

Tunable Phase Structure of Side-chain Liquid Crystalline Polymers Enabled by Molecular Engineering of Dual Mesogenic Cores

Wen-Huan Yao^{a,b*}, Lan-Sheng Liu^b, Jie Zhao^b, Yan-Xia Wang^b, An-Zhi Ma^b, Zheng-Rui Ma^b, Lan-Ying Zhang^{c*}, and Ruo-Chen Lan^{d*}

^a College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

^b Key Laboratory of Eco-Functional Polymer Materials of the Ministry of Education, Key Laboratory of Eco-Environmental Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

^c Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

^d Institute of Advanced Materials & Key Lab of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

Abstract A series of novel side-chain liquid crystalline (SCLC) copolymers were synthesized by attaching two distinct mesogenic units, namely a chiral cholesteryl-based monomer (M1) and an achiral biphenyl-based monomer (M2), to a poly(3-mercaptopropylmethylsiloxane) (PMMS) backbone via thiol-ene click chemistry. The influence of side chain composition on the self-assembly behavior and phase structures of these SCLC copolymers was systematically investigated using different instrument. Results indicate that three distinct liquid crystalline phases and four unique molecular configurations were identified within the polymer series, with the emergence of the liquid crystalline phase being a synergistic outcome of the two distinct side chains. This study underscores the critical influence of side chain dimensions, rigidity, and spatial volume on the self-assembly structures and phase characteristics of liquid crystalline polymers, providing valuable insights for the rational design and development of advanced functional materials with tailored properties.

Keywords Liquid crystalline copolymers; Self-assembly; Phase structure; Chiral molar ratio

Citation: Yao, W. H.; Liu, L. S.; Zhao, J.; Wang, Y. X.; Ma, A. Z.; Ma, Z. R.; Zhang, L. Y.; Lan, R. C. Tunable phase structure of side-chain liquid crystalline polymers enabled by molecular engineering of dual mesogenic cores. *Chinese J. Polym. Sci.* 2024, 42, 1459–1469.

INTRODUCTION

Side-chain liquid crystalline (SCLC) copolymers, characterized by two or more types of mesogenic groups attached to the polymer backbone as side chains, represent a fascinating class of materials that combine the unique properties of liquid crystals with the versatility of copolymer chemistry. These materials have garnered significant attention in the field of polymer science due to their potential applications in various technological domains, including display technologies, sensors, artificial muscles, and actuators.^[1–4]

The versatility of SCLC copolymers arises from the ability to tailor their properties through attaching different side chains with specific functions. Beyond the influence of the common affecting factors, such as backbone flexibility/rigidity,^[5–8] length of flexible spacers,^[9–11] mesogenic content density,^[12–14] molecular weight,^[15–17] topology structure,^[18–22] size^[23–25] and polarity^[26] of the terminal flexi-

ble substituents along with the architecture,^[27–29] on the self-assembly behavior and phase structures of SCLC polymers, the coexistence of multiple mesogenic groups, the ratio and the interactions between them also play a crucial role in determining the characteristics of the resulting self-assembled structures of SCLC copolymers.^[30–36] This tailor-made approach allows for the fine-tuning of characteristics, such as the transition temperatures,^[32,36–38] mechanical strength,^[38,39] and optical properties,^[35,37] which are crucial for the performance of the material in specific applications. For instance, the incorporation of more flexible or rigid monomers can enhance the mechanical flexibility and the thermal stability of the copolymer,^[37,38,40] and the inclusion responsive groups can endow the copolymer responsiveness to external stimuli, such as temperature, light, pressure, humidity, electric/magnetic fields, and solvent exposure, to create smart materials can respond to their environment, providing a dynamic and interactive platform for various applications.^[2,41–46]

In this work, we report the synthesis and characterization of a series of novel SCLC copolymers bearing both chiral cholesteryl-based and achiral biphenyl-based mesogenic units attached to a poly[3-mercaptopropylmethylsiloxane] (PMMS) backbone via thiol-ene click chemistry. By varying the molar ratio of the chiral monomer to the achiral monomer, we aim to elucidate the influence of side chain composition

* Corresponding authors, E-mail: wenhuanyao@163.com (W.H.Y.)
E-mail: zhanglanying@pku.edu.cn (L.Y.Z.)
E-mail: lanruochen@pku.edu.cn (R.C.L.)

Special Issue: Dynamic Polymer Networks

Received April 26, 2024; Accepted May 19, 2024; Published online August 20, 2024

on the self-assembly behavior and phase structures of these SCLC copolymers, provide valuable insights into the complex interplay between chiral and achiral mesogenic units in SCLC copolymers and how their relative proportions dictate the self-assembly behavior and phase structures of these materials.

