications in many fields, including optical data storage, optic, electro-optic, nonlinear optic devices, photomechanical, and so on [1–10]. Generally, liquid-crystalline polymers can be divided into mainchain liquid-crystalline polymers (MCLCPs) and side-chain liquidcrystalline polymers (SCLCPs) according to the positions of mesogens [11]. For SCLCPs, the mesogenic groups incorporated in the SCLCPs can be linked to the backbone via either "terminal" or "lateral" attachment, and the flexible spacers are needed to decouple motions between the main chain and the mesogenic side groups [12,13]. However, when flexible spacers are absent, the phase structures may become more intriguing.

A class of "mesogen-jacketed liquid-crystalline polymers" (MJLCPs) was reported by Zhou et al. in 1987 [14]. In MJLCPs, the

side-chain mesogenic units were connected at their gravity center to the main chain without or with only very short spacers, which could also show liquid-crystalline behavior [14-20]. In the past several years, the MJLCPs have been widely researched by Finklemann [21], Percec [22], Pugh [23,24], Keller [25], Gray [26], Ober [16], and Zhou [15,17–19,27–43]. In these cases, the main chain of the polymer were forced to adopt a more extended conformation because of a strong steric interaction between polymer backbones and bulky side chains, and the conformation of the polymers were similar to that of main-chain liquid-crystalline polymers (MCLCPs), which was different from the conventional SCLCPs with long spacers and their liquid-crystalline behaviors were not absolutely determined by the mesogenic groups. Therefore, MJLCPs exhibited some unique LC phase structures and could form hexatic columnar nematic ( $\Phi_{\text{HN}}$ ) phases [41,43], columnar nematic ( $\Phi_{\text{N}}$ ) [44] and smectic A (S<sub>A</sub>) phase [45,46]. 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 effect on the phase structure [27–46]. However, few reposts are found to study the effects of semirigid side chain on the phase structure and on the ability of mesophase formation. Moreover, the effects of number of

<sup>\*</sup> Corresponding author. Tel.: +86 731 58293377; fax: +86 731 58293264. *E-mail address*: hailiangzhang@xtu.edu.cn (H.L. Zhang).

<sup>0032-3861/\$ -</sup> see front matter  $\odot$  2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.polymer.2009.12.004

the terminal flexible substituents in the semirigid side chain on the phase structure and on the ability of mesophase formation of mesogen-jacketed liquid-crystalline polymers have not been reported.

In this work, we report the synthesis and characterization of a series of vinvl monomers with different numbers of alkoxy terminal groups and their corresponding homopolymers. We try to add one methylene unit between the alkoxybenzene unit and the oxycarbonyl styrene unit of poly {2, 5-bis [(4-methoxyphenyl) oxycarbonyl] styrenes} (PMPCS) to break the rigidity of side-chain mesogen and investigate the effects of the semirigid side chain on the phase structure and the ability of mesophase formation. Moreover, we add different number of alkoxy terminal groups to change spatial steric hindrance, and investigate the effects of the spatial steric hindrance on the ability of mesophase formation. The structures of the monomers and the corresponding polymers and their abbreviations are depicted in Scheme 1. As evidenced by the results of DSC, PLM, and WAXD, all the high molecular weight polymers show stable columnar nematic phase ( $\Phi_N$ ), and the subtle structural change or the number change of terminal groups all lead to a remarkable impact on the ability of mesophase formation.

# 2. Experimental section

## 2.1. Materials

The compound of vinyl terephthalic acid was synthesized using the method previously reported [47]. Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. Chlorobenzene was purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with water, once with 5% sodium carbonate solution, and again with water before being dried with anhydrous calcium chloride and then distilled. 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. 4-Dimethylaminopyridine (DMAP) was purchased from Aldrich Chemical Co. Anhydrous magnesium sulfate was used to dry all organic extracts. All other reagents were used as received from commercial sources.

#### 2.1.1. Synthesis of monomers

The synthetic route of MBCS, DMBCS and TMBCS was shown in Scheme 1. The experimental details of the monomers synthesis and characterization are described below.

