A Series of Novel Side Chain Liquid Crystalline Polysiloxanes Containing Cyano- and Cholesterol-Terminated Substituents: Where will the Structure-Dependence of Terminal Behavior of the Side Chain Reappear?

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ABSTRACT: A series of polysiloxane side chain liquid crystal polymers with strong polarity cyano substitution-terminated achiral side chains and cholesterol-terminated chiral side chains was successfully synthesized via thiol-ene click chemistry. ¹H-NMR, FT-IR, and thermogravimetric analysis were used to confirm their chemical structures and thermal stabilities. Their phase transition behaviors and phase structures were systematically investigated by a combination of analysis methods such as differential scanning calorimetry, polarized optical microscopy, and X-ray. Results revealed that attributing to the decisive role of the polarity interaction, all the polymers only

Polysiloxanes side-chain liquid crystalline polymers (PSCLCPs), as one of the most important branches of soft matter materials that combining the anisotropic characteristics of mesogen pendants with polymeric properties, have been drawn wide-spread attention for both fundamental and applied reasons in the past few decades.^{1–4} Among them, the mesogen pendants with polar substituents such as cyano, fluorine, and so on, which can be oriented in an electrical field, endows PSCLCPs with some special interests.^{5,6}

From the viewpoint of molecular design and structure–properties–performance relationship, previous results have revealed that the self-assembly behaviors and phase structures of SCLCPs can be drastically affected by the polymer backbone,^{7,8} the length of flexible spacers,^{9–11} the size and architecture of the terminal flexible substituents in mesogenic developed a monolayer interdigitated SmA phase in which the period arrangement was determined by the cyano-terminated side chains, the increased content of cholesterol-terminated chiral side chains (X_{chol}) just expanded the distance between neighboring molecules within a layer. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

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core¹²⁻¹⁷ as well as the linkage groups between the rigid core.¹⁸⁻²¹ Beyond that, the polarity of the terminal substituents in the side chains is also one of the most important factors. Sołtysiak et al.^{22,23} prepared cyclic oligosiloxanes with different types of polar terminal groups and found that the polarity reduced the phase transition temperatures of the formed interdigitated smectic A_d phase. By replacing the CH₃ side chain groups with polar CF3 groups, Lee et al.24 found the similar results. Sudhölter et al.²⁵⁻²⁷ and Chen et al.^{28,29} reported that a drastic change in mesogen phase structures was occurred when cyano group was used instead of methoxy group as the terminal group. Zhou et al.^{30,31} synthesized a series of mesogen-jacketed liquid crystalline polymers (MJLCPs) with asymmetric substitutions and found that carboxylic acid terminated asymmetric polymers formed a double layer smectic A phase, while the corresponding alkyl

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terminated polymers showed no liquid crystallinity or exhibited columnar phase. Their later work³² revealed that the introduction of fluorinated substituent weakened the liquid crystallinity of the polymers as well as boosted the glassy temperature.

In our previous work,³³ we have synthesized and characterized a series of PSCLCPs based on poly-[3-mercaptopropylmethylsiloxane] (PMMS) backbone with cholesterol-terminated chiral side chains and methoxy-terminated achiral side chains (PMMSs-OCH₃-based polymers). By virtue of the long polysiloxane skeleton and spacer as well as the synergy between them, smectic E (SmE), which is a high ordered liquid crystalline (LC) phase, was self-assembled at low temperatures for polymers with the molar concentration of chiral cholesteric unit (X_{chol}) below 0.3. Furthermore, a strong dependence of LC phase structures on X_{chob} which showed a layer period saltation as X_{chol} changing from 0.40 to 0.50, was observed. Here in this work, by replacing the weak polarity methoxy substitution with strong polarity cyano substitution as the terminal group of the achiral side chains, we designed and synthesized a series of novel PSCLCPs based on PMMS backbone. We anticipate that by subtle changes in the molecular structure with the polarity alteration of the terminal group in achiral side chains, the resulting PSCLCPs will bring unexpected variation of the self-assembly behaviors and LC properties.