EXPERIMENTAL

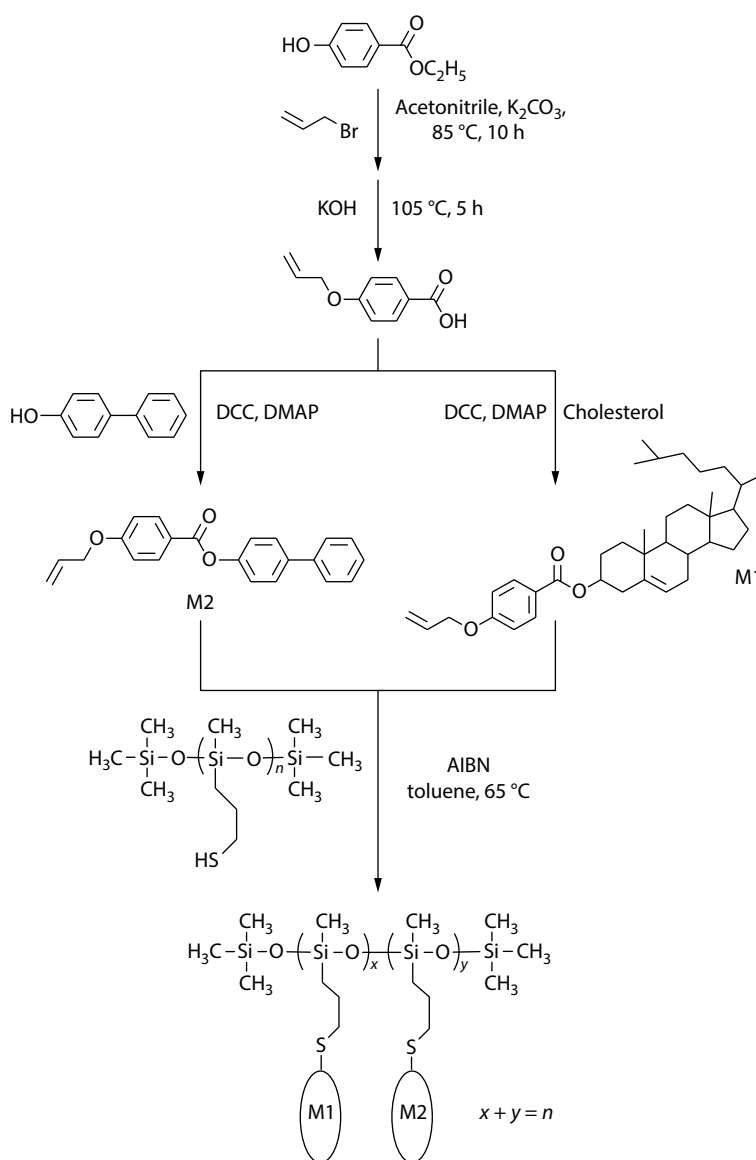
Materials

The materials used in this study include poly(3-mercaptopropylmethylsiloxane) (PMMS, SMS-992, M.W. 4000–7000, 95 cst, Gelest Inc.), ethylparaben (A.R. grade, Sinopharm), cholesterol (A.R. grade, Sinopharm), 3-bromopropene (98%, Beijing Dominant Technology Co.), dimethylaminopyridine (DMAP, 99%, Energy Chemical), *N,N'*-dicyclohexylcarbodiimide (DCC, 98%, Energy Chemical), 4-phenylphenol (98 %, Sinopharm Chemical Reagent Co., Ltd.),

potassium hydroxide (A.R. grade, Beijing Chemical Reagents Co.) and anhydrous potassium carbonate (A.R. grade, Beijing Chemical Reagents Co.). These were utilized without further purification. Toluene (A.R. grade, Beijing Chemical Reagents Co.) was prepared by refluxing over sodium and distilling under a nitrogen atmosphere prior to use. Azodiisobutyronitrile (AIBN) (A.R. grade, Beijing Dominant Technology Co.) was purified by recrystallization in ethanol. All other chemical reagents were used as received without any modification.

Measurements

The materials were characterized using ^1H -NMR spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized optical microscopy (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), following the protocols as previously described procedures.^[36]



Scheme 1 Synthetic routes to the monomers and polymers.

Synthesis

Scheme 1 outlines the synthetic pathway for the precursors, monomers, and target polymers. Precursor 4-(allyloxy) benzoic acid and monomers, cholesteryl-4-(allyloxy) benzoate (M1) and [1,1'-biphenyl]-4-yl 4-(allyloxy) benzoate (M2), were synthesized using methodologies detailed in our previously published literature.^[36]

Synthesis of the Copolymers

The copolymers were synthesized with minor modifications to the literature methods.^[36,47] The preparation of P-2 is described as an illustrative example. M1 (344.60 mg, 0.63 mmol), M2 (831.60 mg, 2.52 mmol), PMMS (412.80 mg, 3.00 mmol —SH), AIBN (49.26 mg, 0.10 mmol) and toluene (4.87 mL) were introduced into a polymerization tube. After degassing and nitrogen exchange through three freeze-thaw cycles, the tube was sealed under vacuum conditions. The reaction was carried out at 65 °C for 24 h. Subsequently, the crude polymer was precipitated by pouring the reaction mixture into methanol, and further purified by dissolving in chloroform, followed by several precipitations from methanol to remove excess unreacted monomers. The polymer was dried under vacuum, yielding a white powder with a purity of 86.3%.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Copolymers

As depicted in **Scheme 1**, the monomers were synthesized with high efficiency through a series of reactions, beginning with the Williamson etherification and concluding with the Steglich esterification. All polymers were obtained in high yields (>86%) via the thiol-ene addition reaction using AIBN as the initiator. The chemical structures of the precursors, monomers, and target polymers were unambiguously confirmed by ¹H-NMR spectroscopy.