2.1.1.1. 2, 5-Bis [(4-methoxy benzyl) oxycarbonyl] styrene (*MBCS*). An amount of vinyl terephthalic acid (1.92 g, 10 mmol) was mixed with thionyl chloride (40 ml). The mixture was stirred for about 4 h at 50 °C till a clear solution was obtained. 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). 4-Methoxybenzalcohol (2.76 g, 20 mmol), DMAP (3.67 g, 30 mmol) and triethylamine (4 mL) were dissolved in dried THF (50 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. A vigorous reaction occurred, leading to a white suspension. 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 were added to dissolve the precipitate, and the product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extracts were dried over anhydrous magnesium sulfate (anhydrous MgSO<sub>4</sub>), and condensed to give a solid. Afterward, the raw product dissolved in dichloromethane was purified first by column chromatography (silica gel,



Scheme 1. Synthetic route of the monomers and polymers.



Fig. 1. <sup>1</sup>H NMR spectra of (a) the monomer MBCS and (b) the polymer PMBCS in  $CDCl_3-d$ .

dichloromethane) and then recrystallized from diethyl ether/ethyl alcohol to MBCS. <sup>1</sup>H NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 8.23–7.87 (m, 3H, Ar–H); 7.42–7.36 (q, 1H, = CH–); 7.39–7.36 (m, 4H, Ar–H); 6.93–6.90 (m, 4H, Ar–H); 5.75–5.70 (dd, 1H, = CH<sub>2</sub>); 5.41–5.38 (dd, 1H, = CH<sub>2</sub>); 5.31, 5.29 (s, 4H,–OCH<sub>2</sub>–); 3.82 (s, 6H,–OCH<sub>3</sub>). <sup>13</sup>C NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 55.32 (–OCH<sub>3</sub>); 67.05, 67.07 (–OCH<sub>2</sub>–); 114.07, 114.17, 127.77, 127.87, 128.20, 128.41, 129.96, 130.26, 132.49, 133.29, 139.65, 159.83 (Ar); 117.78 (CH<sub>2</sub> = ); 134.89 (=C–); 165.70, 166.66 (C=O). Anal. Calcd for C<sub>26</sub>H<sub>24</sub>O<sub>6</sub>: C, 72.21; H, 5.59. Found: C, 72.12; H, 5.56.

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

2.1.1.2. 2, 5-Bis [(3, 5-dimethoxy benzyl) oxycarbonyl] styrene (DMBCS). <sup>1</sup>H NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 8.28–7.95 (m, 3H, Ar–H); 7.47–7.40 (q, 1H, = CH–); 6.60–6.57 (m, 4H, Ar–H); 6.44 (m, 2H, Ar–H); 5.77–5.73 (dd, 1H, = CH<sub>2</sub>); 5.44–5.40 (dd, 1H, = CH<sub>2</sub>); 5.32, 5.30 (s,

 Table 1

 GPC, DSC, and TGA results and thermotropic properties of PMBCSs, PDMBCSs and PTMBCSs.

Sample <sup>a</sup>	$M_n^{b}(\times 10^{-4})$	PDI <sup>b</sup>	DP <sup>b</sup>	Tg <sup>c</sup> (°C)	$T_d^d(^{\circ}C)$	Liquid crystallinity <sup>e</sup>
P1	13.49	2.23	312	52.7	359.6	No
P2	16.17	2.26	374	53.2	371.9	Yes
P3	21.37	2.17	495	55.1	374.5	Yes
P4	5.68	1.72	115	49.8	397.0	No
P5	9.66	2.27	196	51.3	397.5	Yes
P6	24.19	1.96	492	52.9	392.7	Yes
P7	2.82	2.25	51	79.6	364.3	Yes
P8	10.12	2.29	183	82.2	368.5	Yes

<sup>a</sup> P1, P2 and P3 represented PMBCS; P4, P5 and P6 represented PDMBCS; P7 and P8 represented PTMBCS.

<sup>b</sup> Based on GPC measurements.

 $^{\rm c}$  Glass-transition temperature obtained from the second-heating DSC experiments and heating rates were 10  $^{\circ}\text{C/min.}$ 

<sup>d</sup> Temperature at which the weight loss of the polymers reached 5%.

e Determined by PLM.

4H,  $-OCH_2-$ ); 3.88 (s, 12H,  $-OCH_3$ ). <sup>13</sup>C NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 55.39 ( $-OCH_3$ ); 67.03, 67.10 ( $-OCH_2-$ ); 100.23, 100.29, 106.04, 106.22, 128.25, 128.50, 130.51, 132.36, 133.21, 137.87, 137.99, 139.76, 161.06 (Ar); 117.86 (CH<sub>2</sub>=); 134.90 (=C-); 165.50, 166.45 (C=O). Anal. Calcd for C<sub>28</sub>H<sub>28</sub>O<sub>8</sub>: C, 68.28; H, 5.73. Found: C, 68.13; H, 5.68.

