Journal of Materials Chemistry C



CHEMISTRY

View Article Online

PAPER



Cite this: DOI: 10.1039/c5tc04331j

Synthesis and self-assembly behaviours of side-chain smectic thiol—ene polymers based on the polysiloxane backbone[†]

Wenhuan Yao,‡^a Yanzi Gao,‡^b Xiao Yuan,^b Baofeng He,^b Haifeng Yu,^{bc} Lanying Zhang,*^{bc} Zhihao Shen,*^{cd} Wanli He,*^a Zhou Yang,*^a Huai Yang*^{abc} and Dengke Yang^e

A series of polysiloxane side chain liquid crystal polymers (PSCLCPs) with chiral and achiral substitutions in the side chains, denoted as PMMS-X_{chol}-n (n = 0, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5 0.6, 0.7. 0.8, 0.9, and 1.0, respectively, the molar content of the chiral cholesteric unit (X_{chol}) in a specific polymer), were successfully synthesized via thiol-ene click chemistry. The molecular structures of the polymers were confirmed by ¹H-NMR, FT-IR, gel permeation chromatography (GPC) and thermogravimetric analysis (TGA). Their liquid crystalline (LC) properties and self-assembling behaviors were investigated in detail by a combination of various techniques, such as differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction. The results demonstrated that the phase transition behaviour and the self-assembly structure of the polymers were significantly influenced by X_{chol} and temperatures. With increased X_{chol} , the clearing points increased significantly, their mesogenic temperature ranges greatly widened, and abundant mesophases developed. Generally, two different types of LC phase structures and three different molecular arrangements were observed, depending on the two LC building blocks. Polymers with X_{chol} below 0.3 could self-assemble into a smectic E (SmE)-like structure and a single layer smectic A (SmA₂) structure upon heating. When X_{chol} was between 0.4 and 0.7, a single phase structure of a SmA_s or a bilayer smectic A (SmA_d) could be observed. While for polymers with X_{chol} over 0.8, a SmA_d phase structure was self-organized, further heating led to a SmAs structure. Moreover, when the molar ratio of the chiral group or achiral group was about 0.1, a microphase-separated smectic morphology could be found, indicating that the introduction of a small amount of any components in the copolymers might destroy the well-ordered structures.

www.rsc.org/MaterialsC

DOI: 10.1039/c5tc04331j

Received 20th December 2015, Accepted 28th December 2015

1. Introduction

Side Chain Liquid Crystal Polymers (SCLCPs), which combine the anisotropy of liquid crystalline mesogens with the mechanical performance of polymers showing wide potential applications as

^a Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083,

- P. R. China. E-mail: yanghuai@pku.edu.cn, yangz@ustb.edu.cn,
- hewanli@mater.ustb.edu.cn

^b Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, P. R. China. E-mail: zhanglanying@pku.edu.cn

^c Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Peking University, Beijing 100871, P. R. China

^d Beijing National Laboratory for Molecular Sciences, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering,

Peking University, Beijing 100871, P. R. China. E-mail: zshen@pku.edu.cn ^e Chemical Physics Interdisciplinary Program, Liquid Crystal Insititute, Kent State University, Kent, Ohio 44241, USA

- † Electronic supplementary information (ESI) available. See DOI: 10.1039/c5tc04331j
- ‡ Joint first author, these authors contributed equally.

photoactive materials, electro-optic or nonlinear optic materials, high-strength and high-modulus fibers, engineering plastics or other functional materials, have drawn the scientists' extensive attention for the past few decades.^{1–4} Polysiloxane Side Chain Liquid Crystal Polymers (PSCLCPs), distinguishing themselves from traditional polyacrylate based liquid crystal polymers with the characteristics of much lower glass transition temperature (T_g), viscosities, surface energy, and good mechanical and thermal stabilities,⁵ have received considerable interest and have been applied in various fields ranging from optics, electrics to coatings.^{6–9}

Generally, PSCLCPs can be obtained by traditional hydrosilylation reaction between polymethylhydrosiloxane (PMHS) and unsaturated carbon–carbon bond based monomers such as alkene monomers or alkyne monomers, or by grafting mesogenic monomers to poly[3-mercaptopropylmethylsiloxane] (PMMS) *via* thiol–ene click chemistry. Since the first publication of PSCLCPs in 1979,¹⁰ following the traditional hydrosilylation reaction which was invented by Finkelmann, a large amount of PSCLCPs with different structures and unique properties has been designed,

synthesized, and characterized in detail. Furthermore, the relationships between their molecular structures and phase transition behaviours as well as phase structures have also been studied systematically. Percec et al.,^{11–15} Smith et al.¹⁶ and Gasparoux et al.17 synthesized a series of end-on (mesogens are terminally attached) PSCLCPs bearing methoxy groups, biphenyl groups, terphenyl groups and cyano groups, and found that the mesomorphic and thermodynamic properties of these polymers were dramatically influenced by the increasing content of benzene. Zhang et al.¹⁸⁻²⁰ studied a series of end-on PSCLCPs containing methyl groups and found the similar evolution tendency as described in Percec's work. Yang et al. synthesized a series of PSCLCPs by using alkyne hydrosilylation.²¹ Tschirner et al.²² and Ringsdorf et al.²³ synthesized a series of side-on (mesogens are laterally attached) PSCLCPs which formed nematic phases or smectic phases. Zhou et al.24 prepared a series of mesogenjacketed liquid crystal polymers (MJLCPs) with a polysiloxane backbone and found that the mesogen-jacketed effect could still force the polymers to self-organize into supramolecular columnar nematic or smectic liquid crystalline phases. However, for the method of traditional hydrosilylation, the purification difficulty derived from the usage of expensive noble metal platinum catalysts, the complexity of the chemical structures and performance of the products attributing to the coexistence of Markovnikov and anti-Markovnikov addition reaction have limited their wide applications.25

The thiol-ene addition reaction, namely hydrothiolation of a C=C bond, as a representative click reaction with features of high efficiency, strong stereo-selectivity, simple reaction conditions with no side products, etc., has been well known since 1905.²⁶ Since then, it has sparked an enormous amount of interest in the development of organic synthetic chemistry, polymer synthetic chemistry, biological chemistry, and materials science. By virtue of the thiol-ene reaction, functional polymer materials with linear,²⁷⁻²⁹ crosslinked,30-32 or net-worked33,34 structures were designed and synthesized. Reviews about the mechanism of thiol-ene click chemistry and various applications in polymers and materials synthesis were also reasonably elaborated.^{35,36} Recently, Yang et al. prepared a series of main chain liquid crystal polymers (MCLCPs),^{37,38} SCLCPs,³⁹⁻⁴¹ and liquid crystal elastomers (LCEs)^{42,43} by thiol-ene click chemistry, in which only anti-Markovnikov addition products were obtained. The self-assembly properties of the SCLCPs as well as the effect of the molecular structure of the mesogen on the mesophase were also investigated.

In this paper, inspired by the accurate control of the molar ratio between the thiol group and the mesogenic monomer as well as the region-selectivity of thiol–ene click chemistry, and the outstanding performances such as electro-optics,^{44,45,49} piezoelectricity,⁴⁶ ferroelectricity^{47,48} and pyroelectricity⁴⁹ derived from the symmetry breaking by the introduction of the molecular chirality to MCLCPs/PSCLCPs, the first example of PSCLCPs based on the PMMS main chain with different compositions of chiral and achiral mesogenic groups has been presented. A battery of PSCLCPs (PMMS- X_{chol} -n, n means the molar ratio in a specific polymer) with the molar content of the chiral cholesteric group (X_{chol}) ranging from 0, 0.1, 0.15, 0.2,

0.3, 0.4, 0.5 0.6, 0.7. 0.8, 0.9, to 1.0 mol%, respectively, was successfully synthesized and characterized. The resultant PSCLCPs are therefore a model system to investigate the relationship between a single composite change of X_{chol} and the variable in the self-assembly behaviours. Furthermore, different from the work with PMHS-based copolymers and LCEs reported previously in our group,^{50–52} we anticipate that the longer flexible spacer in PMMS may offer the polymers more abundant LC phase structures, interesting properties, and potential applications.