Fig. 1 presents the ¹H-NMR spectra of the chiral monomer M1, the achiral monomer M2, the backbone PMMS, and all the synthesized polymers, respectively. The absence of vinyl group signals from the monomers at 6.05, 5.43 and 5.31 ppm, and the thiol group signal from PMMS at 1.37 ppm in the polymer spectra confirms the complete consumption of PMMS and removal of the monomers during the polymerization. The emergence of proton peaks corresponding to aromatic rings and silicomethyl groups at 0.11 ppm verifies the successful incorporation of the monomers and PMMS into the

polymer structure. Moreover, an inverse relationship is observed between the integral areas of signals at 4.81 ppm (—O—CH— in cholesteryl moiety of M1) and 8.15 ppm (proton peaks of aromatic of M2), as highlighted by the red dotted boxes. The actual molar fractions of M1 in each polymer, relative to the (M1 + M2) ratio, are calculated and summarized in **Table 1**. Interestingly, these fractions are higher than those in the initial feed, suggesting that the substituted vinyl monomer M1, with its larger and more rigid substituent, exhibits greater reactivity than M2. This finding is consistent with our previous observations.^[36,48]

Table 1 and **Fig. 2(a)** present the results of the GPC measurements, which reveal a trend where the number-average molecular weight ($\bar{M}_n$) of the polymers decreases with an increasing proportion of M2. This trend is also reflected in the $\bar{M}_n$ values calculated based on ¹H-NMR results, which can be attributed to the higher molecular weight of M1 compared to M2. Additionally, the copolymers exhibit a broad molecular weight distribution, which is inherited from the polymeric starting material, PMMS.

Thermal and Liquid-Crystalline Properties of Copolymers

The thermal and liquid-crystalline properties of these polymers were thoroughly investigated using DSC, TGA and POM analy-

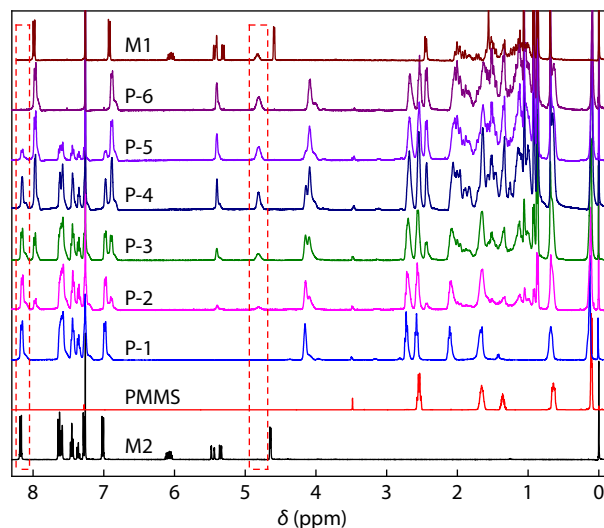


Fig. 1 ¹H-NMR spectra of monomers, PMMS, and polymers in CDCl₃.

Table 1 Thermal properties and molecular characterization of polymers.

Sample	M1/(M1 + M2) (MR) ^a		T_g ^c (°C)	T_i ^c (°C)	$\bar{M}_n$ (g/mol)		PDI ^d	T_d ^e (°C)	ΔT ^f (°C)	Yield (%)
	In feed	Calculated ^b			GPC ^d	Calculated ^b				
PMMS	—	—	—	—	800	6192	2.53	—	—	—
P-1 ^g	0.00	0.000	21.1	133.2	2400	21042	1.67	354	112.1	91.6
P-2	0.20	0.216	31.2	137.1	2900	23132	1.97	329	105.9	86.3
P-3	0.40	0.409	26.3	148.4	3200	25036	1.88	326	122.1	88.5
P-4	0.60	0.613	29.4	173.9	3900	27028	1.71	325	144.5	91.5
P-5	0.80	0.811	30.8	183.1	4400	28961	1.70	324	152.3	89.4
P-6 ^g	1.00	1.000	35.7	204.8	4800	30852	2.04	337	169.1	91.2

^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; ^e 5% Weight loss temperature was evaluated by TGA at a rate of 20 °C/min; ^f Mesogenic temperature ranges determined by $T_i - T_g$; ^g The data of P-1 and P-6 referenced as P-4 and PMMS- $X_{\text{chol}}=1.00$ in Refs. [20] and [36], respectively, and listed here for comparison only.^[20,36]