EXPERIMENTAL

Materials

Cholesterol (A.R. grade, Sinopharm), poly[3-mercaptopropylmethylsiloxane] (PMMS, SMS-992, M.W. 4000-7000, 95 cst, Gelest Inc), ethylparaben (A.R. grade, Sinopharm), acetonitrile (A.R. grade, Sinopharm), 3-bromopropene (98%, Beijing Dominant Technology Co.), dimethylaminopyridine (DMAP) (99%, Energy Chemical), *N*,*N*'-dicyclohexylcarbodiimide (DCC) (98%, Energy Chemical), 4-hydroxybenzonitrile (A.R. grade, Beijing Dominant Technology Co.), potassium hydroxide (A.R. grade, Beijing Chemical Reagents Co.), and anhydrous potassium carbonate (A.R. grade, Beijing Chemical Reagents Co.) were used as purchased. Toluene (A.R. grade, Beijing Chemical Reagents Co.) was refluxed over sodium and distilled under nitrogen atmosphere before use. Azodiisobutyronitrile (AIBN) (A.R. grade, Beijing Dominant Technology Co.) was purified by recrystallization from ethanol. Other chemical reagents were used without any purification.

Measurements

¹H-NMR spectra, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized optical microscope (POM), one-dimensional wide-angle X-ray diffraction (1D-WAXD), small angle X-ray scattering (SAXS), and two-dimensional wide-angle X-ray diffraction (2D-WAXD) were carried out according to the procedures as described previously.³³

Synthesis

The synthetic routes of the monomers and polymers are shown in Scheme 1. The experimental details are described below.



SCHEME 1 Synthetic routes of the monomers and polymers.

Synthesis of the 4-(Allyloxy) Benzoic Acid

The experimental details of the precursor synthesis are in accordance with the literature. 33

FT-IR (KBr, cm⁻¹): 2985–2825 (-CH₂-, H₂C=, and =C-H), 2668–2554 (-OH in -COOH), 1680 (C=O), 1648 (C=C), 1602, 1575, 1503, 1425 (Ar-), 1251 (C-O-C). ¹H-NMR (400 MHz, DMSO, TMS, δ , ppm): 12.61 (1H, s, -COO<u>H</u>), 7.88–7.85 (2H, d, Ar-<u>H</u>), 7.02–7.0 (2H, d, Ar-<u>H</u>), 6.08–5.98 (1H, m, CH₂=C<u>H</u>-CH₂-), 5.41–5.36 (1H, dd, one of C<u>H</u>₂=CH-CH₂-), 5.28–5.25 (1H, dd, one of C<u>H</u>₂=CH-CH₂-), 4.63–4.62 (2H, d, CH₂=CH-CH₂-).

Synthesis of Cholesteryl-4-(Allyloxy) Benzoate (M1)

The experimental details of M1 synthesis are in accordance with the literature.³³ FT-IR (KBr, cm⁻¹): 2946–2884 (—CH₃, —CH₂—, H₂C=, and =C—H), 1712 (C=O), 1648 (C=C), 1606, 1580, 1509, 1464 (Ar—), 1274, 1249 (C—O—C). ¹H-NMR (400 MHz, CDCl₃, TMS, δ , ppm): 8.00–7.98 (2H, dt, Ar—<u>H</u>), 6.93–6.91(2H, dt, Ar—<u>H</u>), 6.09–6.02 (1H, m, CH₂=C<u>H</u>—CH₂—), 5.45–5.42 (1H, dq, one of C<u>H</u>₂=CH—CH₂—), 5.40(1H, t, =C<u>H</u>— in cholesteryl moiety), 5.33–5.30 (1H, dq, one of C<u>H</u>₂=CH—CH₂—), 4.84–4.80(1H, m, —O—C<u>H</u>— in cholesteryl moiety), 4.60–4.59 (2H, d, CH₂=CH—C<u>H</u>₂—), 2.46–2.44(2H, d, —O—CH—C<u>H</u>₂—C— in cholesteryl moiety), 2.04–0.86(38H, m, <u>H</u> in cholesteryl moiety), and 0.69(3H, s, —C<u>H</u>₃ in cholesteryl moiety).



