Side-Chain Liquid-Crystalline Polymers Based on Flexible Rod-Like Mesogen Directly Attached to Backbone

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Received 30 May 2012; accepted 7 August 2012; published online DOI: 10.1002/pola.26337

ABSTRACT: In this article, we report the synthesis and characterization of a new end-on side-chain liquid crystalline polymer (SCLCP), poly[4-(4'-alkoxyphenyloxymethylene)styrene] [denoted as Poly(*n*-POMS), where *n* is the carbon number of the alkyl tail, n = 2, 4, 6, 8, 12, 16], with the flexible rod-like mesogenic side-chain directly attached to the polymer backbone without flexible spacer. The polymer was obtained by using free radical polymerization. The chemical structures of Poly(*n*-POMS) and the corresponding monomer were characterized using various techniques with satisfactory analysis data. A combination analysis of differential scanning calorimetry, polarized light microscopy, small angle X-ray scattering, and wide-angle X-ray diffraction has been conducted to

INTRODUCTION Liquid crystalline polymers (LCPs) have been studied for several decades in both industrial and academic research because they combine the functionality of conventional liquid crystals (LCs) with the advantages of polymer systems. Several molecular design-related concepts have been proposed when constructing various LCPs for different functional properties. In general, mesogens, polymer backbones, and their linkage strategy are mostly considered as the three structural factors of LCP molecular engineering. When designing a side-chain LCP,¹ rod-like, disk-like, or other shaped mesogens were frequently introduced into the side-chain with different attachment method. Typically, for rod-like mesogenic side-chain, end-on or side-on type sidechain LCPs (SCLCPs) could be achieved. It should be noted that the thermodynamic behaviors of mesogenic side-chain and polymer backbone are quite different. The chain backbone tends to be disordered and coil-like driven by maximization of conformational entropy, whereas the mesogenic side-chains tend to self-assembly into ordered structures

investigate the phase behavior of Poly(*n*-POMS). Poly(2-POMS), Poly(4-POMS), and Poly(6-POMS) are amorphous. Poly(8-POMS) develops partially into the liquid crystal phase, and Poly(12-POMS) and Poly(16-POMS) self-assembly into the smectic A (SmA) phase. Upon increasing temperature, the phase transition of Poly(16-POMS) follows the sequence of SmA1 \leftrightarrow SmA2 \leftrightarrow isotropic (I), which may be attributed to the conformation isomerization of the flexible rod-like mesogens. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: liquid crystalline polymers (LCP); phase behavior; radical polymerization; s(LCP)

driven by maximization of their enthalpic interaction. Therefore, in case of mesogenic side-chain directly attached to the polymer backbone, the coil conformation of polymer backbone may disturb the mesogenic side-chain to form ordered LC phases to some extent. Thus, flexible spacers are purposefully introduced to decouple the dynamics of the polymeric backbone and the mesogenic side-chain to maintain the liquid crystallinity of side-chains.^{2,3} This "decoupling concept" suggested by Ringsdorf and Finkelmann has become an useful guideline for the molecular design of SCLCPs. Accordingly, nematic or semctic LC phases can be readily obtained from end-on SCLCPs. Percec and coworkers first introduced the concept of microphase separation between the backbone and side groups into end-on SCLCP systems by using immiscible polymer backbone and side groups.⁴⁻⁶ Consequently, highly or even completely decoupled end-on SCLCP can be realized. On the other side, it has been found that, in side-on type SCLCPs, attaching the mesogenic side-chains to the polymer backbone with short or no spacers can induce a

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Poly(n-POMS), n=2,4,6,8,12,16

SCHEME 1 Chemical structure and conformational isomerism of Poly(*n*-POMS).

strong "jacketing effect" of side-chains to the backbone especially, resulting in the SCLCP called mesogen-jacketed LCP (MJLCP) vividly.⁷⁻⁹ In this case, the mesogen jacket covered around the polymer backbone forces the flexible backbone stretching to a great extent. So each jacketed polymer could be considered as a rod-like polymer chain, which can pack parallel to others forming supramolecular columnar LC structure.¹⁰ When increasing the rigidity of the mesogen or the length of rod-like mesogens of MJLCP, those sidechains could overwhelm the disturbance from the polymer backbone and self-organize into smectic layer-like mesophase.^{11,12}