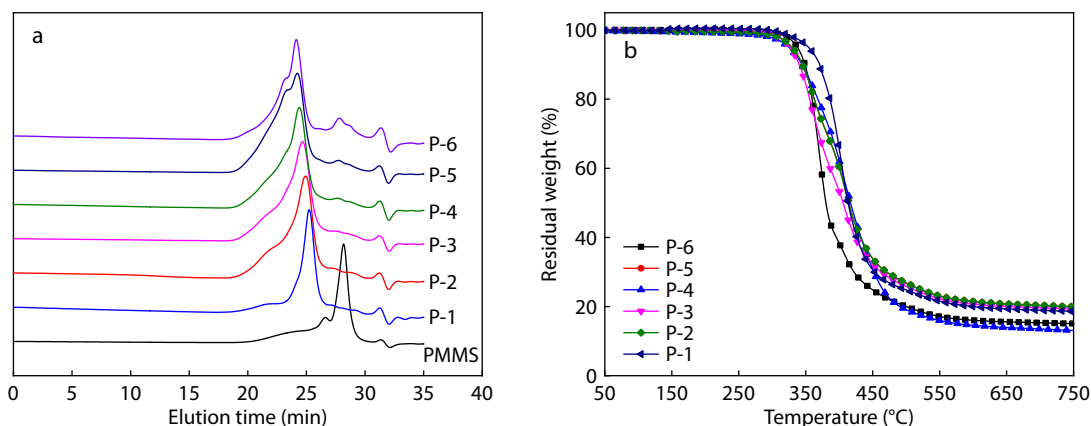


Fig. 2 (a) GPC curves of all the polymers and PMMS; (b) TGA thermograms of polymers in nitrogen at a rate of 20 °C/min.

ses. The results, summarized in Table 1 and Fig. 2(b), highlight the exceptional thermal stability of the copolymers. The TGA curves reveal that the temperature at which the copolymers experienced a 5% weight loss exceeds 324 °C under a nitrogen atmosphere. Interestingly, a slight decrease in thermal stability is observed with increasing content of the chiral cholesteric monomer M1. This observation suggests that the benzene ring structure in M2 contributes to a higher thermal stability compared to the cholesteryl group in M1.

The phase transition characteristics of the copolymers were

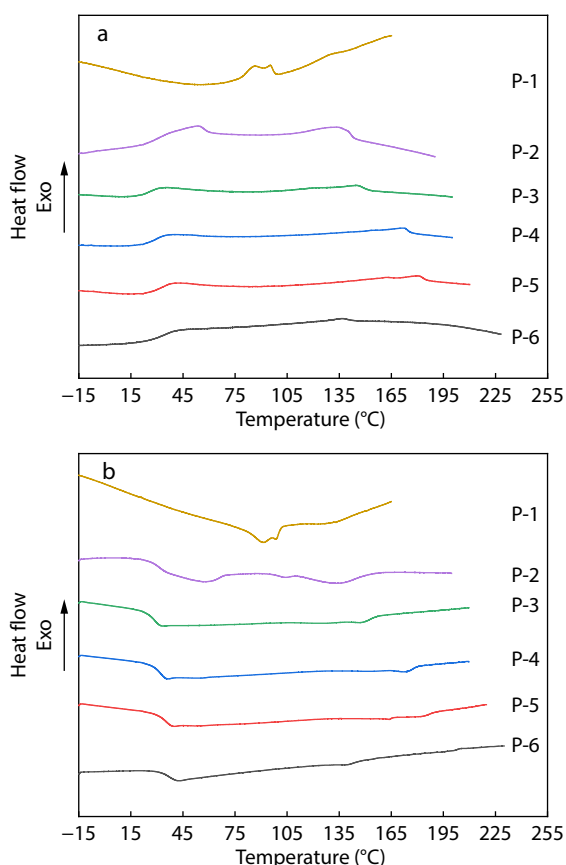


Fig. 3 DSC thermograms of the homopolymers during (a) the first cooling and (b) subsequent second heating scans at a rate of 10 °C/min.

investigated using DSC experiments, and the results presented in Fig. 3. To minimize the impact of prior thermal history, DSC scans were conducted during the initial cooling and subsequent second heating cycles at a rate of 10 °C/min under a controlled nitrogen atmosphere. The copolymers exhibited diverse liquid-crystalline phases, identifiable by their characteristic thermal transitions. For instance, copolymers P-2 and P-5 displayed three or four distinct exothermic/endothermic peaks during their cooling/heating processes, whereas copolymers P-3 and P-4 exhibited only two peaks. This pattern suggests the potential existence of multiple mesophase structures within the mesogenic temperature ranges for P-2 and P-5, in contrast to the single mesophase observed for P-3 and P-4. Consistent with our expectations, the glassy transition temperature (T_g) and the clearing point temperature (T_i) of the copolymers increased progressively with increasing content of the rigid monomer M1, reflecting the modulated side chain rigidity. Remarkably, due to the synergistic effect of the flexible polysiloxane backbone PMMS and the less rigid side chains, the T_g of the copolymers remained below 31.2 °C.

The liquid crystalline birefringence of all copolymers was observed under POM with powder samples, and representative textures are displayed in Fig. 4. Pronounced birefringence was observed for samples P-2, P-3 and P-5 during cooling at specific temperatures of 135, 142 and 177 °C, respectively. These temperatures were slightly lower than the mesophase transitions identified in the DSC analysis, attributing to the super cooling. The observation of birefringence confirms the presence of liquid-crystalline phases in these copolymers and provides valuable insights into their mesomorphic behavior.