2. Experimental

2.1 Materials and methods

2.1.1 Materials. Poly[3-mercaptopropylmethylsiloxane] (PMMS, SMS-992, M.W. 4000-7000, 95 cst, Gelest Inc.), ethylparaben (A.R. grade, Sinopharm), cholesterol (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-methoxyphenol (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 without any further purification. Toluene (A.R. grade, Beijing Chemical Reagents Co.) was refluxed over sodium and distilled under a nitrogen atmosphere before use. Azodiisobutyronitrile (AIBN) (A.R. grade, Beijing Dominant Technology Co.) was purified by recrystallization from ethanol. Other chemical reagents were used as received.

2.1.2 Methods. All ¹H-NMR spectra were collected using a Bruker HW400 MHz spectrometer (ADVANCE III-400) using deuterated chloroform (CDCl₃) or dimethylsulfoxide (DMSO) with tetramethylsilane (TMS) as the internal standard at room temperature.

The FT-IR spectra were recorded on a PerkinElmer spectrum 100 spectrophotometer by the KBr method.

A PerkinElmer DSC8000 with a mechanical refrigerator was used to obtain the phase transition of the monomers and polymers under dry nitrogen at a heating and a cooling rate of 10 $^{\circ}$ C min⁻¹; the temperature and heat flow scale were calibrated using zinc and indium as standard.

Thermogravimetric analysis (TGA) was performed on a TA Q600 at a heating rate of 20 $^\circ \rm C~min^{-1}$ under nitrogen.

Gel permeation chromatography (GPC) was performed on a Waters 2410 instrument equipped with a Waters 2410 refractive index detector and three waters μ -styragel columns (10³, 10⁴, and 10⁵ Å). The column packing allowed the separation of polymers over a wide molecular weight range of 2200–600 000. All GPC data were gathered by using tetrahydrofuran (THF) (HPLC grade, Fisher Scientific) as the eluent at a flow rate of 1.0 ml min⁻¹ at 35 °C and calibrated using polystyrene standards.

Polarized optical microscopy (POM) was carried out to observe the liquid crystal textures of the samples using a Carl Zeiss Axio Vision SE64 polarized optical microscope with a Linkam LTS420 hot stage. One-dimensional wide-angle X-ray diffraction (1D-WAXD), Small Angle X-ray scattering (SAXS), and Two-dimensional wideangle X-ray diffraction (2D-WAXD) were used to study the selfassembly structures and transitions of the binary copolymers. All the background patterns were collected and subtracted from the sample patterns.

1D-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 the wavelength λ is 0.1542 nm), an X'celerator detector, and a Paar Physica YCU 100 hot stage in the reflection mode at 40 kV and 40 mA and protected by a nitrogen atmosphere. The heating and cooling rates in all 1D-WAXD experiments were 10 °C min⁻¹. The samples were prepared by dissolving about 30 mg of powder samples in tetrahydrofuran (THF, ~1 ml) and drop-casting into a film on a monocrystalline silicon substrate.

SAXS experiments were carried out on an Anton Paar SAXSess high-flux small-angle X-ray scattering instrument equipped with a Kratky block-collimation system and a Philips PW3830 sealed-tube X-ray generator with the Cu target (Cu K α and the wavelength λ is 0.1542 nm) in the transmission mode at 40 kV and 40 mA. The samples were sandwiched with about 3–5 mg of powder samples between aluminium films.

2D-WAXD experiments were executed on a Bruker D8 Discover diffractometer with a 2D detector of GADDS in the transmission mode at 40 kV and 40 mA. The samples were oriented by mild mechanical shearing at an appropriate temperature of the liquid crystal phase and the point-focused X-ray beam was aligned perpendicular to the shear direction.

An unpolarized UV/VIS/IR spectrophotometer (Perkin-Elmer Lambda 950) was used for the spectral characterization in transmission mode at normal incidence, or in reflection mode with a reflectance accessory (150 nm Int. Sphere).

2.2 Synthetic procedures

2.2.1 Synthesis of 4-(allyloxy) benzoic acid. 3-Bromopropene (7.26 g, 0.06 mol) was added drop-wise to a mixture of ethyl 4-hydroxybenzoate (8.30 g, 0.05 mol), anhydrous potassium carbonate (6.90 g, 0.05 mol), and 150 ml of acetonitrile at room temperature and refluxed under magnetic stirring for 10 h. After filtration and removal of solvent, the buff liquid was obtained as the intermediate product.

Then the buff liquid and potassium hydroxide (8.40 g, 0.15 mol) were dissolved in the ethanol/water (1/5) mixture and refluxed at 105 °C for 5 h. After removal of ethanol, the unhydrolyzed reactants were extracted three times with ether. The aqueous phase was acidified to pH 2.0 with hydrochloric acid. After filtration, the residue was recrystallized from ethanol to give 4-(allyloxy) benzoic acid as a white needle crystal. Yield: 93%. 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, -COOH), 7.88–7.85 (2H, d, Ar–H), 7.02–7.0 (2H, d, Ar–H), 6.08–5.98 (1H, m, CH₂=CH–CH₂–), 5.41–5.36 (1H, dd, one of CH₂=CH–CH₂–), 5.28–5.25 (1H, dd, one of CH₂=CH–CH₂–), 4.63–4.62 (2H, d, CH₂=CH–CH₂–).

2.2.2 Synthesis of cholesteryl-4-(allyloxy) benzoate (M1). A solution of N,N'-dicyclohexylcarbodiimide (DCC) (12.36 g, 0.06 mol) in dichloromethane was added drop-wise slowly to a mixture of 4-(allyloxy) benzoic acid (8.40 g, 0.05 mol), cholesterol (11.60 g, 0.03 mol), dimethylaminopyridine (DMAP) (0.92 g, 7.50 mmol), and 200 ml of dichloromethane, and then stirred at room temperature for 24 h. After filtration and removal of dichloromethane, the concentrated solution was purified by silica gel column chromatography with dichloromethane as the eluent to give M1 as a white crystal. Yield: 91%. 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-H), 6.93-6.91 (2H, dt, Ar-H), 6.09-6.02 (1H, m, CH2==CH-CH2-), 5.45-5.42 (1H, dq, one of CH2==CH-CH₂-), 5.40 (1H, t, =CH- in the cholesteryl moiety), 5.33-5.30 (1H, dq, one of CH2==CH-CH2-), 4.84-4.80 (1H, m, -O-CH- in the cholesteryl moiety), 4.60-4.59 (2H, d, CH2=CH-CH2-), 2.46-2.44 (2H, d, -O-CH-CH2-C- in the cholesteryl moiety), 2.04-0.86 (38H, m, \underline{H} in the cholesteryl moiety), 0.69 (3H, s, $-C\underline{H}_3$ in the cholesteryl moietv).

2.2.3 Synthesis of 4-methoxyphenyl 4-(allyloxy) benzoate (M2). The synthesis of M2 used the same method as described for the preparation of M1. FT-IR (KBr, cm⁻¹): 3081–2836 (-CH₃, -CH₂-, H₂C=, and =C-H), 1733 (C=O), 1648 (C=C), 1604, 1579, 1502, 1460 (Ar-), 1269, 1246 (C-O-C). ¹H-NMR (400 MHz, CDCl₃, TMS, δ , ppm): 8.16–8.13 (2H, dt, Ar-H), 7.13–7.10 (2H, dt, Ar-H), 7.01–6.99 (2H, dt, Ar-H), 6.95–6.92 (2H, dt, Ar-H), 6.11–6.03 (1H, m, CH₂=CH-CH₂-), 5.47–5.43 (1H, dq, one of C H_2 =CH-CH₂-), 5.35–5.32 (1H, dq, one of C H_2 =CH-CH₂-), 4.64–4.62 (2H, dt, CH₂=CH-C H_2 -), 3.82 (3H, s, -OC H_3).