FIGURE 1 FT-IR spectra of monomers and all the polymers. [Color figure can be viewed at wileyonlinelibrary.com]

Synthesis of 4-Cyanophenyl 4-(Allyloxy) Benzoate (M2)

The synthesis of M2 used the same method as described for the preparation of M1. 4-(allyloxy) benzoic acid (8.40 g, 0.05 mol), 4-hydroxybenzonitrile (7.14 g, 0.06 mol), dimethylaminopyridine (DMAP) (0.92 g, 7.50 mmol), and 200 mL dichloromethane were premixed, then a dichloromethane solution of N,N'-dicyclohexylcarbodiimide (DCC) (12.36 g, 0.06 mol) was added dropwise slowly to the premixture, and reacted at room temperature for 24 h. After filtration and removal of the solvent, the coarse products were purified by silica gel column chromatography with dichloromethane as the eluent to give M2 as a white crystal. FT-IR (KBr, cm^{-1}): 3104–2862 (-CH₃, -CH₂-, H₂C=, and =C-H), 2229 (-CN), 1737 (C=0), 1633 (C=C), 1603, 1579, 1509, 1467 (Ar-), 1275, 1261 (C-O-C). ¹H-NMR (400 MHz, CDCl₃, TMS, δ, ppm): 8.2–8.12 (2H, dt, Ar–<u>H</u>), 7.79–7.72 (2H,dt, Ar-H), 7.41-7.35 (2H, dt, Ar-H), 7.08-7.00 (2H, td, Ar-<u>H</u>), 6.16-6.03 (1H, m, CH₂=C<u>H</u>-CH₂-), 5.52-5.43 (1H, dq, one of CH2=CH-CH2-), 5.40-5.34 (1H, dq, one of C<u>*H*</u>₂=CH-CH₂-), 4.70-4.64 (2H, dt, CH₂=CH-C<u>*H*</u>₂-).

Synthesis of the Polymers

The synthetic routes of all the polymers were similar to those reported in the literature with minor modification.^{33,34} Taking the preparation of polymer P-3 as a typical procedure. M1 (361.00 mg, 0.66 mmol), M2 (122.76 mg, 0.44 mmol), PMMS (137.60 mg, 1.00 mmol-SH), AIBN (16.40 mg, 0.10 mmol), and toluene (1.85 mL) were sealed in a polymerization tube after degassed via three freeze-pump-thaw cycles to obtain a vacuum environment, then stirred at 65 °C for 24 h. After removal of the solvent, the coarse polymer was purified by several precipitate-dissolve-precipitate cycles to give P-3 as white powders. Yield: 90.7%.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Polymers

The synthetic routes of monomers consisted of Williams etherification reaction and Steglich esterification reaction in an efficient sequential order as shown in Scheme 1. AIBN was used as the initiator in the thiol-ene addition reaction to obtain the polymers, and the yields of all the polymers were higher than 86%. The chemical structures of all the above compounds were confirmed by FT-IR and $^1\mathrm{H}\text{-}\mathrm{NMR}$ spectroscopic methods.

The FT-IR and ¹H-NMR spectra of monomers, PMMS, and all the polymers are illustrated in Figures 1 and 2, respectively. The disappearance of the weak vibrational bands at 2552 cm^{-1} [assigned as the S–H stretching, as shown in Fig. 1(a)] as well as the signal of the thiol group in PMMS at 1.37 ppm (as shown in Figure 2), indicated that hydrogen atoms of all the S-H groups were substituted completely. The appearance of the vibrational bands, which were derived from methylene (-CH₂-), cyanogroup (-CN), ester carbonyl (C==0), aromatic (Ar--), Si--C, and Si--O--Si at 2965-2836, 2229, 1737/1712, 1603-1467, 1260, and 1072-1018 cm⁻¹ (as shown in Fig. 1), respectively, and the proton peak of aromatic (as shown in Figure 2), suggested the successful preparation of polymers via thiol-ene addition reaction. Additionally, the weak vibrational bands at 1633 cm^{-1} [assigned as the C=C stretching, the partially amplified FT-IR spectra as shown in Figure 1(b)] and the representative signals of the vinyl group in monomers at 6.05, 5.43, and 5.31 ppm (as shown in Figure 2) disappeared, indicating the