2.1.1.3. 2, 5-Bis [(3, 4, 5-trimethoxy benzyl) oxycarbonyl] styrene (*TMBCS*). <sup>1</sup>H NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 8.28–7.93 (m, 3H, Ar–H); 7.44–7.39 (q, 1H,=CH–); 6.68–6.66 (m, 4H, Ar–H); 5.78–5.74 (dd, 1H,=CH<sub>2</sub>); 5.44–5.41 (dd, 1H,=CH<sub>2</sub>); 5.31, 5.29 (s, 4H, –OCH<sub>2</sub>–); 3.88, 3.85 (s, 18H, –OCH<sub>3</sub>). <sup>13</sup>C NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 56.19, 60.82 (–OCH<sub>3</sub>); 67.40, 67.44 (–OCH<sub>2</sub>–); 105.71, 105.95, 128.22, 128.44, 130.42, 131.13, 131.24, 132.48, 133.21, 138.23, 139.61, 153.43 (Ar); 117.79 (CH<sub>2</sub>=); 134.84 (=C–); 165.50, 166.52 (C=O). Anal. Calcd for C<sub>30</sub>H<sub>32</sub>O<sub>10</sub>: C, 65.21; H, 5.84. Found: C, 65.13; H, 5.81.

### 2.2. Polymerization

All polymers were obtained by conventional solution radical polymerization (see Scheme 1). A typical polymerization procedure was carried out as follows. For example, MBCS (0.5 g, 1.16 mmol), 0.01 M chlorobenzene solution of AIBN (300  $\mu$ L,) and chlorobenzene (1.2 mL) were transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed off under vacuum. Polymerization was carried out at 60 °C for 24 h. The tube was then opened, and the reaction mixture was diluted with THF (10 mL), and then reprecipitated in methanol. After purification, the polymers were dried to a constant weight.

## 2.3. Measurement and characterization

Elemental analysis was carried out with an Elementar Vario EL instrument. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker ARX400 spectrometer at room temperature, using deuterated chloroform (CDCl<sub>3</sub>) as the solvent and tetramethylsilane (TMS) as the internal standard.

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  $\mu$ -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 (PSt). The TGA was performed on a TA SDT 2960 instrument at a heating rate of 20 °C/min in nitrogen atmosphere.



**Fig. 2.** The second-heating DSC curves of all polymers at a heating rate of 10 °C/min (*P*1, P2 and P3 represented PMBCS; P4, P5 and P6 represented PDMBCS; P7 and P8 represented PTMBCS).



Fig. 3. Representative textures of (a) PMBCS (P3), (b) PDMBCS (P6) and (c) PTMBCS (P8) at 220 °C with PLM.

DSC examination was carried out on a TA DSC Q100 calorimeter with a programmed heating procedure in nitrogen. The temperature and heat flow were calibrated, using standard materials (indium and zinc) at cooling and heating rates 10 °C/min. Samples with a typical mass of 3–10 mg were encapsulated in sealed aluminum pans.

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 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 KR) 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. Fibers were drawn at a stretching rate of about 1 m s<sup>-1</sup> at 200 °C and quenched to room temperature for measurements.

#### 3. Results and discussion

#### 3.1. Synthesis of the monomers

As shown in Scheme 1, all the monomers MBCS, DMBCS and TMBCS were successfully synthesized through multistep reactions. The structures of the monomers have been confirmed by elemental analysis, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. Fig. 1a gave the <sup>1</sup>H NMR spectra of the monomer MBCS.

## 3.2. Synthesis of the polymers

Fig. 1b showed the <sup>1</sup>H NMR spectra of the polymer PMBCS. The characteristic resonance peaks of the vinyl substituent of monomer MBCS were presented at 5.75–5.38 and 7.42–7.36 ppm, respectively. After polymerization, these signals disappeared completely, and the chemical shifts of polymers were quite broad, consistent with the expected polymer structure.