2.2.4 Synthesis of polymers. All the polymers were prepared according to the synthetic routes similar to those reported in the literature with minor modifications.⁴⁰ The preparation of PMMS- X_{chol} -0.50 (0.50 means X_{chol} in the polymer) was taken as a typical procedure. M1 (302.00 mg, 0.55 mmol), M2 (156.30 mg, 0.55 mmol), PMMS (137.60 mg, 1.00 mmol –SH), AIBN (16.40 mg, 0.10 mmol), and toluene (2.20 ml) were transferred into a polymerization tube. The polymerization tube was sealed under the conditions of vacuum after degassing and exchanging with nitrogen *via* three freeze-thaw cycles. The reaction was carried out at 65 °C for 24 h. Then the coarse polymer was precipitated by pouring the reaction mixture into methanol, and further purified by dissolving in chloroform, precipitating from methanol several times in order to remove the excessive unreacted monomers and drying in a vacuum. A white powder polymer was obtained. Yield: 91%.

3. Results and discussion

3.1 Synthesis and characterization of monomers and polymers

As shown in Scheme 1, the monomers were synthesized successfully and efficiently by starting from the Williams etherification reaction and ending up with Steglich esterification reaction. All the polymers were obtained with high yields over 87% by the thiol–ene addition reaction using AIBN as the initiator. The chemical structures of



Scheme 1 Synthetic route of the monomers and polymers.

precursors, monomers, and target polymers were confirmed by FT-IR and ¹H-NMR spectroscopic methods.

Fig. 1 and 2 show the FT-IR and ¹H-NMR spectra of chiral M1, achiral M2, PMMS, and all the polymers, respectively. As shown in Fig. 1a and b, the disappearance of the weak vibrational bands at 2552 cm⁻¹ (assigned as the S–H stretching) and 1648 cm⁻¹ (assigned as the C=C stretching), and the appearance of the vibrational bands at 2965–2836, 1737/1717, 1606–1464, 1260, and 1071–1018 cm⁻¹, which were attributed to the vibrations

from methylene (-CH₂-), ester carbonyl (C=O), aromatic (Ar-), Si-C, and Si-O-Si, respectively, indicated the successful thiol-ene addition reaction and complete removal of the unreacted monomers. Furthermore, in the ¹H-NMR spectra shown in Fig. 2, the complete disappearance of the representative signals of the vinyl group in monomers at 6.05, 5.43, and 5.31 ppm, the signal of the thiol group in PMMS at 1.37 ppm in the spectra of all the polymers, and the appearance of the proton peak of the aromatic group confirmed the success of the reaction and high purity of the products once again. Additionally, a reciprocal relationship between the integral area of the signals at 4.82 ppm (-O-CH- in the cholesteryl moiety) in M1 and 3.82 ppm (-OCH₃) in M2 (as remarked by red dotted boxes in Fig. 2) as well as the vibrational band of C=O at about 1711 cm^{-1} in M1 and 1737 cm^{-1} in M2 (as remarked in Fig. 1b) can be observed and the actual molar fraction of M1 based on (M1 + M2) in a specified polymer was calculated and is summarized in Table 1, which was relatively large compared to that in the feed, indicating that the substituted vinyl monomer M1 was more reactive than M2 although the substituent of the former was much larger and more rigid than that of the latter.^{53,54}

As listed in Table 1 and Fig. S1 (ESI[†]), GPC measurements showed that the number-average molecular weight (\bar{M}_n) of polymers decreased with the increasing content of M2, and the calculated \bar{M}_n according to the ¹H-NMR results also exhibited a similar variation tendency, which was in accordance with that the molecular weight of M1 is greater than that of M2.

3.2 Thermal and liquid-crystalline properties of polymers

DSC, TGA, and POM were used to investigate the thermal and liquid-crystalline properties of the homopolymers and copolymers. As shown in Table 1 and Fig. S2 (ESI†), all the polymers have good thermal stabilities with the temperatures at 5% weight loss above 310 $^{\circ}$ C in nitrogen. And the thermal stability decreases slightly with the increasing content of the chiral cholesteric monomer M1, indicating that the thermal stability of the benzene ring is superior to the cholesteryl moiety.

DSC experiments were carried out to investigate the phase transition behaviours of the homopolymers and the copolymers. Considering the influence of the thermal history, the traces during the first cooling and subsequent second heating were recorded at a rate of 10 $^{\circ}$ C min⁻¹ under nitrogen as shown



Fig. 1 FT-IR spectra of monomers, PMMS, and all the polymers.



Fig. 2 ¹H-NMR spectra of monomers, PMMS, and polymers.

Table 1 Thermal properties and molecular characterization of polymers

	$M1/(M1 + M2) (MR)^a$				$\bar{M}_{n} (\text{g mol}^{-1})$				
Sample	In feed	Calculated ^b	$T_{\rm g}^{\ c}$ (°C)	T_{i}^{c} (°C)	GPC^d	Calculated ^b	PDI^d	$T_{\rm d}^{\ e}$ (°C)	Yield (%)
PMMS-X _{chol} -1.00	1.00	1.00	35.7	204.8	4800	30 852	2.04	337	91.2
PMMS-X _{chol} -0.90	0.90	0.909	35.6	189.9	4700	29771	1.89	338	89.6
PMMS-X _{chol} -0.80	0.80	0.820	31.9	174.4	4600	28713	1.82	337	90.3
PMMS-X _{chol} -0.70	0.70	0.714	30.3	164.4	4600	27454	1.76	337	89.4
PMMS-X _{chol} -0.60	0.60	0.632	22.8	132.4	4400	26 4 8 0	2.58	320	87.3
PMMS-X _{chol} -0.50	0.50	0.519	21.9	114.7	3900	25 1 38	2.01	313	91.0
PMMS-X _{chol} -0.40	0.40	0.419	20.2	110.7	3700	23 950	1.94	316	88.2
PMMS-X _{chol} -0.30	0.30	0.329	16.0	102.5	3600	22 880	1.78	341	87.5
PMMS-X _{chol} -0.20	0.20	0.208	7.9	80.0	2500	21 443	1.57	346	92.1
PMMS-X _{chol} -0.15	0.15	0.146	9.4	79.6	2500	20706	1.53	353	90.8
PMMS-X _{chol} -0.10	0.10	0.109	11.4	90.0	2400	20267	1.48	366	92.7
PMMS-X _{chol} -0.00	0.00	0.000	17.1	95.5	2400	18972	1.45	362	88.9
PMMS	—	—	—	—	800	6192	2.53	—	—

^{*a*} Molar ratio. ^{*b*} Calculated according to the ¹H-NMR results. ^{*c*} Evaluated by DSC during the second heating at the rate of 10 °C min⁻¹. ^{*d*} Determined by GPC in THF using polystyrene standards. ^{*e*} 5% weight loss temperature was evaluated by TGA at a rate of 20 °C min⁻¹.

in Fig. 3. As expected, the whole series of polymers had very low glass transition temperatures (T_g) below 36 °C attributing to the polysiloxane backbone. Both of the T_g and the clearing point temperature (T_i) gradually decreased first and then increased with the increasing content of the chiral monomer M1, which might be attributed to the synergistic effect of the less rigid side-chain structure and the flexible polysiloxane backbone. Additionally, besides the phase transitions of T_g and T_i , there were other endothermic peaks with relatively small values of enthalpic changes, which might be attributed to phase transitions involving LC phases.