FIGURE 2 ¹H-NMR spectra of monomers and all the polymers. [Color figure can be viewed at wileyonlinelibrary.com]



TABLE 1	L	Thermal	Properties	and	Molecular	Characterization	of	Polymers
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$M1/(M1 + M2) (MR)^{a}$			M _n (g/mol)					
n feed	Calculated ^b	T _g ^c (°C)	τ _i ^c (°C)	GPC ^d	Calculated ^b	PDI ^d	<i>T</i> d ^e (°C)	Yield (%)
_	_	_	_	800	6192	2.53	-	_
0.00	0.000	2.4	92.1	2200	18747	2.84	349	86.2
.20	0.221	10.5	96.3	3300	21412	2.28	302	87.4
.40	0.425	18.7	111.7	3700	23872	2.23	301	89.5
.60	0.604	23.6	176.8	4000	26031	1.67	334	90.7
.80	0.819	33.1	189.4	4400	28624	1.89	329	92.3
.00	1.000	35.7	204.8	4800	30852	2.04	337	91.2
r.	- .00 .20 .40 .60 .80 .00	a feed Calculated ^b - - .00 0.000 .20 0.221 .40 0.425 .60 0.604 .80 0.819 .00 1.000	Introduct A line (introduct) (introduct) Introduction (introduct) a feed Calculated ^b $T_g^{\circ}(^{\circ}C)$ - - - 00 0.000 2.4 .20 0.221 10.5 .40 0.425 18.7 .60 0.604 23.6 .80 0.819 33.1 .00 1.000 35.7	Introduct + M2/ (MH)a feedCalculatedb $T_g^{c}(^{\circ}C)$ $T_i^{c}(^{\circ}C)$ 000.0002.492.1.200.22110.596.3.400.42518.7111.7.600.60423.6176.8.800.81933.1189.4.001.00035.7204.8	Introduct + ML2 (MH) Introduct + ML2 (MH) Introduct + ML2 (MH) a feed Calculated ^b $T_g^{\circ}(^{\circ}C)$ $T_i^{\circ}(^{\circ}C)$ GPC ^d - - - - 800 .00 0.000 2.4 92.1 2200 .20 0.221 10.5 96.3 3300 .40 0.425 18.7 111.7 3700 .60 0.604 23.6 176.8 4000 .80 0.819 33.1 189.4 4400 .00 1.000 35.7 204.8 4800	Introduct + MLP (MM) $T_9^{c}(^{\circ}C)$ $T_i^{c}(^{\circ}C)$ GPC^d Calculatedb $ -$ 8006192 000 0.000 2.4 92.1 2200 18747 20 0.221 10.5 96.3 3300 21412 40 0.425 18.7 111.7 3700 23872 60 0.604 23.6 176.8 4000 26031 80 0.819 33.1 189.4 4400 28624 00 1.000 35.7 204.8 4800 30852	Intrinsit of fieldCalculatedb $T_g^{c}(^{\circ}C)$ $T_i^{c}(^{\circ}C)$ GPCdCalculatedbPDId80061922.53.000.0002.492.12200187472.84.200.22110.596.33300214122.28.400.42518.7111.73700238722.23.600.60423.6176.84000260311.67.800.81933.1189.44400286241.89.001.00035.7204.84800308522.04	IntrinsitionIntrinsitionIntrinsitionIntrinsitiona feedCalculatedb $T_g^{\circ}(^{\circ}C)$ $T_i^{\circ}(^{\circ}C)$ GPC ^d CalculatedbPDI ^d $T_d^{\circ}(^{\circ}C)$ 80061922.53000.0002.492.12200187472.84349.200.22110.596.33300214122.28302.400.42518.7111.73700238722.23301.600.60423.6176.84000260311.67334.800.81933.1189.44400286241.89329.001.00035.7204.84800308522.04337

^a Molar ratio.

^b According to the ¹H-NMR results.

^c Evaluated by DSC during the second heating at the rate of 10 °C/min.