From the previous SCLCP research work, we can be aware of that the mechanism of LC formation in polymeric system is really not as direct as we thought, especially considering that the side-chain and polymer backbone have complex and subtle interaction between each other. Nonetheless, if we could take advantage of the interaction between them, we may realize novel self-assembled LC structure through rational molecular design. In this article, we design and synthesize a series of end-on SCLCP containing rod-like benzyl ether mesogens directly attached to polyethylene backbone without any flexible spacer [see Scheme 1, denoted as Poly(n-POMS), where n is the carbon number of the alkyl tail]. Because of the free rotation around the ether bonds, the mesogenic side-chain incorporated in Poly(n-POMS) presents conformational isomerism (Scheme 1). On the basis of the difference between the rotational energy barrier of different configurational isomers or conformers of calamitic mesogens, rod-like mesogens could be classified into three categories: rigid shape, semi-rigid, or flexible rod-like mesogens.¹³⁻¹⁶ Percec and coworkers have introduced the flexible mesogen into SCLCPs,^{13,14,16,17} main-chain LCPs,^{15,18-26} as well as polymers containing mesogens with more complex topology based on conformational isomerism²⁷ and systematically studied their phase behaviors.²⁸⁻³⁴ When compared with other rigid calamitic mesogens, the flexible rod-like mesogen can adjust its conformation. For Poly(*n*-POMS), because the benzyl ether mesogen is attached directly to

the polyethylene backbone, it will give us a good opportunity to investigate how the conformation isomerism of flexible mesogenic side-chain interplays with polymer backbone thermodynamically.

Although this kind of directly linkage sounds not good to LC formation, we first intend to observe if the flexibility owned by the mesogen itself can facilitate the formation of LC phases. We presume that the mesogens with the majority of trans conformation at low temperatures may favor smectic structures. Moreover, considering that the gauche conformation of mesogen may bring the 4'-alkoxyphenyl group much closer to the backbone, we are also interested in if the chain backbone can feel strong "jacketing effect" when more and more side-chains adopt gauche conformation with increasing temperature. If it is the case, Poly(n-POMS) may form supramolecular columnar phase, and thus, the sample will display a phase transition of smectic-to-columnar. We investigated the phase behavior of Poly(n-POMS) using differential scanning calorimetry (DSC), polarized light microscopy (PLM), and wide-angle X-ray diffraction (WAXD). It is found that Poly(n-POMS) with reasonably long alkyl tails can render stable smectic A (SmA) phase at low temperatures, showing the tail length influence on the formation of LC phases. Although the smectic-to-columnar transition which we desired was not realized, we observed that Poly(16-POMS)



SCHEME 2 Synthetic route of monomers (*n*-POMS) and corresponding polymers (Poly(*n*-POMS)).

TABLE 1 Molecular Weight Characterization of Poly(*n*-POMS)^a

Poly(<i>n</i> -POMS)	n					
	2	4	6	8	12	16
$M_{ m w} imes 10^{-5b}$	1.87	1.69	1.74	1.25	1.40	1.46
$M_{ m n} imes 10^{-4 m c}$	7.80	6.61	7.02	5.42	7.05	6.48
$M_{\rm w}/M_{\rm n}$	2.40	2.56	2.47	2.30	1.99	2.26

 $^{\rm a}$ Molecular weights and polydispersity were measured by GPC, using tetrahydrofuran as an eluent at 35 $^{\circ}$ C, polystyrene as the standard.

^b $M_{\rm w}$, weight average molecular weight.