The liquid crystalline birefringence of all the polymers was observed under POM with powder samples. Some typical POM

textures are shown in Fig. 4. All the polymers exhibited apparent birefringence during the heating and cooling procedures below the isotropic state, and the observed colour of some samples altered obviously with the temperature changes (as shown in Fig. 4a and b). However, no characteristic textures were observed except samples PMMS- X_{chol} -1.00 and PMMS- X_{chol} -0.90, which developed a representative focal-conic texture of the smectic liquid crystalline phase (Fig. 4c–f) when the samples were cooled slowly to a temperature higher than T_{g} .^{55,56} Furthermore, the texture showed no significant difference upon heating even there was phase transition in the DSC experiment. Interestingly, a distinguished texture with blue colour was observed at high temperatures for the polymers with the chiral content of 0, 0.10,



Fig. 3 DSC thermograms of the polymers during the first cooling (a) and subsequent second heating (b) scans at a rate of 10 °C min⁻¹.

0.15, 0.20, 0.30, and 0.80, as well as during the whole mesomorphic state for the samples with the chiral content between 0.40 and 0.70 (as shown in Fig. 4g and h). In order to elucidate whether the phenomenon occurred occasionally, we tried a long annealing time, a sheared method, and different heating/cooling rates several times, and the blue colour appeared and maintained repeatedly.

3.3 Phase structure identification of polymers

Variable-temperature 1D-WAXD, SAXS, and 2D-WAXD experiments were performed to further investigate the self-assembly structures of the polymers, due to the insufficient information for the identification of the specific self-assembly structure based on the DSC and POM results.

Parts a and b of Fig. 5 show the 1D-WAXD patterns of PMMS- $X_{\rm chol}$ -0.00 during the first heating and subsequent cooling processes, respectively. In accordance with the result of the DSC experiment, there were two phase transition processes in the whole temperature range. Upon first heating in Fig. 5a, three peaks with the q ($q = 4\pi \sin \theta / \lambda$) values of 14.28, 15.53 and 19.88 nm^{-1} (*d*-spacings were 0.44, 0.40 and 0.32 nm, respectively) were observed in the high-angle region at low temperatures, indicating the existence of a molecular packing on the subnanometer scale. Upon heating, the intensity of the diffraction peaks dramatically decreased, the peak at a q value of 14.28 nm⁻¹ became diffused, and the peaks at q values of 15.53 and 19.88 nm^{-1} vanished after heating to 90 °C, suggesting the loss of molecular packing on the subnanometer scale and the birth of a new phase. When the temperature exceeded 100 °C, the diffraction peak disappeared and became a scattering halo, indicating that the sample might become isotropic. Upon subsequent cooling as shown in Fig. 5b, the broad halo at high-angle shifted slightly to a lower-angle and a diffraction peak developed again when the sample was cooled to 90 °C. The peaks at about q values of 14.28, 15.53, and 19.88 nm^{-1} could also be restored at 80 °C and remained at room temperature. However, there are no other diffraction peaks presented in the low-angle region in Fig. 5a and b, even repeated experiments with larger sample amounts and larger exposure time were performed. Because the calculated length

of the chiral and achiral groups from the Si atom in the backbone to the last C atom of the side chain with the alkyl chains in all-trans conformation were 3.09 nm and 2.31 nm, respectively, as well as the insensitivity of the ID-WAXD test, we presumed that there might be some diffraction peaks at even lower angles. After the cooling process of 1D-WAXD, SAXS experiments were employed to confirm this conjecture. As expected, four peaks with d-spacings of 2.62, 0.88, 0.66 and 0.52 nm were observed below 100 °C as shown in Fig. 5c, the ratio of the scattering vectors $q (q = 2\pi/d)$ of these peaks was approximately 1:3:4:5 (see the inset of Fig. 5c), indicating a smectic packing of PMMS-Xchol-0.00, and no other diffraction peaks could be observed at even higher temperatures. The isotropic temperature of 100 °C for PMMS-X_{chol}-0.00 decided from the 1D-WAXD and SAXS results was consistent with the DSC results. Combining the results of 1D-WAXD and SXAS, we concluded that the self-assembly structure of PMMS-X_{chol}-0.00 at low temperature could be smectic E (SmE) as a result of the four diffraction peaks in the low-angle region which was assigned as (001), (003), (004), and (005) as well as the three diffraction peaks in the high-angle region which was assigned as (110), (200) and (210) diffractions of SmE with a and b values of 0.81 nm and 0.52 nm (see the inset of Fig. 5a and b), respectively.^{57,58} And a simple smectic phase structure of smectic A (SmA) or smectic C (SmC) could be confirmed for PMMS-X_{chol}-0.00 at higher temperatures due to the q ratio of 1:3:4:5 in the low-angle region and the diffused high-angle scattering halo.

The DSC traces, 1D-WAXD and SAXS patterns of polymers PMMS- X_{chol} -0.15, PMMS- X_{chol} -0.20, and PMMS- X_{chol} -0.30 were similar to those of PMMS- X_{chol} -0.00, thus similar phase transition behaviours and self-assembly structures could be confirmed.

The self-assembly behaviour of homopolymer PMMS- X_{chol} -1.00 were quite different from those of PMMS- X_{chol} -0.00. As shown in Fig. 6a, two diffraction peaks with a scattering vector ratio of about 1:2 (*q* values were 0.95 and 1.97 nm⁻¹, assigned as (001) and (002), respectively) (see the inset of Fig. 6a) in the low-angle region and an amorphous broad halo in the high-angle region (as shown in Fig. 6b) developed upon heating, demonstrating a long-range ordered smectic phase (SmA or SmC). Upon further heating over 180 °C, the first sharp diffraction peak disappeared but the second



Fig. 4 Representative textures of the samples PMMS- X_{chol} -0.15 (a and b), PMMS- X_{chol} -0.90 (c and d), PMMS- X_{chol} -1.00 (e and f), PMMS- X_{chol} -0.50 (h), and PMMS- X_{chol} -0.40 (g) at different temperatures cooled from the isotropic state, and (i) photographs of samples observed with the naked eye; samples in the first row were gradually cooled from the isotropic state to room temperature by 1 °C min⁻¹ without any other treatment, and samples in the second row were quenched from high temperatures of the liquid crystal phases.

one still remained, and the peak shifted to a lower angle, indicating the formation of a new lamellar LC packing. When the temperature

was over 210 $^\circ C$, the sharp diffraction peak in the low-angle region disappeared, accompanied with the amorphous broad halo in the



Fig. 5 1D-WAXD patterns of PMMS- X_{chol} -0.00 during the first heating (the inset shows the enlarged patterns in the high-angle region) (a) and the subsequent cooling (the inset shows the enlarged patterns in the high-angle region) (b) and SAXS pattern (the inset shows the enlarged patterns in the low-angle region) (c) of PMMS- X_{chol} -0.00 during the first heating process.



Fig. 6 SAXS (the inset shows the enlarged patterns in the low-angle region) (a) and 1D-WAXD (the inset shows the enlarged patterns in the high-angle region) (b) patterns of PMMS-X_{chol}-1.00 during the heating process.

high-angle region becoming more diffused and the position shifting to a higher angle, indicating that the sample entered into the isotropic state, which was consistent with the DSC results. It was worth noticing that the intensity of the second-order diffraction peak was stronger than that of the first-order diffraction peak for the polymer PMMS- X_{chol} -1.00, whose possible reason was that the cumulative intensity of crystal face (002) was stronger or the arrangement of crystal face (002) was more ordered than that of the (001) crystal face.⁵⁹⁻⁶²

The DSC traces, 1D-WAXD and SAXS patterns of polymer PMMS- X_{chol} -0.80 were similar to those of PMMS- X_{chol} -1.00, thus similar phase transition behaviour and self-assembly structures could be confirmed. However, as mentioned in the POM results, PMMS- X_{chol} -0.80 could reflect blue colour at high temperatures

while PMMS-*X*_{chol}-1.00 could not, although they have the same self-assembly structure.