^d Determined by GPC in THF using polystyrene standards.

completely removal of the excessive allyl ether monomers. Furthermore, as summarized in Table 1, the actual molar fraction of M1 based on (M1 + M2) (assigned as X_{chol}) in a specified polymer could be calculated on the basis of reciprocal relationship between the integral area of the signals at 4.82 ppm (-O-CH- in cholesteryl moiety) in M1 and 7.76 ppm (Ar-H) in M2 (as remarked by red dotted boxes in Figure 2), and the variation of X_{chol} could also be reflected by the gradually weakened relative intensity of cyano absorption peak [as shown in Figure 1(a)] as well as the reciprocal relationship between the vibrational band of C=O at about 1712 cm^{-1} in M1 and 1737 cm^{-1} in M2 [as remarked in Figure 1(b)]. In agreement with our previously reported work,³³ the calculated X_{chol} were relatively bigger than that in the feed, indicating that the substituted vinyl monomer M1 with much larger space and stronger rigid was more reactive than M2.35,36

As listed in Table 1 and Supporting Information, Figure S1, GPC measurement showed that the number-average molecular weight (M_n) of polymers decreased with the increasing content of M2 along with broad molecular weight distribution of polymers which was derived from parent skeleton molecules PMMS, and the calculated M_n according to the ¹H-NMR results also exhibited the similar variation tendency, which were in line with that the molecular weight of M1 is greater than that of M2. Furthermore, as a result of the molecular weight of monomeric unit of sample (413 or 695 g/mol) was much larger than that of polystyrene standards (104 g/mol), the hydrodynamic volume of former was smaller than that of the latter, which led to the significant difference between the calculated M_n based on ¹H-NMR spectra and the measured M_n according to the GPC method.

Phase Structures and Phase Transition Identification

Figure 3 shows the POM images of all the polymers, which were obtained by cooling the samples from isotropic state to room temperature at a rate of 1 $^{\circ}$ C/min. The birefringence of P-1, P-2, P-3, P-4, and P-5 appeared rapidly upon cooling when the temperature reached to 78, 95, 110, 172, and 185 $^{\circ}$ C,

^e 5% weight loss temperature was evaluated by TGA at a rate of 20 °C/min. ^f The data of P-6 referenced as PMMS- X_{Chol} -1.00 in ref. 33 and listed here for comparison only.

respectively. A focal-conic texture, which was a characteristic of smectic phase,^{37,38} was developed following by isothermal annealing for a short time, then it maintained to the room temperature. These observations indicated that all the polymers had at least one smectic phase. Considering the only structure changes of the terminal groups in achiral monomer, we speculated that these polymers might have the similar period arrangement scale with previously reported PMMSs-OCH₃-based polymers.³³

As shown in Table 1 and Supporting Information, Figure S2, the temperatures of all the polymers at 5% weight loss in nitrogen were all above 300 $^{\circ}$ C, indicating that the polymers had good thermal stabilities.

DSC experiments were performed to examine the phase transitions of all the polymers. The traces of the first cooling and the subsequent second heating process were recorded at a rate of 10 °C/min under nitrogen as shown in Figure 4. As expected, the synergistic effect of the relatively less rigid sidechain structure and the flexible polysiloxane backbone endowed all the samples with low glass transition temperatures (T_{g}) below 33 °C, which was gradually increased with the increasing content of chiral monomer M1. Additionally, comparing the glass transition temperatures (T_g) of the polymers in this study with those of the corresponding PMMSs- OCH_3 -based polymers, the T_g of the polymers in this study was slightly higher except P-1, which might be attributed to the combined effect of the more rigid side-chain structure and the strong polarity with the introduction of cyano substitution. Besides the apparent glass transition, only one endothermic/ exothermic peak at higher temperature in the whole heating/ cooling processes was observed for all the polymers, and displayed a similar evolution tendency as T_g with altering the content of M1, suggesting that there might exist only one LC phase structure in the whole mesogenic temperature ranges.

To systematically investigate whether there were phase transitions in the mesogenic state and the self-assembly structures of all the polymers, variable-temperature 1D-WAXD, SAXS, and 2D-WAXD experiments were carried out.