For samples P-2 and P-5, as clearly depicted in Figs. 4(a)–4(c) and Figs. 4(g)–4(i), a focal-conic texture emerged upon cooling from the isotropic state to 135 and 177 °C, respectively. These textures are characteristic of a smectic liquid-crystalline phase. As the temperature decreased further to 130 °C for P-2 and 154 °C for P-5, a fascinating coexistence of focal-conic and fan-shaped textures became evident. This dual texture persisted essentially unchanged down to room temperature, despite the observation of three and two phase transitions in the DSC experiments for P-2 and P-5, respectively. The only discernible change was a subtle alteration in color. The appearance of fan-shaped texture, which are charac-

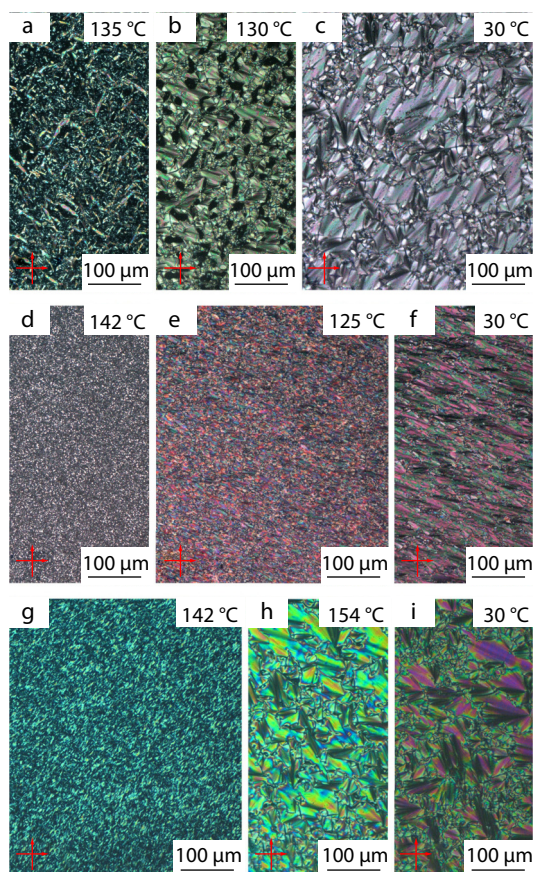


Fig. 4 Representative textures of samples (a–c) P-2, (d–f) P-3, and (g–i) P-5 at different temperatures cooled from isotropic state.

teristic of smectic liquid crystalline phase,^[49,50] suggests that P-2 and P-5 may possess a series of sub-smectic phase throughout their entire mesomorphic temperature range.

In contrast, copolymer P-3 exhibited a unique behavior. Initially, a gritty texture was observed as the sample cooled from the isotropic state to 142 °C, as depicted in Figs. 4(d) and 4(e). This texture evolved into a fan-shaped pattern upon further cooling to 125 °C, which was retained at room temperature, accompanied by subtle color variations (Fig. 4f).

Overall, the appearance of the fan-shaped texture, which is a characteristic of a smectic liquid crystalline phase, indicates that P-2, P-3, and P-5 may all possess a series of sub-smectic phase throughout their entire mesomorphic temperature range.

Phase Structures and Phase Transition Identification

To systematically explore the existence of phase transitions within the mesogenic state and the self-assembly structures of all polymers, comprehensive studies were conducted using variable-temperature 1D-WAXD, SAXS, and 2D-WAXD experiments.

Fig. 5(a) and Fig. 5(b) present the 1D-WAXD and SAXS patterns of P-2 throughout the heating process, respectively. At low temperatures, a distinct diffraction peak with a q ($q = 4\pi\sin\theta/\lambda$) value of 2.12 nm^{-1} (corresponding to a d -spacing of 2.96 nm) is detected in the low-angle region. Additionally, three diffraction peaks in the high-angle region, with q values of 14.19 , 15.33 and 19.75 nm^{-1} , indicate the existence of molecular packing at the sub-nanometer scale. The combination of these diffraction peaks suggests the existence of a smectic phase characterized by highly ordered molecular packing. Upon heating to 70 °C , two peaks in the high-angle region, specifically those with q values of 15.33 and 19.75 nm^{-1} , disappear completely. Meanwhile, the peak at a q val-