SAXS and 1D-WAXD profiles of PMMS-X_{chol}-0.10 during the heating process are shown in Fig. 7a and b, respectively. Four diffraction peaks with *q* values of 2.4, 7.12, 9.7 and 12.1 nm⁻¹ (the corresponding ratio of the scattering vectors q ($q = 2\pi/d$) of these peaks was approximately 1:3:4:5) in the low-angle region, indicating a layer packing of an ordered phase, and three diffraction peaks with *q* values of 14.18, 15.46 and 19.45 nm⁻¹ in the high-angle region which were assigned as (110), (200) and (210), were observed and a characteristic SmE with *a* and *b* of 0.81 nm and 0.53 nm was identified below 70 °C (see the inset of Fig. 7b). When the temperature exceeded 70 °C, the intensity of the four diffraction peaks decreased

Paper



Fig. 7 SAXS (the inset shows the enlarged patterns in the low-angle region) (a) and 1D-WAXD (the inset shows the enlarged patterns in the high-angle region) (b) patterns of PMMS-X_{chol}-0.10 during the heating process.

significantly, the peak at a q value of 14.18 nm^{-1} became diffused and the peaks at q values of 15.46 and 19.45 nm^{-1} vanished, suggesting a simple smectic phase structure of SmA or SmC developed. After 90 °C, the diffused peaks in the lowangle region disappeared and the amorphous halo in the highangle became more diffused, indicating that the sample became isotropic. However, one diffused halo at a lower q value of 2.27 nm⁻¹ with the *d*-spacing of about 2.77 nm was observed below 50 °C (see the inset of Fig. 7a), which was larger than that of the first diffraction peak of PMMS-X_{chol}-0.00, but close to half of the *d*-spacing of the first diffraction peak of PMMS- X_{chol} -1.00, we assumed that the introduction of the chiral mesogen in the copolymer might force the system to self-organize into two kinds of smectic phases of the same type with periodic arrangement on different scales, thus a micro-phase separation and a poorly ordered packing were developed at low temperatures. Combining the 1D-WAXD, SAXS and DSC results, the self-assembly behaviour with increasing temperatures of the sample PMMS-X_{chol}-0.10 could be summarized as follows: SmE with micro-phase separation, SmE with well-ordered structure, a simple smectic phase structure of the SmA or SmC and isotropic state.

Similarly, the phase transition behaviour and self-assembly structures of sample PMMS- X_{chol} -0.90 were also investigated. SAXS and 1D-WAXD experiments were carried out at different temperatures from RT to 210 °C (as shown in Fig. 8). Two diffraction peaks with a scattering vector ratio of 1:2 (*q* values were 0.95 and 2.01 nm⁻¹, respectively), and an amorphous broad halo in the high-angle region were observed, demonstrating a long-range ordered smectic phase (SmA or SmC). When the temperature exceeded 140 °C, the first sharp diffraction peak disappeared but the second one still remained and the intensity became more concentrated, suggesting the construction of a new LC packing. After heating to higher temperatures over 190 °C, the sharp diffraction peak in the low-angle region vanished, and the amorphous broad halo in the high-angle

region became more diffused, indicating that the sample entered into the isotropic state. The isotropic temperature for PMMS- X_{chol} -0.90 (about 190 °C) decided from the SAXS and 1D-WAXD results was consistent with the DSC results. Interestingly, another diffuse halo at a relatively high q value of 1.12 nm^{-1} with the *d*-spacing of about 5.6 nm was observed below 60 $^\circ$ C (see the inset of Fig. 8a), which was about two times of the d-spacing of the first diffraction peak of PMMS-X_{chol}-0.00, thus our speculation was confirmed. The introduction of a small amount of any components in the copolymers might destroy the original wellordered structures and force the system to self-organize into two kinds of smectic phases of the same type with different periodic arrangement scales. Consequently, the self-assembly behaviour of the sample PMMS-X_{chol}-0.90 with increasing temperatures could be summarized as follows: simple smectic phase structure of SmA or SmC with micro-phase separation, simple smectic phase structure of SmA or SmC with well-ordered structure and isotropic state.

The SAXS and 1D-WAXD patterns of samples PMMS-X_{chol}-0.40 and PMMS-X_{chol}-0.50 at various temperatures are illustrated in Fig. 9 and 10, respectively. There were broad halos in high-angle regions for both of the polymers during the whole heating scan, indicating the absence of nanometer ordered packing. For sample PMMS-X_{chol}-0.40, there was one diffraction peak located at a q value of 2.06 nm^{-1} (corresponding to a d-spacing of 3.05 nm) (see the inset of Fig. 9a). While two diffraction peaks with a scattering vector ratio of 1:2 (q values were 0.98 and 1.96 nm^{-1} and corresponding *d*-spacing were 6.41 nm and 3.21 nm respectively) (see the inset of Fig. 10a), indicating a characteristic layer structure, were observed for sample PMMS-X_{chol}-0.50. Because the layer spacing of sample PMMS- X_{chol} -0.50 (6.41 nm) was about twice as that of sample PMMS- X_{chol} -0.40 (3.05 nm), we speculated that there might be a self-assembly structure of double layer arrangement. After heating to higher temperatures, the diffraction peaks in lowangle regions for both of the samples disappeared, indicating

J. Mater. Chem. C



Fig. 8 SAXS (the inset shows the enlarged patterns in the low-angle region) (a) and 1D-WAXD (the inset shows the enlarged patterns in the high-angle region) (b) patterns of PMMS-X_{chol}-0.90 during the heating process.



Fig. 9 SAXS (the inset shows the enlarged patterns in the low-angle region) (a) and 1D-WAXD (the inset shows the enlarged patterns in the high-angle region) (b) patterns of PMMS-X_{chol}-0.40 during the heating process.

that the samples entered into the isotropic state. Additionally, it was worth noticing that the isotropic temperature for PMMS- X_{chol} -0.50 (about 110 °C) decided from the SAXS and 1D-WAXD results was in agreement with the DSC and POM results, while the isotropic temperature for PMMS- X_{chol} -0.40 decided from the SAXS and 1D-WAXD results (about 85 °C) was much lower than that of the DSC and POM results (about 110 °C). The possible reason was that the poor-ordered self-assembly structure of PMMS- X_{chol} -0.40 led to the weak diffraction intensity of the XRD results.

The DSC traces, 1D-WAXD and SAXS patterns of polymers PMMS- X_{chol} -0.60 and PMMS- X_{chol} -0.70 were similar to those of PMMS- X_{chol} -0.50, thus similar phase transition behaviours and self-assembly structures could be confirmed.

Since the 1D-WAXD and SAXS patterns lack dimensionality, 2D-WAXD experiments were carried out to identify the smectic structures of all the polymers. The samples were mechanically sheared and annealed at different temperatures after cooling from the isotropic state. Fig. 11 shows the representative 2D-WAXD patterns of some polymers recorded at room temperature with the X-ray incident beam perpendicular (along the *Z* direction) to the shear direction (*X* direction). For the sample PMMS- X_{chol} -1.00 as shown in Fig. 11a, two pairs of strong diffraction arcs corresponding to the first-order and second-order diffractions of the smectic structure could be clearly seen on the equator, indicating that the order structure developed parallel to the shear direction on the nanometer scale, which was perfectly in agreement with the results of 1D-WAXD. Meanwhile, two



Fig. 10 SAXS (the inset shows the enlarged patterns in the low-angle region) (a) and 1D-WAXD (the inset shows the enlarged patterns in the high-angle region) (b) patterns of PMMS-X_{chol}-0.50 during the heating process.