^c M_n, number average molecular weight.

exhibits a transition of SmA1 \leftrightarrow SmA2, which should be largely related to the conformational isomerism of the flexible rod-like mesogens.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Polymers

Monomers *n*-POMS were prepared as shown in Scheme 2 using two subsequent etherification reactions. Monoalkoxy substituted 4-alkoxyphenols were first produced by etherification of bromoalkane and hydroquinone. The second etherification step of the obtained 4-alkoxyphenol with a 10% excess amount of vinylbenzyl chloride in the presence of a catalytic amount of tetrabutylammonium bromide (TBAB) afforded monomers *n*-POMS in 80–90% yield. The unreacted vinylbenzyl chloride is easy to remove by recrystallization from corresponding solvents. The structures of the monomers and precursors were confirmed by ¹H NMR, ¹³C NMR, and elemental analysis. All the monomers exhibited as white crystals at ambient temperature and could melt into isotropic state around 60–70 °C, which were detected under

PLM. No further phase structural studies of those monomers were performed due to their easily thermal polymerization.

Poly(*n*-POMS) was obtained by conventional free radical polymerization. Number average molecular weights (M_n) of these polymers ranged from 5.4 × 10⁴ to 7.8 × 10⁴ g/mol, with the polydispersity of 2.0–2.4 were measured by gel permeation chromatography (GPC) using polystyrene (PS) standards (Table 1). The ¹H NMR spectrum of 12-POMS and corresponding polymer Poly(12-POMS) are shown in Figure 1. In Figure 1(a), representative resonances of the vinyl group of 12-POMS at 5.24–5.28 and 5.74–6.77 ppm can be seen clearly. After polymerization, these signals completely disappear [see Fig. 1(b)]. The resonance peaks of the spectrum of polymer were broad due to the slower motion of the protons. All other monomers and polymers were characterized similarly, and the results were in accordance with the desired structures.

Phase Transitions and Phase Structures of Polymers

Phase transitions of Poly(*n*-POMS) were first examined by DSC. Figure 2(a) shows the DSC traces of the six samples recorded during the second heating at a rate of 10 °C/min. For n = 2, 4, and 6, typical glass transitions are observed in the temperature range from 30 to 60 °C, of which the glass transition temperature (T_g) decreases with increasing *n*. Poly(*n*-POMS) can also be viewed as a derivate of PS. When compared with that of PS, the lower T_g 's of Poly(*n*-POMS) implies that the directly attached flexible mesogen enhance the chain mobility, and moreover, increasing the length of alkyl tail depresses more the T_g of Poly(*n*-POMS). Poly (8-POMS) exhibits a broad and weak endotherm peaked at ~50 °C right after the glass transition. This implies that liquid crystallinity of the sample may be partially developed. The DSC curve of Poly(12-POMS) displays an endothermic



FIGURE 1 ¹H NMR spectra of 12-POMS (a) and Poly(12-POMS) (b).



FIGURE 2 Differential scanning calorimetry thermograms of Poly(n-POMS) at a rate of 10 °C/min (a) and Poly(16-POMS) at different heating and cooling rate (b).

transition peaked at 75 °C. For Poly(16-POMS), a relatively broad and strong endotherm appears in the temperature range of \sim 20 to 50 °C. Afterward, two highly overlapped endothermic transitions between 65 and 80 °C can be observed. The DSC results demonstrate clearly that some ordered structure of Poly(12-POMS) and Poly(16-POMS) are melted during heating. The transition is in fact enantiotropic, which could be also detected upon cooling from the isotropic state. It is interesting to note that Poly(16-POMS) with the longest alkyl tails we investigated possesses multiple transitions and the glass transition could not be observed directly. The broad melting endothermic peak and the plot shifting upward slightly indicate the possibility of a combination of $T_{\rm g}$ and melting endotherm. Figure 2(b) presents a set of cooling and subsequent heating DSC curves of Poly (16-POMS), showing that the transitions exhibit almost no

heating and cooling rate dependence. This can be taken as an indicative of LC transitions.

We used PLM to study the LC behavior of Poly(*n*-POMS). The results confirmed that the samples with n = 2, 4, and 6 were amorphous. Although a sort of LC structure of Poly(8-POMS) might be partially developed as suggested by the DSC result [see Fig. 2(a)], no clear birefringence of the sample could be observed. Figure 3(a,b) depicts the PLM pictures of Poly(12-POMS) and Poly(16-POMS), respectively, which were taken after the samples were cooled slowly from their isotropic state at a rate of 1 °C/min. Thread-like texture [Fig. 3(a)] of Poly(12-POMS) and sanded-like texture [Fig. 3(b)] of Poly(16-POMS) indicate the existence of LC structures.