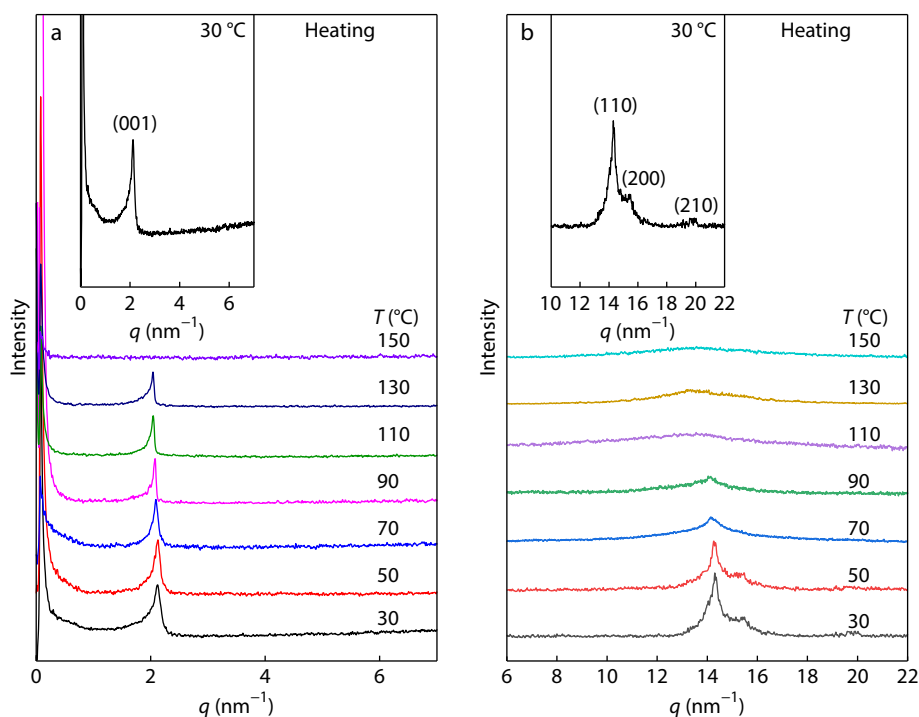


Fig. 5 (a) SAXS (the inset shows the enlarged patterns in the low-angle region) and (b) 1D-WAXD (the inset shows the enlarged patterns in the high-angle region) patterns of P-2 during the heating process.

ue of 14.19 nm^{-1} weakens, and shifts to a slightly lower angle (14.16 nm^{-1} , corresponding to a d -spacing of 0.44 nm). The sharp diffraction peak observed in the low-angle region persists, indicating the loss of molecular packing at the sub-nanometer scale and the emergence of a new phase. As the temperature reaches 110°C , the diffraction pattern in the high-angle region transforms into an amorphous broad halo, with a blue shift in the centre position. Concurrently, the intensity of the low-angle region diffraction peak decreases while shifting to an even lower angle (2.04 nm^{-1}). These alterations suggest further loss of molecular packing on the sub-nanometer scale and the formation of a simple smectic phase structure, resembling SmA or smectic C (SmC). Upon further heating to 145°C , the low-angle diffraction peak disappears, and the high-angle scatter halo becomes more diffuse, indicating that sample P-2 has entered the isotropic state.

Notably, the variations observed in the diffraction patterns of copolymer P-2 closely resemble those previously reported for homopolymer P-1, which exhibited a phase transition sequence of $G \leftrightarrow \text{Smectic E} \leftrightarrow \text{Smectic B} \leftrightarrow \text{Smectic A} \leftrightarrow \text{Iso}$.^[20] The sole distinction between copolymer P-2 and homopolymer P-1 lies in the minor inclusion of the chiral monomer M1 in the side chain composition of P-2. Given this similarity and considering the fan-shaped texture captured by POM analysis, along with the four phase transitions detected in the DSC traces, we hypothesize that copolymer P-2 likely exhibits a comparable phase transition sequence to that of homopolymer P-1.

Based on our observations, we infer that the self-assembly structure of copolymer P-2 at lower temperatures is likely the smectic E (SmE) phase, characterized by the low-angle diffraction peak attributed to the (001) plane and the three high-an-

gle diffraction peaks corresponding to the (110), (200), and (210) planes of SmE, with lattice parameters a and b measuring 0.82 and 0.54 nm , respectively.^[20,32,36,51] Upon heating to intermediate temperatures, a loosely hexagonal packed smectic B (SmB) phase emerges from the SmE phase with an orthorhombic structure. Furthermore, at higher temperatures, the low-angle diffraction peak and the high-angle amorphous broad halo suggest that P-2 adopts a simple smectic phase structure, resembling either SmA or SmC.

In contrast, the self-assembly behavior of P-5 and P-3 differs significantly from that of P-2, as shown in Figs. 6 and 7 across various temperatures, respectively. Notably, both samples exhibited a broad amorphous halo in the high-angle regions during the heating process, indicating a lack of nanometer-scale ordered molecular packing. In the case of sample P-3, only a single diffraction peak with q value of 2.04 nm^{-1} (corresponding to a d -spacing of 3.08 nm) was observed prior to entering the isotropic state. However, for sample P-5, below 165°C , two distinct diffraction peaks with q values of 0.97 and 1.93 nm^{-1} (featuring a scattering vector ratio of 1:2 and corresponding d -spacings of 6.48 and 3.26 nm , respectively) were observed, suggestive of a characteristic layer structure. Upon further heating, the first sharp diffraction peak vanishes, while the second one persists and becomes more intense, signaling the emergence of a new liquid crystalline phase. As the temperature reaches 190°C , the low-angle diffraction peak disappears, and the high-angle amorphous broad halo becomes increasingly diffuse, indicating the transition of the sample into the isotropic state. The fan-shaped texture observed in POM and the layer spacing of P-5 (approximately twice that of P-3) suggest a double layer arrangement in P-5, akin to samples with a M1 molar ratio exceeding 0.4 in prior studies.^[36]