FIGURE 3 POM textures of (a) P-1, (b) P-2, (c) P-3, (d) P-4, and (e) P-5 were recorded by cooling the samples from isotropic state to room temperature at a rate of 1 °C/min. [Color figure can be viewed at wileyonlinelibrary.com]

Distinctively, different from the apparent diffraction pattern variations of PMMSs-OCH₃-based polymers, the diffraction patterns of polymers in this work seemed to be simply or not variety enough. Taking the performance of sample P-4 as a typical example, parts a and b of Figure 5 show the SAXS and 1D-WAXD patterns of P-4 during the heating processes,



FIGURE 4 DSC thermograms of polymers during (a) the first cooling and (b) subsequent second heating scans at a rate of 10 $^{\circ}$ C/min.

respectively. There was a scattering halo at high-angle region with the center position slightly blue shifted during the whole heating scanning, indicating the absence of nanometer ordered packing. While only one diffraction peak was observed (corresponding to a *d*-spacing of 3.20 nm) [see the inset of Figure 5(a)], and the intensity gradually weakened upon heating. When the temperature reached 185 °C, the sharp diffraction peak at low-angle region vanished, accompanied with the amorphous broad high-angle halo becoming more diffused and the center position shifting to a higher angle, demonstrating that the sample entered into isotropic state. Therefore, combining the results of DSC, POM, 1D-



FIGURE 5 (a) SAXS (inset shows the enlarged patterns in the low-angle region) and (b) 1D-WAXD (inset shows the enlarged patterns in the high-angle region) patterns of P-4 during the heating process. [Color figure can be viewed at wileyonline-library.com]

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FIGURE 6 2D-WAXD pattern of (a) P-4 and (b) the shear geometry. [Color figure can be viewed at wileyonlinelibrary.com]

WAXD, and SAXS, a low ordered smectic phase structure of SmA or SmC in the whole mesogenic state was demonstrated, which was on account of the representative fan-shaped texture under POM along with the sharp low-angle diffraction peak and the diffused scattering halo at high-angle region under SAXS and 1D-WAXD.

2D-WAXD experiments were carried out to remedy the dimensionality absence of the 1D-WAXD and SAXS patterns to further confirm the smectic structures of polymers. Taking the 2D-WAXD pattern of P-4 as a representative example, the sample was mechanically sheared and annealed at 89 °C and then cooled to room temperature. As depicted in Figure 6(a), the 2D-WAXD pattern of P-4 was recorded at room temperature with the X-ray incident beam (along Z direction) perpendicular to the shear direction (X direction). A pair of strong low-angle diffraction arcs, which was originated from the layer structure, could be observed on the equator (Y direction). Meanwhile, a pair of scattering halos at $q \approx$ 12.56 nm^{-1} (corresponding to a *d*-spacing of 0.50 nm) were more or less concentrated on the meridian (X direction) with rather broad azimuthal distributions, and its center azimuthal had an offset of 90° with that of the low-angle diffraction arcs. These results proved that a typical SmA phase structure was formed for P-4 sample.^{13,39}

Accordingly, the DSC traces, POM textures, 1D-WAXD, and SAXS patterns of polymers P-1, P-2, P-3, and P-5 were quite



FIGURE 7 (a) SAXS and (b) 1D-WAXD patterns of all the polymers at room temperature. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 8 $d_{(100)}$ and $d_{n-\pi}$ as a function of X_{chol} at room temperature. [Color figure can be viewed at wileyonlinelibrary.com]

similar to those of P-4, an SmA phase structure in the whole mesogenic state could be confirmed consequently.

Dependence of the Phase Structure on the Two LC Building Blocks and Interplay Between Them

Parts a and b of Figure 7 show the SAXS and 1D-WAXD patterns of all the polymers at room temperature, respectively. The corresponding *d*-spacing of the strong diffraction peak in the low-angle region (assigned as $d_{(100)}$) and the amorphous broad halo (assigned as $d_{\pi-\pi}$) in the high-angle region as a function of X_{chol} are shown in Figure 8. The values of $d_{(100)}$ and $d_{\pi-\pi}$ along with the phase transitions of all the polymers are also summarized in Table 2. Obviously, the position of the diffraction peaks in the low-angle region, which indicated the distance of minimized layer spacing of the period arrangement, were almost unchanged with the increasing of X_{chol} . While the central positions of the amorphous broad halos in high-angle region, which represented the distance between the molecules within a layer, were shifted to the lower angle obviously (blue shift).