The phase structures of the polymers were further characterized by X-ray diffraction experiments. Sets of one-dimensional (1D) WAXD profiles recorded at room temperature of



FIGURE 3 Polarized light microscope pictures of Poly (12-POMS) at 72 °C (a) and Poly(16-POMS) at 79 °C (b).



FIGURE 4 1D-WAXD profiles of Poly(n-POMS).

Poly(n-POMS) after heating and subsequent cooling processes are presented in Figure 4. Poly(2-POMS) and Poly (4-POMS) at room temperature display a broad halo both in the low angle region and high angle region, representing the amorphous state. For Poly(6-POMS), we notice that the lowangle scattering halo possesses a smaller full-width of half maximum (FWHM) compared with that of the samples with smaller n. This may suggest that some ordered molecular packing tends to develop in Poly(6-POMS). However, the sample should be still most likely amorphous. The WAXD pattern of Poly(8-POMS) displays a rather strong diffraction peak at q of 1.65 nm⁻¹ ($q = 4\pi \sin\theta/\lambda$, where λ is the X-ray wavelength and 2θ the scattering angle) in the low angle region. Careful examination can reveal a weak and small bump at $q = 3.24 \text{ nm}^{-1}$, which can be assigned as the second-order diffraction. In this case, although clear LC texture of the sample was absence under PLM, Poly(8-POMS) may form a smectic structure. Here, we observe the tendency to develop LC phase with increasing the tail length. We consider that when the alkyl tails are short the motion of the polyethylene backbone dominates the dynamics of whole molecule and hence prevents the formation of LC phase of flexible mesogens. Increasing the alkyl tail length may enhance the degree of microphase separation between the backbones and side-chains. Consequently, the smectic phase can be achieved in Poly(*n*-POMS) with large *n*.

The WAXD pattern of Poly(12-POMS) shows clearly two diffraction peaks in the low angle region with q-ratio of 1:2, indicating a smectic structure. The d-spacing of 4.6 nm corresponding to the first-order diffraction is comparable with twice the length of the side chain estimated under the assumption that the alkyl tail adopts an all-trans conformation which is 2.4 nm. For Poly(16-POMS), we observe a very strong low-angle diffraction with a d-spacing of 5.28 nm, which is less than twice the calculated side-chain length of 3.0 nm. In addition, a bump peaked at $q = 15.4 \text{ nm}^{-1}$ is superimposed on the high-angle amorphous halo, which should arise from the partial crystallization of the long alkyl tails. It should be reasonable to assume that Poly(16-POMS) also possesses a smectic phase at low temperatures.

Two-dimensional (2D) WAXD experiments were carried out to study the polymer mesophase structure as well, to get more information of the phase structure. Specimens were obtained by mechanical shearing the sample at temperatures slightly lower than that of the isotropic transition. The oriented films were annealed at the shear temperature for several hours and then quenched to room temperature. Figure 5(a,b) shows the 2D-WAXD pattern of the sheared films of Poly(12-POMS) and Poly(16-POMS) obtained at room temperature with the X-ray incident beam perpendicular to the shear direction, respectively. For both of the polymers, the 2D-WAXD results elucidate the existence of SmA structure. With the shear direction along the meridian, the low-angle diffractions with the *q*-ratio of 1:2:3 appear on the equator, indicating that the smectic layer normal is perpendicular to the shear direction. On the other hand, the high-angle scattering halo is more or less concentrated on the meridian. Therefore, the side-chains should be largely parallel to the layer normal. We found that mechanical shear could greatly enhance the smectic ordering of Poly(16-POMS). As shown in Figure 5(b), the layer diffractions up to the third order can be seen. When compared with that of Poly(12-POMS), the high-angle scattering of Poly(16-POMS) is stronger. A pair of diffraction arc with d-spacing of 0.41 nm can be found on the meridian [pointed by the arrow in Fig. 5(b)], which should be associated with the partially crystallization of the long alkyl tails. Considering that the layer spacing is nearly twice the side-chain length, the SmA phase of Poly(12-POMS) and Poly(16-POMS) should be a bilayer structure with slight interdigital.