GPC analysis was performed to determine the apparent MW and molecular weight distributions of the polymers. Table 1 summarized the results of the characterization of PMBCSs, PDMBCSs and PTMBCSs. For the three monomers MBCS, DMBCS and TMBCS, we endeavored to synthesize the polymers via the atomic transfer radical polymerization (ATRP), and different ligands and different initiators were used in the ATRP system. However, we found that it was very difficult to obtain the high molecular weight polymers via the ATRP, probably because of the chain transfer reactions with the multi-benzylic protons in the side groups during atomic transfer radical polymerization. In this study, we synthesized a series of the polymers with different MWs



Fig. 4. Sets of WAXD powder patterns in both 2 $\theta$  angle region of 2–30P<sup>oP</sup>. (a) PMBCS (P3), (b) PDMBCS (P6), (c) PTMBCS (P8) all obtained during the heating of the as-cast films.

by radical polymerization and all the polymers had approximately the same MW distributions (Table 1).

# 3.3. Thermal properties and mesomorphic properties

TGA was employed to characterize the thermal stabilities of the polymers. As could be seen from Table 1, all the polymers were quite stable with the temperatures at 5% weight loss above 350 °C in nitrogen atmosphere. The phase transitions of the polymers were studied by DSC. To eliminate the effect of thermal history, we first heated all the samples from 0 to 240 °C at a rate of 10 °C/min. The DSC thermal diagrams were recorded at 10 °C/min during the second-heating process, of which the DSC traces were shown in Fig. 2. From Fig. 2, we could observe that each of the polymers showed only a glass transition, and that the temperatures of glass transition of PTMBCSs were obviously greater than those of PMBCSs were the lowest. The reason may be that the temperatures of glass

transition are influenced by the situation of the alkoxy terminal group and the number of the alkoxy terminal group simultaneously. Moreover, compared with PMPCS, the glass transition temperature of PMBCS was obviously lower than 60 °C. For example, the glass transition temperature of the PMPCS samples reached a plateau of 116 °C when the Mn exceeded approximately  $1.0 \times 10^4$  [48]. It indicated that the glass-transition temperature obviously decreased as the rigidity of side-chain group decreased.

Birefringence of the polymers was observed by PLM with the samples cast from THF solution and slowly dried at room temperature. For the polymer PMBCS (P1), no birefringence could be observed under PLM in the consecutive heating and cooling process, and for the polymers PMBCSs (P2, P3), focal conic fanlike textures appeared in the heating process and the textures still retained before decomposed temperature, while, the textures could be maintained during the cooling process (Fig. 3a). The birefringence of the polymer PDMBCS (P4) did not appear in the consecutive heating and cooling process, and birefringence could be



Fig. 5. (a, b and c) 2D WAXD patterns of the oriented PMBCS (P3), PDMBCS (P6) and PTMBCS (P8) recorded at room temperature, respectively. The X-ray incident beam was perpendicular to the fiber axis.

observed in the polymers PDMBCSs (P5, P6), when the samples were heated to a temperature much higher than Tg (Fig. 3b). For the polymers PTMBCSs (P7, P8), focal conic fanlike textures appeared and the textures retained before decomposed temperature, and the textures remained in consecutive cooling (Fig. 3c).

To elucidate the phase structures and transitions clearly, we performed WAXD experiments under different temperatures. All the samples exhibited similar results, although the testing temperature was different. Herein, we will use the WAXD measurement results of the typical sample PMBCS (P3) as the example to elucidate the evolution. Contrast to common MJLCPs, it was interesting that the PMBCS (P3) obviously exhibited two scattering halos at  $2\theta = 15.5^{\circ}$  (*d* spacing of 5.7 Å) and at  $2\theta = 22.5^{\circ}$ (d spacing of 4.0 Å) during the heating in the high  $2\theta$  region in 1D WAXD patterns (as shown in Fig. 4a). Moreover, with increasing temperatures, the center of the two halos slightly shifts to lower  $2\theta$ angles, then, followed by sudden jump to  $2\theta = 14.9^{\circ}$  (*d* spacing of 5.9 Å) and at  $2\theta = 21.5^{\circ}$  (*d* spacing of 4.1 Å) at 200 °C, respectively. Above 200 °C, the two center positions continuously and slightly shifts to lower  $2\theta$  angles caused by the thermal expansion. At the same time, the scattering halo of the sample in the low  $2\theta$  region of  $3.0-6.5^{\circ}$  was observed when the temperature was below 200 °C. Upon heating, a diffraction peak gradually developed at the right side of the scattering halo, of which the intensity increased and the peak position slightly shifted toward a lower angle. At 200 °C, the diffraction peak positions were at the  $2\theta = 5.12^{\circ}$  with a *d* spacing of 17.3 Å (Fig. 4a). Further heating the samples led to a substantial enhancement of the reflection peak intensity, and the peak position continuously and slightly shifted to lower  $2\theta$  angles. The low-angle