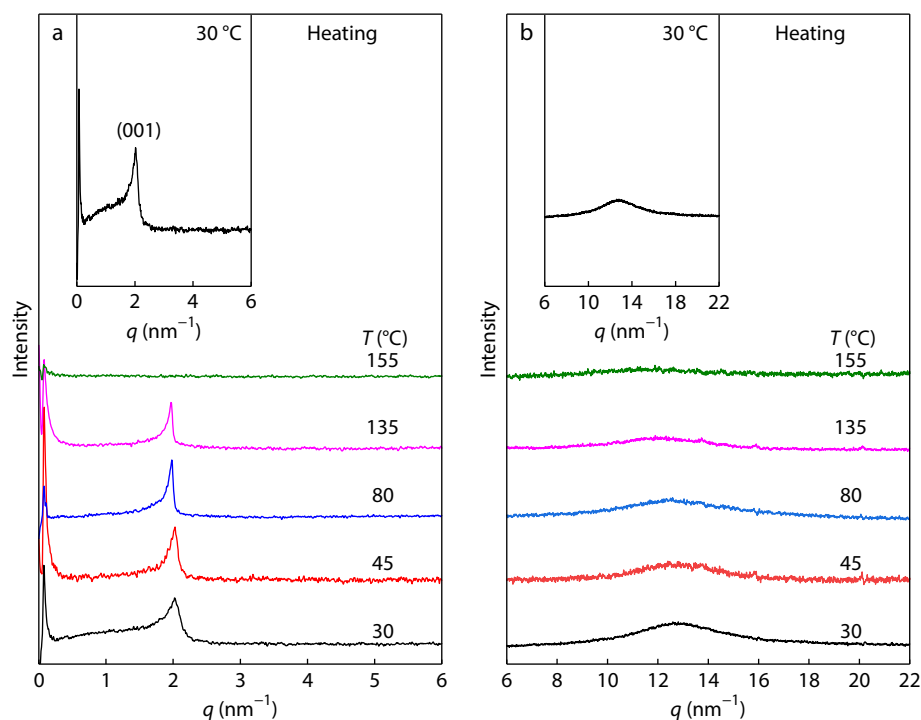


Fig. 6 (a) SAXS (the inset shows the enlarged patterns in the low-angle region) and (b) 1D-WAXD (the inset shows the enlarged patterns in the high-angle region) patterns of P-3 during the heating process.

The DSC traces, 1D-WAXD and SAXS patterns of copolymer P-4 are highly similar to those of P-3, confirming their analogous phase transition behavior and self-assembly structures.

Given the limitations of 1D-WAXD and SAXS patterns in terms of dimensionality, 2D-WAXD experiments were conducted to accurately identify the smectic structures of all the copolymers. For samples other than P-2, the specimens were mechanically sheared and annealed at varying temperatures after cooling from the isotropic state. However, for sample P-2, its unexpected brittleness and continuous phase transition during cooling precluded the successful formation of sheared films at low temperatures. Fortunately, we overcame this challenge by employing a quenching procedure, which allowed us to obtain sheared films at high temperatures.

Fig. 8 shows representative 2D-WAXD patterns of selected copolymers recorded at room temperature, with the X-ray incident beam aligned perpendicular (along the Z direction) to the shear direction (X direction). On the equator, one or two pairs of strong diffraction arcs corresponding to the low-

angle diffraction peaks are clearly visible, indicating the development of an ordered structure parallel to the shear direction on the nanometer scale. Additionally, two scattering halos in the high-angle region are more or less focused on the meridians, exhibiting a relatively broad azimuthal distribution at low angles. This indicating the existence of only short-range order along the shear direction. In conclusion, the 2D-WAXD patterns demonstrate the presence of a typical SmA phase structure in these polymers.^[52,53]

Dependence of Phase Structures on the Two LC Building Blocks and Their Interplay

Fig. 8 and Table 2 provide an in-depth analysis of the phase transition temperatures and minimized layer spacings, highlighting the dependency of these properties on polymer composition. As illustrated in Fig. 8, a noticeable trend emerges in the minimized layer spacing (denoted as c) of the periodic smectic phase for each polymer. Intriguingly, an increase in the molar ratio of the chiral monomer M1 is correlated with an ex-