FIGURE 5 2D-WAXD patterns collected from the sheared sample of Poly(12-POMS) (a) and Poly(16-POMS) (b) at RT and (c) is the shear geometry of polymer film.





FIGURE 6 Set of 1D-WAXD powder patterns in the low 2θ angle region (a) and in the high 2θ angle region (b) of Poly(16-POMS) obtained during the first heating of the as-cast film.

Mesophase Phase Behavior of Poly(16-POMS)

As shown in Figure 2(a), the DSC result reveals that the phase transition of Poly(16-POMS) is more complicated than other samples. We performed thermal 1D-WAXD experiments to follow the phase transition process during heating, of which the result is shown in Figure 6. After the sample was slowly cooled from isotropic state to room temperature followed by prolonged annealing, we can see clearly a diffraction peaked at 2θ of 21.5° [see Fig. 6(b), 30 °C], which can be taken as an indicative of the crystalline parking of the long alkyl tails. Upon heating to 60 °C, this diffraction completely disappears, and only a typical amorphous halo can be observed in the high-angle region. Combining the DSC and 1D-WAXD results, we can conclude that the low temperature endotherm is associated with the melting of the alkyl tails. However, this transition does not affect the smectic structure too much. As shown in Figure 6(a), the low-angle diffraction looks largely unchanged. In Figure 7, we plot the *d*-spacing and FWHM of the low-angle diffraction as functions of temperature measured upon heating. With heating from 35 to 60 °C, accompanying with the continuous melting of tails, the *d*-spacing increases from 5.1 to 5.3 nm, which should be

mainly due to the thermal expansion of the smectic layers. The value of FWHH of the low-angle diffraction decreases during the melting of tails. This may be due to that the increased tail mobility promotes a better smectic packing.

For Poly(16-POMS), of particular interesting is that the two transitions occur in the high temperature range, which are largely overlapped with each other. Figure 6(a) shows that the low-angle diffraction is remained until the temperature becomes higher than 80 °C. Afterward, the diffraction peak becomes diffused, indicating that the sample enters into isotropic state (I). In the case, we presume that before the isotropization the sample keeps the smectic structure. As shown in Figure 7, after entering the temperature range of the middle transition, the FWHM shows a maximum at ${\sim}75$ °C, which is the peak temperature of corresponding endotherm of Poly(16-POMS) (see Fig. 2). On the other hand, the d-spacing of the low-angle diffraction decreases monotonically from 5.3 nm at 65 °C to 4.2 nm at 80 °C. It sounds easily to assign that the middle transition leads the SmA to SmC. However, if it is the case, the phase transition sequence of SmA-SmC-I would be contrary to the normal one of most LCs which shall be SmC-SmA-I. We suggest that



FIGURE 7 *d*-Spacing and FWHM data of the low angle peak as functions of temperature measured during heating of Poly(16-POMS).

Poly(16-POMS) remains the feature of SmA during heating until the isotropization, and the transition sequence is SmA1-SmA2-I. Considering the flexible nature of the rod-like mesogen incorporated in this polymer, we propose that the middle transition is associated with the fact that more and more gauche conformers of mesogenic groups prefer to exist with increasing temperature. The bended gauche conformation certainly brings the side-chain tails to be more closed to the chain backbone, resulting in the decrease of the smectic layer spacing. It is worth to mention here that Poly(12-POMS) only exhibits the transition of SmA-I, which takes place in the same temperature range of the middle transition of Poly(16-POMS). Seemingly, the long alkyl tail of Poly(16-POMS) can retard the trans-to-gauche conformational isomerism to some degrees, and thus let the sample to form the additional SmA2 with smaller layer spacing. Following the picture of "microphase separation" of SCLCP, we consider that the nano-segregation between the mesogen core and the alkyl tail can help to stabilize the layer-like self-assemble structure.