diffraction evolved during the first heating all remained upon cooling. Moreover, the similar results could be observed in the 1D WAXD patterns of PDMBCS (P6, Fig. 4b) and PTMBCS (P8, Fig. 4c). For the three samples (P3, P6 and P8), the changes and positions of the two scattering halos in the high  $2\theta$  region of  $10-30^{\circ}$  were similar. However, the *d* spacing of the polymers in the low  $2\theta$  region slightly increased as the number of the alkoxy terminal group increased, for example, at 200 °C, the *d* spacing of the polymer P3 was 17.3 Å ( $2\theta = 5.12^{\circ}$ ), but for polymer P6 the one was 18.4 Å  $(2\theta = 4.80^\circ)$ , and for the polymer P8 it was 18.5 Å  $(2\theta = 4.77^\circ)$  (as shown in Fig. 4). The difference of the *d*-spacing suggests that the main chain of polymer may take more extended conformation with the number of the alkoxy terminal group increased. On the other hand, all the previous MILCPs only exhibits one scattering halo in the high  $2\theta$  region, however, we can observe two scattering halos at the high  $2\theta$  regions of the polymers in the 1D WAXD patterns. This phenomenon hardly was investigated in MJLCPs. In general, the halo at  $2\theta = 21.5^{\circ}$  (*d* spacing of 4.1 Å) presented the lateral packing of the mesogens [18,32,41,46]. However, for the scattering halo at  $2\theta = 15.5^{\circ}$  (*d* spacing of 5.7 Å), we still do not get a reasonable interpretation about the packing.

To further confirm the structures of the polymers, 2D WAXD experiments needed to carry out. Parts a, b and c of Fig. 5 were the 2D WAXD patterns of the oriented PMBCS (P3), PDMBCS (P6) and PTMBCS (P8) samples at room temperature with the X-ray incident beam perpendicular to the shear direction, respectively. In these three figures, only the higher angle amorphous scattering halos are observed to be more or less concentrated on the meridians with rather broad azimuthal distributions, which shall

be ascribed to the short-range orders existing along the fiber direction. On the other hand, a pair of strong diffraction arcs can be seen on the equators at  $2\theta = 5.12^{\circ}$  (*d*-spacing was 17.3 Å), 4.80° (*d*-spacing was 18.4 Å) and 4.77° (*d*-spacing was 18.5 Å) for PMBCS (P3), PDMBCS (P6) and PTMBCS (P8), respectively, indicating that the order structures have developed along the direction perpendicular to the fiber axis on the nanometer scale. Therefore, the LC phase in PMBCS (P3), PDMBCS (P6) and PTMBCS (P6) and PTMBCS (P8) shall be a  $\Phi_{\rm N}$  phase, respectively [48].

From all these results, we found that the mesophase formation of the polymers all showed remarkable MW dependence (see Table 1). Compared with those MJLCPs, the side chains based on a more rigid and straight mesogen core, the ability of mesophase formation of the polymers with the semirigid side groups were lower. For example, when the MWs of the PMPCS samples were higher than 10,200 ( $DP_{GPC} = 25$ ), the amorphous samples cast from solution developed into an LC phase above the glass-transition temperature upon the first heating [31,48]. However, when we added one methylene unit between the alkoxybenzene unit and the oxycarbonyl styrene unit of PMPCS to break the rigidity of side-chain mesogen, we found the PMBCS samples with MWs higher than  $13.5\times10^4\,(\text{DP}_{GPC}\,{=}\,312)$  could form LC phase. So, we presumed that the ability of mesophase formation of the PMBCSs was obviously lower than the PMPCSs and the ability of mesophase formation of the polymers decreased as the rigidity of side-chain group decreased. As could be seen from Table 1 in combination with the results of PLM, the ability of mesophase formation of the polymers increased as the number of the alkoxy terminal group increased. For example, for PMBCSs, PDMBCSs and PTMBCSs, the samples could show liquid-crystalline behaviors when DP<sub>GPC</sub> exceeded 312, 115 and 51, respectively. It meant that the samples were much easier to form liquid-crystalline state with the number of the methoxy terminal group increased. We presumed that for MJLCPs, because of the spatial requirement of bulky mesogenic units, the main chain had to take an extended and stiffened conformation and the steric hinderance caused by the number of methoxy terminal group increased. So the ability of mesophase formation increased with the steric hinderance increasing due to the increase of the number of the methoxy terminal group. And all the polymers with high molecular weight showed stable columnar nematic phase  $(\Phi_N)$ .