Comparing the value of $d_{(100)}$ with the calculated length of the side chains, where the calculated length of the chiral and achiral side chains from the Si atom in the main chains to the last C/N atom of the side chains were 3.09 nm (L_1) and 2.33 nm (L_2) under the perfect assumption that the alkyl chains were in an all-trans conformation, it could be easily found that $L_2 < L_1 < d_{(100)} < 2L_2 < 2L_1$. Further analysis and probe showed that $d_{(100)} \approx L_{\rm m} + 2L_{\rm s}$, where $L_{\rm s}$ (1.07 nm) is the calculated length of the spacers from the O atom in the ether groups to the Si atom in the backbones, and $L_{\rm m}$ (1.28 nm) is the calculated length of the achiral mesogenic cores from the O atom in the ether groups to the last N atom of the achiral side chains, respectively. Additionally, previous reports have revealed that the dipole interaction of the strong polarity cyano substituent could induce the side chains to organize in antiparallel pairs to force the cyano away from each other and to minimize the system energy, which played a decisive role on the self-organization of the molecule.^{26,27,40} Combining the comprehensive analysis and judgment of above results, as shown in Scheme 2, we

TABLE 2 d-Spacing and Phase Transitions of Polymers

	Phase transitions ^a (°C)								
	Heating								
Sample	Cooling	<i>d</i> ₍₁₀₀₎ ^b (nm)	$d_{\pi \cdot \pi}{}^{b}$ (nm)	c ^c (nm)					
P-1	G2.4SmA _s 92.1Iso Iso81.3SmA _s -1.4G	3.20	0.44	3.20					
P-2	G10.5SmA₅96.3 Iso Iso98.5SmA₅8.8G	3.20	0.46	3.20					
P-3	G18.7SmA _s 111.7Iso Iso113.4SmA _s 16.4G	3.20	0.49	3.20					
P-4	G23.6SmA _s 176.8Iso Iso175.8SmA _s 19.5G	3.20	0.50	3.20					
P-5	G33.1SmA _s 189.4lso lso186.7SmA _s 29.9G	3.20	0.50	3.20					
P-6 ^d	G35.7SmA _d 139.9SmA _s 204.8lso lso197.9SmA _s 136.6SmA _d 34.6G	6.61	_	6.61					

 $^{\rm a}$ According to the DSC results: G, glass state; SmA_s, smectic A phase with single layer; SmA_d, smectic A phase with double layer; Iso, isotropic state.

^b Calculated at room temperature for all the polymers and according to the XRD results.

speculated that for this series of polysiloxanes-containing cyano-terminated side chains, a monolayer SmA phase with side chains partially interdigitated was self-assembled, in



SCHEME 2 Schematic of molecules packing of polymer. [Color figure can be viewed at wileyonlinelibrary.com]

^c The minimized layer spacing of the periodic arrangement.

^d The data of P-6 referenced as PMMS- X_{Chol} -1.00 in ref. 33 and listed here for comparison only.

which the layer period was dominated by the achiral side chains with cyano unit. Moreover, the chiral side chains with large space volume and steric hindrance were forced to adopt compression or partially coiled conformation, and the increased content of chiral cholesteric side chains just expanded the distance between the molecules within a layer.

CONCLUSIONS

In summary, a series of novel PSCLCPs based on cholesterol and benzonitrile groups as side groups was successfully designed and synthesized via efficient thiol-ene click addition chemistry reaction. Results indicated that a drastic change in mesogenic state was observed when the cyano substitution was used instead of methoxy substitution. With increasing $X_{\rm chol}$, polymers with cyano-terminated side chains in this work developed a single monolayer interdigitated SmA phase, while the corresponding PMMS-OCH₃-based polymers formed abundant LC phase structures including SmE phase, a monolayered SmA phase as well as a bilayered SmA phase. Attributing to the decisive role of the polarity interaction, a strong dependence of LC phase structures on X_{chol} was not reappeared in this series of cyano-terminated polymers. This work reproduced the mysterious force of the polarity terminal groups in construction of the LC phase structures of SCLCPs.

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