Fig. 11 2D-WAXD Patterns of PMMS- X_{chol} -1.00 (a), PMMS- X_{chol} -0.40 (b), and PMMS- X_{chol} -0.30 (c), and the shear geometry (d).

scattering halos in the high-angles were more or less concentrated on the meridians with rather broad azimuthal at low directions, indicating that only the short-range order existed along the shear direction. The 2D-WAXD pattern demonstrated that PMMS- X_{chol} -1.00 self-assembled into a typical SmA phase structure instead of the SmC phase structure at low

temperatures.^{63,64} Similar patterns were obtained for samples PMMS- X_{chol} -0.90, PMMS- X_{chol} -0.80, PMMS- X_{chol} -0.70, PMMS- X_{chol} -0.60 and PMMS- X_{chol} -0.50.

For polymer PMMS-X_{chol}-0.40, in consistent with the 1D-WAXD result, as shown in Fig. 11b, a pair of strong low-angle diffraction arcs appeared on the equator, which was perpendicular to the shear



Fig. 12 SAXS Patterns of Polymers at 40 °C.

direction, indicating that the normal of the smectic layers was perpendicular to the shear direction. Meanwhile, the high-angle scattering halo was more or less concentrated on the meridian with rather broad azimuthal distributions, proving that a typical SmA phase structure was self-organized in sample PMMS-X_{chol}-0.40.

For samples with X_{chol} below 0.4, due to the brittleness and the continuous phase transition during the cooling scan, we failed to obtain the sheared films at low temperatures and it was difficult to conduct 2D WAXD experiments on the samples, although we tried different methods. Then by quenching sheared samples from high temperatures, we obtained the 2D patterns of samples PMMS- X_{chol} -0.30 and PMMS- X_{chol} -0.20, which were in accordance with the investigation of liquid crystalline properties we have shown in Fig. 4i. The 2D WAXD pattern in Fig. 11c proved that PMMS- X_{chol} -0.30 formed a typical SmA phase at high temperatures, and a similar pattern and self-assembly structure were also confirmed for PMMS- X_{chol} -0.20.

Sample			Phase Transitions ^b (°C)		
			Heating		<i>c^d</i> (nm)
	$d_{(001)}{}^{a}$ (nm)	$d_{(002)}{}^{a}$ (nm)	Cooling	Lattice parameter ^{<i>a,c</i>} (nm)	
PMMS-X _{chol} -1.00	6.61	3.19	G35.7SmA _d 139.9SmA _s 204.8I I197.9SmA _s 136.65SmA _d 34.6G	_	6.61
PMMS-X _{chol} -0.90	6.61	3.13	G35.6SmA _d ′59.6SmA _d 152.2SmA _s 189.9I I185.5SmA _s 154.9SmA _d 59.0SmA _d ′34.1G	_	6.61
PMMS-X _{chol} -0.80	6.61	3.31	G31.9SmA _d 145.1SmA _s 174.4I I171.8SmA _s 144.6SmA _d 27.8G	_	6.61
PMMS-X _{chol} -0.70	6.16	3.13	G30.3SmA _d 164.4I I161.5SmA _d 28.9G	_	6.16
PMMS-X _{chol} -0.60	6.41	3.24	G22.8SmA _d 132.4I I129.8SmA _d 22.6G	_	6.41
PMMS-X _{chol} -0.50	6.41	3.21	G21.9SmA _d 114.7I I117.7SmA _d 20.1G	_	6.41
PMMS-X _{chol} -0.40	3.05	—	G20.2SmA _s 110.7I I108.3SmA _s 18.6G	_	3.05
PMMS-X _{chol} -0.30	2.96	_	G16.0SmE55.9SmA _s 102.5I I99.83SmA _s 5I.3SmE11.8G	<i>a</i> = 0.81, <i>b</i> = 0.53	2.96
PMMS-X _{chol} -0.20	2.77	_	G7.9SmE70.6SmA _s 80.0I I72.5SmA _s 63.4SmE9.6G	<i>a</i> = 0.81, <i>b</i> = 0.53	2.77
PMMS-X _{chol} -0.15	2.82	_	G9.4SmE53.4SmA _s 79.6I I82.9SmA _s 59.8SmE8.6G	<i>a</i> = 0.81, <i>b</i> = 0.53	2.82
PMMS-X _{chol} -0.10	2.62	_	G11.4SmE′46.8SmE71.9SmA _s 90.0I I76.5SmA _s 71.9SmE57.4SmE′8.91G	<i>a</i> = 0.81, <i>b</i> = 0.53	2.62
PMMS-X _{chol} -0.00	2.62	_	G17.1SmE83.4SmA _s 95.5I 180 5SmA 68 6SmE15 2G	<i>a</i> = 0.81, <i>b</i> = 0.52	2.62

^{*a*} Calculated at the temperature of 40 °C for all the polymers. ^{*b*} According to the DSC results, G: glass state; SmE: Smectic E phase; SmE': Smectic E phase with microphase separation; SmA_s: smectic A phase with a single layer; SmA_d: smectic A phase with a double layer; SmA_d': SmA_d phase with microphase separation; I: isotropic state. ^{*c*} Parameters of the SmE lattice. ^{*d*} The minimize layer spacing of the periodic arrangement.

3.4 Dependence of the phase structure on the two LC building blocks and interplay between them

The SAXS patterns of all the polymers at 40 °C are presented in Fig. 12 and the corresponding *d*-spacing values of the low-angle peaks are summarized in Table 2. Table 2 also lists the calculated lengths (L) of the side groups of the polymers along with the phase transitions of all the polymers. As shown in Fig. 12, the location of the first diffraction peaks of each polymer shifted to the lower angle region with the increased molar ratio of the chiral monomer M1, and had a jump when the chiral molar ratio was changed from 0.40 to 0.50 (with the corresponding d-spacing increased from 3.05 nm to 6.41 nm). Comparing the *d*-spacing of the first diffraction peaks of all the polymers with the calculated lengths of the side group, it is found that the *d*-spacing values were comparable to the calculated lengths of the side chains under the assumption that the alkyl tails were in an all-trans conformation, indicating that the low-angle peak was associated with the size of the side groups, which affected the self-assembly structure. On the other hand, the *d*-spacing of the first diffraction peaks was close to the calculated length of the achiral side group or the chiral side group when the chiral molar ratio was less than 0.4, and close to twice of the calculated length of the chiral side group when the chiral molar ratio was more than 0.4, we speculated that at low-temperatures, a single layer SmE or SmA phase structure was self-organized when the X_{chol} was less than 0.4 and a double layer SmA phase was formed when the X_{chol} was more than 0.4. Furthermore, with the chiral molar ratio changing from 0.00 to 0.40, the *d*-spacing values gradually approached the calculated length of the chiral side group, indicating that the *n*-alkyl tails of the chiral side chain might adopt a partially

interdigitated packing in the initial and a fully extended packing in the end. In other words, the chiral side group might play an important role increasingly in the formation of the self-assembly structure with the chiral molar ratio increasing. It was worth noticing that an obvious microphase-separated structure in the smectic phase morphology was observed when the polymers had an X_{chol} value of about 0.1 or 0.9, respectively, indicating that the introduction of a small amount of any components in the copolymers might destroy the original well-ordered structures.