EXPERIMENTAL

Materials

Vinylbenzyl chloride (Aldrich) and hydroquinone (Beijing Chemical Reagent Company) were used as received. Ethyl bromide, bromobutane (98%), bromohexane (98%), bromooctane (98%), bromododecane (98%), and bromohexadecane (98%) were all purchased from Alfa Aesar and used as received. Benzoyl peroxide (BPO) was recrystallized from chloroform and methanol. Chlorobenzene was washed with concentrated H_2SO_4 , then with aqueous NaHCO₃ and H_2O , drying first with CaCl₂ and then distilling from CaH₂ under N₂ atmosphere. All other solvents and reagents were obtained commercially and used without further purification.

Instruments and Measurements

Elemental analysis was performed with an Elementar Vario EL instrument. 1 H NMR (400 MHz) spectra were recorded



on a Bruker ARX400 spectrometer using deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the internal standard. GPC was carried out on a Waters 515 pump combined with Waters 2410 refractive-index detector at 35 °C, and THF was used as the eluent at a flow rate of 1.0 mL/min. Three Water Styragel columns with 10 μ m bead size were connected in series. All GPC data were calibrated with PS standards.

DSC (Perkin-Elmer Pyris I) was used to examine the thermal behaviors of polymers. The temperature and heat flow were calibrated with benzoic acid and indium. The samples were encapsulated in hermetically sealed aluminum pans, with a typical sample weight of \sim 3.5 mg.

LC textures of the polymers was examined under PLM (Leica DMLP) coupled with a Mettler-Toledo hot stage (FP82HT). The thickness of film samples was kept several micrometers.

To identify the LC structures of the polymers, WAXD experiments were performed with several X-ray instruments. 1D-WAXD experiments were carried out with a high-flux SAXS instrument (SAXSess, Anton Paar) and a PANalytical X'Pert Pro diffractometer. For SAXSess, the diffraction pattern was recorded on an imaging-plate, which covers the *q* range from 0.06 to 29 nm^{-1} . The X'Pert Pro is equipped with an X'celerator detector and a temperature control unit (Anton Paar TTK450). 2D-WAXD experiments were carried out using a Bruker D8 Discover diffractometer in a transmission mode using a GADDS detector. The macroscopically oriented samples prepared by mechanical shear were mounted on the sample stage with the point-focused X-ray incident beam perpendicular the shear direction. For all the X-ray instruments we used, the X-ray sources (Cu K α) were provided by 3 kW ceramic tubes. The diffraction peak positions were calibrated with silicon powder ($2\theta > 15^{\circ}$) and silver behenate $(2\theta < 10^\circ)$. The background scattering was recorded and subtracted from the sample patterns.

Synthesis of Monomers

The monomers *n*-POMS were synthesized by etherification of hydroquinone with 1-bromoalkane followed by etherification with vinylbenzyl chloride in the presence of K_2CO_3 and a catalytic amount of TBAB (Scheme 1). 4-Alkoxyphenol was synthesized according to the ref. ³⁵. The monomers were synthesized as in the following example of 4-(4'-dodecoxy-phenyloxymethylene)styrene (12-POMS).

Synthesis of 12-POMS

Into a single-necked 100 mL round-bottom flask equipped with a condenser, 1.39 g (5 mmol) of 4-dodecoxyphenol, 0.88 g (5.75 mmol) of vinylbenzyl chloride, 0.69 g (5 mmol) of K_2CO_3 , a catalytic amount of TBAB, and 40 mL of acetone were added. The reaction mixture was refluxed until 4-dodecoxyphenol was completely exhausted by TCL analysis under an atmosphere of nitrogen. After the mixture was cooled to room temperature, acetone was removed by a rotary evaporator. The residue was dissolved in dichloromethane (200 mL) and washed three times in total with 150 mL of aqueous NaCl solution. The organic phase was dried over MgSO₄ and

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filtered, and the solvent was removed by rotary evaporator to yield the crude product. Recrystallization from absolute ethanol gave 1.82 g of 12-POMS as white crystals (yield: 92%).