It is of interest to further examine the alkoxy length of alkoxy terminal group effect on the phase structure. We speculate that increasing the length of the alkoxy tails will gradually increase the side-chain mobility. Once the steric hindrance can be overcome, the polymers with long alkoxy tails shall pack into more intriguing structures. The results will be reported in the near future.

#### 4. Conclusion

In summary, we synthesized a series of vinyl monomers with different numbers of alkoxy terminal groups. Upon using conventional radical polymerization, we further obtained their corresponding homopolymers. The chemical structures of the monomers and polymers were confirmed by various characterization techniques. The phase transition behaviors were studied using DSC, and the phase structures and the ability of mesophase formation have been investigated by PLM and WAXD. DSC results revealed that each of the polymers showed only a glass transition and the  $T_g$  of PTMBCSs were obviously greater that those of PMBCSs and PDMBCSs, and those of PDMBCSs were the lowest. Compared with PMPCS, the glass-transition temperatures of the polymers obviously decreased as the rigidity of side-chain group decreased. Moreover, the ability of mesophase formation of the polymers decreased as the rigidity of side-chain group decreased. For

PMBCSs, PDMBCSs and PTMBCSs, the samples could show liquidcrystalline behaviors when  $DP_{GPC}$  exceeded 312, 115 and 51, respectively. It indicated that the ability of mesophase formation of the polymers increased as the number of the alkoxy terminal group increased.

## Acknowledgment

This research was financially supported by the New Century Excellent Talents in University (NCET-05-0707), the Scientific Research Fund of Hunan Provincial Education Department (06A068), the Key Project of Chinese Ministry of Education for Science and Technology (NO.207075) and the National Nature Science Foundation of China (20874082).