On the basis of comprehensive analysis and judgment of the DSC, POM, 1D-WAXD, SAXS and 2D-WAXD results, for this series of polymers, two different types of LC phases and three different molecular arrangements were observed, depending on the two LC building blocks. A schematic representation is shown in Fig. 13 which exhibits different self-assembly structures of the polymers with different molar contents of the chiral cholesteric group (X_{chol}) and temperatures.

3.5 The mechanism of the samples exhibiting blue colour

To further investigate the optical properties of the samples and what the interesting characteristics of blue colour represent, a UV/VIS/IR spectra study was conducted, as shown in Fig. 14. An obvious reflection bulge with different intensities between 380 and 500 nm, which corresponded to the blue band, is observed in Fig. 14a and the maximal reflectance could approach 42%. Combining the layered smectic phase structure of the samples and the refractive index difference between the polysiloxane backbone and the rigid aromatic side chain, we speculated that it might form a structure of a one-dimensional photonic crystal which had a periodical variation of the reflective index in a certain direction.^{65,66} The periodical variation of the refractive



Fig. 13 Schematic drawing of the proposed model for the self-assembly of all the polymers with different X_{chol} and temperatures.



Fig. 14 Optical properties of some typical samples at ambient temperature, sample PMMS- X_{chol} -0.20 (quenched) was quenched from the SmA phase, and other samples were obtained by cooling from the isotropic state at 1 °C min⁻¹.

index of the samples, which was derived from the alternative arrangement of the main chain and the side chain, resulted in the reflection of blue colour. However, we noticed that some of the samples did not exhibit apparent blue colour, and the reflection colour of some samples has temperature sensitive characteristics. Fig. 14b shows the transmittance spectra of some typical samples. We can see that the transmittance of the samples with apparent blue colour was much higher than that of the samples without the blue colour. For a representative temperature sensitive sample PMMS- X_{chol} -0.20, the transmittance at higher temperature (corresponded to the quenched sample) was also much higher than that at ambient temperature, and we considered that the unapparent blue colour of samples was associated with the low transmittance, which possibly ascribe to the molecular orientation relative to the substrate.

4. Conclusions

In summary, by efficient thiol-ene click addition chemistry reaction, a series of novel PSCLCPs of PMMS-Xchol-n with different molar ratios of chiral and achiral groups were rationally designed and successfully synthesized. As expected, all the polymers were thermally stable and had low T_{g} values. Their LC phase structures depended greatly on the molar content of the chiral groups. For the polymers with X_{chol} below 0.3, two different types of LC phase structures, a SmE phase at low temperatures and a single layer SmA (SmAs) phase at high temperatures, could be observed. When X_{chol} was between 0.4 and 0.7, the polymers exhibited a single LC phase (SmAs or bilayer SmA, SmA_d) during the whole mesomorphic state. While for polymers with X_{chol} over 0.8, a SmA_d structure was self-assembled at low temperatures, and the LC phase transformed into SmAs upon heating. Additionally, for polymers with X_{chol} about 0.1 or 0.9, respectively, an obvious microphase-separated structure in the

smectic phase morphology was observed, illustrating that the introduction of a small amount of any components in the copolymers might destroy the original well-ordered structures. Interestingly, the periodical variation of the refractive index of the samples, which was derived from the alternative arrangement of the main chain and side chain, results in the reflection of blue colour. It is believed that the newly obtained PSCLCPs with low T_g and abundant LC phase structures will possess interesting properties and potential applications. Future work will be focused on the potential applications of SmE with high carrier mobility in the organic semiconductor field.

Acknowledgements

Financial support from the Major Project of International Cooperation of the Ministry of Science and Technology (Grant No. 2013DFB50340), the National Natural Science Foundation (Grant No. 51203003, 51303008, 51302006, 51373024, and 51573003), the Fok Ying Tung Education Foundation (Grant No. 142009), and the Major Project of Beijing Science and Technology Program (Grant No. Z151100003315023, Z141100003814011) is gratefully acknowledged.

Notes and references

- 1 V. P. Shibaev, I. V. Yakovlev and S. G. Kostromin, *Vysokomol. Soedin., Ser. A*, 1990, **32**, 1552.
- 2 V. P. Shibaev, S. G. Kostromin and S. A. Ivanov, *Polymers as Electroactive and Photooptical Active Media*, Springer, Berlin, 1996, p. 37.
- 3 C. S. Hsu, Prog. Polym. Sci., 1997, 22, 829-871.
- 4 V. P. Shibaev, Vysokomol. Soedin., Ser. A Ser. B, 2014, 56, 593-630.

- 5 R. J. West, Chem. Educ., Organosilicon Chem., Parts I and II, 1980, 57, 165, 334.
- 6 F. Sun, B. Liao, L. Zhang, H. G. Du and Y. D. Huang, *J. Appl. Polym. Sci.*, 2011, **120**, 3604–3612.
- 7 M. L. Swinburne, D. Willmot and D. Patrick, *Eur. J. Orthod.*, 2011, 33, 407–412.
- 8 F. Hosseinzadeh, M. Galehassadi and M. Mahkam, *J. Appl. Polym. Sci.*, 2011, **122**, 2368–2373.
- 9 K. Mojsiewicz-Pienkowska, M. Jamrogiewicz, M. Zebrowska, M. Sznitowska and K. Centkowska, J. Pharm. Biomed. Anal., 2011, 56, 131–138.
- 10 H. Finkelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, 1980, 1, 31–34.
- 11 C. S. Hsu and V. Percec, Polym. Bull., 1987, 18, 91-98.
- 12 C. S. Hsu and V. Percec, J. Polym. Sci., Part A: Polym. Chem., 1987, 25, 2909–2923.
- 13 C. S. Hsu and V. Percec, Polym. Bull., 1987, 17, 49-54.
- 14 C. S. Hsu and V. Percec, *Makromol. Chem., Rapid Commun.*, 1987, **8**, 331–337.
- 15 C. S. Hsu and V. Percec, J. Polym. Sci., Part A: Polym. Chem., 1987, 25, 2909–2923.
- 16 M. A. Apfel, H. Finkelmann, G. M. Janini, R. J. Laub, B. H. Luehmann, A. Price, W. L. Roberts, T. J. Shaw and C. A. Smith, *Anal. Chem.*, 1985, 57, 651–658.
- 17 M. Mauzac, F. Hardouin, H. Richard, M. F. Achard, G. Sigaud and H. Gasparoux, *Eur. Polym. J.*, 1986, **22**, 137–142.
- 18 J. S. Hu, B. Y. Zhang, W. Pan and A. J. Zhou, *Liq. Cryst.*, 2005, 32, 441–447.
- 19 J. S. Hu, S. C. Ren, B. Y. Zhang and C. Y. Chao, J. Appl. Polym. Sci., 2008, 109, 2187–2194.
- 20 J. S. Hu, K. Q. Wei, B. Y. Zhang and L. Q. Yang, *Liq. Cryst.*, 2008, 35, 925–935.
- 21 W. Zhao, B. P. Lin, X. Q. Zhang, Y. Sun and H. Yang, *Chin. J. Polym. Sci.*, 2015, **33**, 1431–1441.
- M. Engel, E. Hisgen, R. Keller, W. Kreuder, B. Reck, H. Ringsdorf, H. W. Schadt and P. Tschirner, *Pure Appl. Chem.*, 1985, 57, 1009–1014.
- 23 S. Diele, B. Hisgen, B. Reck and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, 1986, 7, 267–271.
- 24 L. Y. Zhang, S. Chen, Z. H. Shen, X. F. Chen, X. H. Fan and Q. F. Zhou, *Macromolecules*, 2010, 43, 6024–6032.
- 25 O. Mukbaniani, G. Titvinidze, T. Tatrishvili, N. Mukbaniani,
 W. Brostow and D. Pietkiewicz, J. Appl. Polym. Sci., 2007,
 104, 1176–1183.
- 26 T. Posner, Ber. Dtsch. Chem. Ges., 1905, 38, 646-657.
- 27 V. S. Khire, D. S. W. Benoit, K. S. Anseth and C. N. Bowman, J. Polym. Sci., Part A: Polym. Chem., 2006, 44, 7027–7039.
- 28 V. S. Khire, Y. Yi, N. A. Clark and C. N. Bowman, *Adv. Mater.*, 2008, **20**, 3308–3313.
- 29 V. S. Khire, A. Kloxin, C. L. Clouch, K. S. Anseth and C. N. Bowman, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, 46, 6896–6906.
- 30 J. Justynska and H. Schlaad, Macromol. Rapid Commun., 2004, 25, 1478–1481.
- 31 J. Justynska, H. Hordyjewicz and H. Schlaad, *Polymer*, 2005, 46, 12057–12064.