2-POMS

White solid; yield 88%. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ (ppm) = 7.46–7.30 (m, 4H, CH₂=CHAr*H*), 6.91–6.86 (m, 2H, 2-*H*, 3-*H*), 6.84–6.79 (m, 2H, 1-*H*, 4-*H*), 6.76–6.68 (m, 1H, CH₂=CHAr), 5.78–5.72 (m, 1H, CH*H*=CHAr), 5.27–5.23 (m, 1H, C*H*H=CHAr), 5.00–4.99 (d, 2H, OC*H*₂Ar), 4.00–3.94 (m, 2H, OC*H*₂CH₂), 1.39–1.36 (t, 3H, CH₃). Anal. Calcd. for C₁₇H₁₈O₂: C, 80.28; H, 7.04; Found: C, 80.27; H, 7.04.

4-POMS

White solid; yield 80%. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ (ppm) = 7.46–7.30 (m, 4H, CH₂=CHArH), 6.91–6.87 (m, 2H, 2-H, 3-H), 6.85–6.80 (m, 2H, 1-H, 4-H), 6.76–6.68 (m, 1H, CH₂=CHAr), 5.79–5.72 (m, 1H, CHH=CHAr), 5.27–5.23 (m, 1H, CHH=CHAr), 5.00 (s, 2H, OCH₂Ar), 3.92–3.89 (m, 2H, OCH₂CH₂), 1.77–1.70 (m, 2H, OCH₂CH₂), 1.53–1.43 (m, 2H, O(CH₂)₂CH₂), 0.98–0.95 (t, 3H, CH₃). Anal. Calcd. for C₁₉H₂₂O₂: C, 80.82; H, 7.85; Found: C, 80.43; H, 7.73.

6-POMS

White solid; yield 79%. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ (ppm) = 7.46–7.29 (m, 4H, CH₂=CHArH), 6.92–6.86 (m, 2H, 2-H, 3-H), 6.84–6.79 (m, 2H, 1-H, 4-H), 6.76–6.68 (m, 1H, CH₂=CHAr), 5.79–5.72 (m, 1H, CHH=CHAr), 5.27–5.23 (m, 1H, CHH=CHAr), 5.00 (s, 2H, OCH₂Ar), 3.92–3.88 (m, 2H, OCH₂CH₂), 1.78–1.71 (m, 2H, OCH₂CH₂), 1.50–1.39 (m, 2H, O(CH₂)₂CH₂), 1.38–1.25 (m, 4H, O(CH₂)₃(CH₂)₂), 0.92–0.88 (t, 3H, CH₃). Anal. Calcd. for C₂₁H₂₆O₂: C, 81.25; H, 8.44; Found: C, 81.04; H, 8.34.

8-POMS

White solid; yield 80%. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ (ppm) = 7.46–7.30 (m, 4H, CH₂=CHArH), 6.92–6.86 (m, 2H, 2-H, 3-H), 6.84–6.80 (m, 2H, 1-H, 4-H), 6.76–6.68 (m, 1H, CH₂=CHAr), 5.79–5.72 (m, 1H, CHH=CHAr), 5.27–5.23 (m, 1H, CHH=CHAr), 5.00 (s, 2H, OCH₂Ar), 3.92–3.88 (m, 2H, OCH₂CH₂), 1.78–1.71 (m, 2H, OCH₂CH₂), 1.49–1.40 (m, 2H, O(CH₂)₂CH₂), 1.39–1.20 (m, 8H, O(CH₂)₃(CH₂)₄), 0.90–0.87 (t, 3H, CH₃). Anal. Calcd. for C₂₃H₃₀O₂: C, 81.61; H, 8.93; Found: C, 81.19; H, 8.81.