#### References

- [1] Ikeda T, Tsutsumi O. Science 1995;268:1873-5.
- [2] Natansohn A, Rochon P. Chem Rev 2002;102:4139-76.
- [3] Yoneyama S, Yamamoto T, Tsutsumi O, Kanazawa A, Shiono T, Ikeda T. Macromolecules 2002;35:8751–8.
  - [4] Tamai N, Miyasaka H. Chem Rev 2000;100:1875-90.
  - [5] Yu Y, Nakano M, Ikeda T. Nature 2003;425:145.
  - [6] Yu HF, Iyoda T, Ikeda T. J Am Chem Soc 2006;128:11010-1.
  - [7] Bubulac TV, Hamciuc C. Polymer 2009;50:2220-7.
  - [8] Bhowmik PK, Han H, Nedeltchev AK, Mandal HD, Jimenez-Hernandez JA, McGannon PM. Polymer 2009;50:3128–35.
     [9] Rodríguez-Hidalgo MDR, Soto-Figueroa CS, Martínez-Magadán JM, Luís-
  - Vicente. Polymer 2009;50:4596–601.
- [10] Kawatsuki N, Koezuka Y. Polymer 2009;50:2349-56.
- [11] Zhou QF, Li HM, Feng XD. Synthesis of a new class of side chain liquid crystal polymers. In: International conference on liquid crystak polymers. Bordeaux, France: 1987. p. 401.
- [12] Finkelmann H, Wendorff HJ. Structure of nematic side chain polymers. In: Blumstein A, editor. Polymeric liquid Crystals. New York: Plenum Press; 1985. p. 295.
- [13] Hessel F, Finkelmann H. Polym Bull 1985;14:375-8.
- [14] Zhou QF, Li HM, Feng XD. Macromolecules 1987;20:233-4.
- [15] Zhou QF, Zhu XL, Wen ZQ. Macromolecules 1989;22:491-3.
- [16] Pragliola S, Ober CK, Mather PT, Leon HG. Macromol Chem Phys 1999;200: 2338-44.
- [17] Zhang D, Zhou QF, Ma YG, Wan XH, Feng XD. Polym Adv Technol 1997;8: 227-33.
- [18] Zhang D, Liu YX, Wan XH, Zhou QF. Macromolecules 1999;32:5183-5.
- [19] Yu ZN, Wan XH, Zhang HL, Chen XF, Zhou QF. Chem Commun 2003:974-5.
- [20] Chen XF, Tenneti KK, Li CY, Bai YW, Zhou R, Wan XH, et al. Macromolecules 2006;39:517–27.
- [21] Hessel F, Herr RP, Finkelmann H. Makromol Chem 1987;188:1597-661.
- [22] Percec V, Tomazos DJ. Matter Chem 1993;3:643-50.
- [23] Pugh C, Schrock RR. Macromolecules 1992;25:6593-604.
- [24] Pugh C, Liu Y, Arehart SV, Narayannan R. Macromol Symp 1995;98:293-310.
- [25] Keller P, Hardouin R, Mauzac M, Achard M. Mol Cryst Liq Cryst 1988;155: 171-8.
- [26] Gray GW, Hill JS, Lacey D. Mol Cryst Liq Cryst 1991;197:43-55.
- [27] Zhou QF, Wan XH, Zhu XL, Zhang F, Feng XD. Mol Cryst Liq Cryst 1993;231: 107–17.
- [28] Zhou QF, Wan XH, Zhu XL, Zhang D, Feng XD. In: Isayev AI, Kyu T, Cheng SZD, editors. Liquid crystalline polymer Systems-Technological Advances. ACS Symposium Book series 632. Washington, DC: American Chemical Society; 1996. p. 344–57.
- [29] Tu YF, Wan XH, Zhang D, Zhou QF, Wu C. J Am Chem Soc 2000;122:10201-5.
- [30] Tu YF, Wan XH, Zhang HL, Fan XH, Chen XF, Zhou QF, et al. Macromolecules 2003;36:6565–9.
- [31] Zhang H, Yu Z, Wan X, Zhou QF, Woo EM. Polymer 2002;43:2357-3261.
- [32] Guan Y, Chen XF, Shen ZH, Wan XH, Zhou QF. Polymer 2009;50:936-44.
- [33] Wang P, Chuai YT, Chai CP, Wang FZ, Zhang GL, Ge GP, et al. Polymer 2008;49:455–60.
- [34] Zhang HL, Sun XY, Wang XY, Zhou QF. Macromol Rapid Commun 2005;26:407–11.
- [35] Wang XZ, Zhang HL, Shi M, Wang XY, Zhou QF. J Polym Sci Part A Polym Chem 2005;43:733–41.
- [36] Xie HL, Hu TH, Zhang HL, Chen EQ, Zhou QF. J Polym Sci Part A Polym Chem 2008;46:7310-20.
- [37] Yu ZN, Tu HL, Wan XH, Chen XF, Zhou QF. J Polym Sci Part A Polym Chem 2003;41:1454–64.
- [38] Fan XH, Dong HC, Chen XF, Wan XH, Zhou QF. Acta Polym Sin 2004;4:620–4.
   [39] Tu HL, Zhang D, Wan XH, Chen XF, Liu YX, Zhang H, et al. Macromol Rapid Commun 1999:20:549–51.
- [40] Wan XH, Tu HL, Liu YX, Zhang D, Chen XF, Zhang H, et al. Chin J Polym Sci 2003;21:21–7.

- [41] Tu HL, Wan XH, Liu YX, Chen XF, Zhang D, Zhou QF, et al. Macromolecules 2000;33:6315-20.
- [42] Yin XY, Chen EQ, Wan XH, Zhou QF. Chin J Polym Sci 2003;21:9–14. [43] Yin XY, Ye C, Ma X, Chen EQ, Qi XY, Duan XF, et al. J Am Chem Soc 2003;125:6854–5.
- [44] Li CY, Tenneti KK, Zhang D, Zhang H, Wan X, Chen EQ, et al. Macromolecules 2004;37:2854-60.
- [45] Chai CP, Zhu XQ, Wang P, Ren MQ, Chen XF, Xu YD, et al. Macromolecules 2007;40:9361-70.
- [46] Chen S, Gao LC, Zhao XD, Chen XF, Fan XH, Xie PY, et al. Macromolecules 2007;40:5718-25.
- [47] Liu YX, Zhang D, Wan XH, Zhou QF. Chin J Polym Sci 1998;16:283–8.
  [48] Ye C, Zhang H, Huang Y, Chen EQ, Lu YL, Shen DY, et al. Macromolecules 2004;37:7188–96.