- 32 J. Justynska, H. Hordyjewicz and H. Schlaad, *Macromol. Symp.*, 2006, **240**, 41–46.
- 33 C. Y. Li, M. J. Birnkrant, L. V. Natarajan, V. P. Tondiglia, P. F. Lloyd, R. L. Sutherland and T. J. Bunning, *Soft Matter*, 2005, 1, 238–242.
- 34 M. J. Birnkrant, H. K. McWilliams, C. Y. Li, L. V. Natarajan, V. P. Tondiglia, R. L. Sutherland, P. F. Lloyd and T. J. Bunning, *Polymer*, 2006, 47, 8147–8154.
- 35 E. H. Charles and C. N. Bowman, Angew. Chem., Int. Ed., 2010, 49, 1540–1573.
- 36 B. L. Andrew, Polym. Chem., 2010, 1, 17-36.
- 37 H. Yang, L. X. Wang, R. F. Shao, N. A. Clark, J. COrtega, J. Etxebarria, P. A. Albouy, D. M. Walba and P. Keller, *J. Mater. Chem.*, 2009, **19**, 7208–7215.
- 38 H. Yang, J. M. Richardson, D. M. Walba, C. H. Zhu, R. F. Shao, N. A. Clark, J. Ortegad, J. Etxebarriae and P. Keller, *Liq. Cryst.*, 2010, 37, 325–334.
- 39 H. Yang, Q. Zhang, B. P. Lin, G. D. Fu, X. Q. Zhang and L. X. Guo, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, 50, 4182–4190.
- 40 H. Yang, M. X. Liu, Y. W. Yao, P. Y. Tao, B. P. Lin, P. Keller, X. Q. Zhang, Y. Sun and L. X. Guo, *Macromolecules*, 2013, 46, 3406–3416.
- 41 H. Yang, Y. J. Lv, B. P. Lin, X. Q. Zhang, Y. Sun and L. X. Guo, J. Polym. Sci., Part A: Polym. Chem., 2014, 52, 1086–1098.
- 42 H. Yang, A. Buguin, J. M. Taulemesse, K. Kaneko, S. Méry,
 A. Bergeret and P. Keller, *J. Am. Chem. Soc.*, 2009, 131, 15000–15004.
- 43 H. Yang, J. J. Liu, Z. F. Wang, L. X. Guo, P. Keller, B. P. Lin,
 Y. Sun and X. Q. Zhang, *Chem. Commun.*, 2015, 51, 12126–12129.
- 44 D. M. Walba, H. Yang, R. K. Shoemaker, P. Keller, R. Shao and D. A. Coleman, *Chem. Mater.*, 2006, **18**, 76–84.
- 45 C. Y. Li, S. Z. D. Cheng, J. J. Ge, F. Bai, J. Z. Zhang and I. K. Mann, *J. Am. Chem. Soc.*, 2000, **122**, 72–79.
- 46 A. C. Charif, N. Diorio, K. Fodor-Csorba, J. E. Puskas and A. Jakli, *RSC Adv.*, 2013, 3, 17446–17452.
- 47 L. L. Hsu, T. C. Chang, W. L. Tsai and C. D. Lee, J. Polym. Sci., Part A: Polym. Chem., 1997, 35, 2843–2855.
- 48 M. Kozlovsky and K. Skarp, J. Polym. Sci., Part B: Polym. Phys., 2005, 43, 1779–1784.
- 49 B. Helgee, T. Hjertberg, K. Skarp, G. Andersson and F. Gouda, *Liq. Cryst.*, 1995, **18**, 871–878.
- 50 Z. H. Cheng, H. Cao, D. Y. Zhao, W. Hu, W. L. He, X. T. Yuan, J. M. Xiao, H. Q. Zhang and H. Yang, *Liq. Cryst.*, 2011, 38, 9–15.
- 51 X. J. Wu, H. Cao, R. W. Guo, K. X. Li, F. F. Wang, Y. Z. Gao, W. H. Yao, L. Y. Zhang, X. F. Chen and H. Yang, *Macromolecules*, 2012, 45, 5556–5566.
- 52 X. F. Zhang, L. Y. Zhang, J. F. Tan, X. J. Wu, B. R. Li, F. F. Wang, H. Yang and Z. Yang, *J. Mater. Sci.*, 2014, 49, 4927-4937.
- 53 H. Tang, Z. G. Zhu, X. H. Wan, X. F. Chen and Q. F. Zhou, *Macromolecules*, 2006, **39**, 6887–6897.
- 54 P. Gopalan and K. C. Ober, *Macromolecules*, 2001, 34, 5120-5124.

- 55 H. L. Xie, T. H. Hu, X. F. Zhang, H. L. Zhang, E. Q. Chen and Q. F. Zhou, J. Polym. Sci., Part A: Polym. Chem., 2008, 46, 7310–7320.
- 56 C. G. Nardele and S. K. Asha, J. Phys. Chem. B, 2014, 118, 1670–1684.
- 57 M. Takahito, Y. Yasuhisa, H. Mafumi, N. Shigenori, M. A. Maria and S. Kazuya, *J. Phys. Chem. B*, 2013, **117**, 8293–8299.
- 58 H. L. Xie, C. K. Jie, Z. Q. Yu, X. B. Liu, H. L. Zhang, Z. H. Shen, E. Q. Chen and Q. F. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 8071–8080.
- 59 Q. W. Pan, X. F. Chen, X. H. Fan, Z. H. Shen and Q. F. Zhou, *J. Mater. Chem.*, 2008, **18**, 3481–3488.
- 60 Y. D. Xu, W. Qu, Q. Yang, J. K. Zheng, Z. H. Shen, X. H. Fan and Q. F. Zhou, *Macromolecules*, 2012, **45**, 2682–2689.

- 61 L. Y. Zhang, Q. K. Zhang and Y. D. Zhang, *Liq. Cryst.*, 2013, 40, 1263–1273.
- 62 V. Percec, T. K. Bera, M. Glodde, Q. Y. Fu, V. S. K. Balagurusamy and P. A. Heiney, *Chem. – Eur. J.*, 2003, 9, 921–935.
- 63 S. Chen, L. C. Gao, X. D. Zhao, X. F. Chen, X. H. Fan, P. Y. Xie and Q. F. Zhou, *Macromolecules*, 2007, 40, 5718–5725.
- 64 Y. H. Cheng, W. P. Chen, Z. H. Shen, X. H. Fan, M. F. Zhu and Q. F. Zhou, *Macromolecules*, 2011, 44, 1429–1437.
- 65 R. Yagi, H. Katae, Y. Kuwahara, S. N. Kim, T. Ogata and S. Kurihara, *Polymer*, 2014, 55, 1120–1127.
- 66 M. Moritsugu, T. Ishikawa, T. Kawata, T. Ogata, Y. Kuwahara and S. Kurihara, *Macromol. Rapid Commun.*, 2011, 32, 1546–1550.