12-POMS

White solid; yield 92%. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ (ppm) = 7.47–7.32 (m, 4H, CH₂=CHArH), 6.93–6.87 (m, 2H, 2-H, 3-H), 6.85–6.80 (m, 2H, 1-H, 4-H), 6.77–6.69 (m, 1H, CH₂=CHAr), 5.79–5.74 (m, 1H, CHH=CHAr), 5.28–5.24 (m, 1H, CHH=CHAr), 5.00 (s, 2H, OCH₂Ar), 3.92–3.88 (t, 2H, OCH₂CH₂), 1.79–1.72 (m, 2H, OCH₂CH₂), 1.49–1.40 (m, 2H, O(CH₂)₂CH₂), 1.39–1.20 (m, 16H, O(CH₂)₃(CH₂)₈), 0.90–0.87 (t, 3H, CH₃). Anal. Calcd. for C₂₇H₃₈O₂: C, 82.18; H, 9.71; Found: C, 82.16; H, 9.73.

16-POMS

White solid; yield 95%. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ (ppm) = 7.49–7.33 (m, 4H, CH₂=CHAr*H*), 6.95–6.90 (m, 2H, 2-*H*, 3-*H*), 6.87–6.80 (m, 2H, 1-*H*, 4-*H*), 6.79–6.72 (m, 1H, CH₂=CHAr), 5.82–5.76 (m, 1H, CH*H*=CHAr), 5.34–5.27

(m, 1H, CHH=CHAr), 5.03 (s, 2H, OCH_2Ar), 3.94–3.91 (t, 2H, OCH_2CH_2), 1.81–1.75 (m, 2H, OCH_2CH_2), 1.49–1.40 (m, 2H, $O(CH_2)_2CH_2$), 1.41–1.20 (m, 24H, $O(CH_2)_3(CH_2)_{12}$), 0.92–0.90 (t, 3H, CH₃). Anal. Calcd. for $C_{31}H_{46}O_2$: C, 82.61; H, 10.29; Found: C, 82.73; H, 10.17.

Polymer Synthesis

All polymers [Poly(*n*-POMS) in Scheme 1] were obtained by conventional solution free radical polymerization with the ratio of monomer to initiator being 200. A typical experimental procedure for the polymerization of 12-POMS is given below. A total of 200 mg (0.506 mmol) of 12-POMS, 80 μ L of chlorobenzene solution of 5 mg/mL BPO, 0.8 mL of chlorobenzene, and a magnetic stir bar were added into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed off under vacuum. Polymerization was carried out at 90 °C for 12 h. The tube was then opened, and the reaction mixture was diluted with 5 mL of THF. Then, the solution was dropped slowly into 80 mL of the mixture of methanol/THF (3/1). The dissolution and precipitation were repeated three times. After drying under vacuum, 0.1 g of polymer was obtained. Yield: 50%.

CONCLUSIONS

In summary, we synthesized a series of SCLCP, Poly(n-POMS) with the flexible rod-like benzyl ether mesogens attached directly onto the polyethylene backbone. We find that the liquid crystallinity of Poly(*n*-POMS) is dependent on the length of alkyl tail. With short alkyl tails, that is, n = 2, 4, and 6, the polymers are amorphous. For $n \ge 8$, the sample without flexible spacer between the mesogen and the backbone can form smectic phases at low temperatures, which is partially attributed to the flexible rod-like mesogens can adjust properly their conformation to fit in the mesophase. Our 2D-WAXD experiments reveal the SmA packing of Poly(12-POMS) and Poly(16-POMS). We also observe that Poly(16-POMS) possesses a rich phase transition behavior. At sufficiently low temperatures, the alkyl tails can partially crystallize inside the smectic structure. Upon heating, the smectic structure remains until the isotropization. We suggest that Poly(16-POMS) can possess two SmA phases, and the trans-to-gauche conformational isomerism of the side-chain results in the second SmA with smaller layer spacing. As mentioned in "Introduction" section, we intend to see if the conformational isomerism of flexible rod-like mesogen can lead to smectic-tocolumnar phase transition. This idea is not realized in this study. However, as Poly(16-POMS) provides some insights that the long alkyl tail contributes to stabilize additional LC phase, we may propose that further increasing the tail length or the number of tails may lead to a stable columnar phase of such a kind of SCLCP when the gauche conformation of the flexible mesogen becomes dominant at high temperatures. Detailed experiments and the mechanism study of the LC formation in this series of polymer were still ongoing.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NNSFC Grant 20990232 and 21104001) and the MOST (2011CB606004).

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