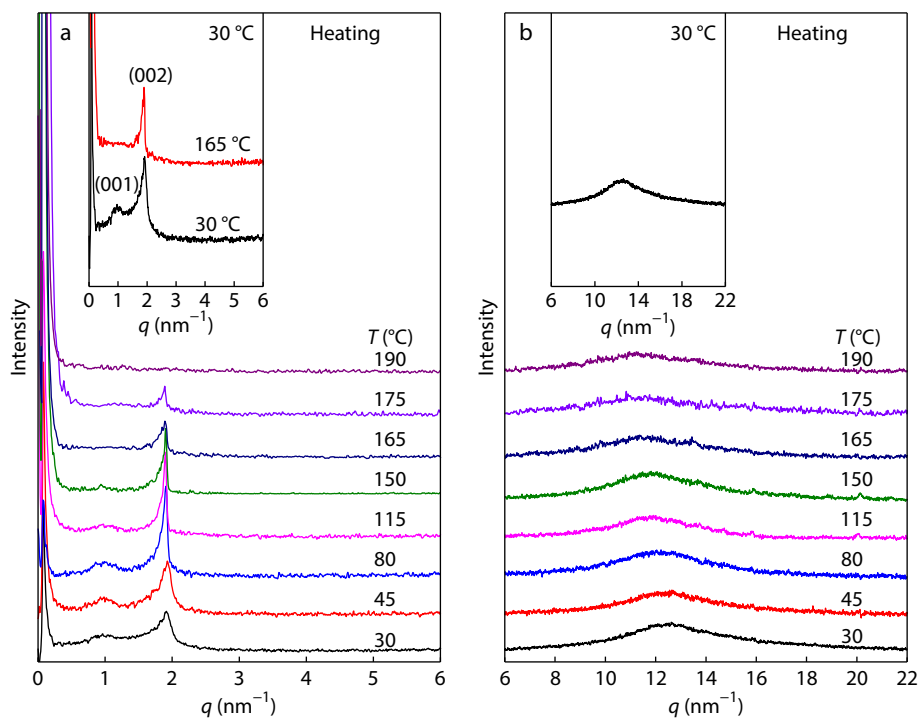


Fig. 7 (a) SAXS (the inset shows the enlarged patterns in the low-angle region) and (b) 1D-WAXD (the inset shows the enlarged patterns in the high-angle region) patterns of P-5 during the heating process.

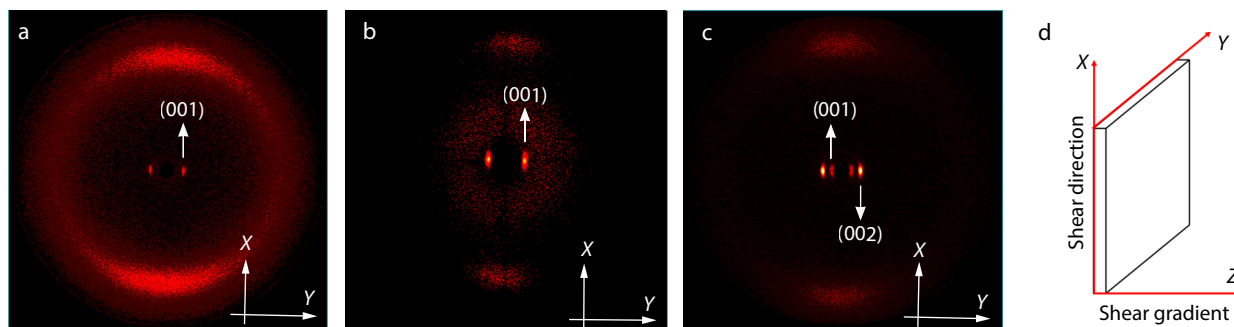


Fig. 8 2D-WAXD patterns of (a) P-2, (b) P-4, and (c) P-5 recorded at room temperature, and (d) the shear geometry.

Table 2 *d*-Spacing, phase transition, and lattice parameter of homopolymers.

Sample	$d_{(001)}$ ^a (nm)	$d_{(002)}$ ^a (nm)	Phase transitions ^b (°C)	Lattice parameter ^a (nm)	c ^c (nm)
			Heating		
			Cooling		
P-1 ^d	2.90	—	G21.1SmE90.6SmB98.9SmA _s 133.3Iso Iso129.6SmA _s 95.5SmB85.8SmE19.1G	$a=0.81$, $b=0.52$	2.90
P-2	2.96	—	G31.2SmE60.5SmB103.7SmA _s 137.2Iso Iso137.0SmA _s 108.6SmB54.5SmE29.0G	$a=0.82$, $b=0.54$	2.96
P-3	3.08	—	G26.3SmAs148.4Iso Iso145.4SmAs24.9G	—	3.08
P-4	3.17	—	G29.4SmAs173.9Iso Iso172.6SmAs28.2G	—	3.17
P-5	6.48	3.26	G30.8SmA _d 163.5SmA _s 183.1Iso Iso181.0SmA _s 162.1 SmA _d 30.1G	—	6.48
P-6 ^d	6.61	3.19	G35.7SmA _d 139.9SmA _s 204.8Iso Iso197.9SmA _s 136.6SmA _d 34.6G	—	6.61

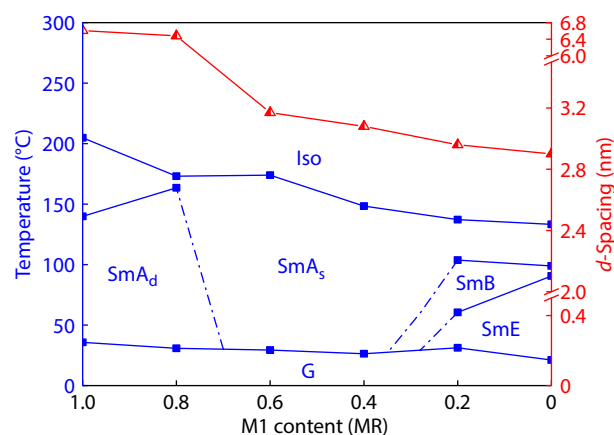
^a Calculated at room temperature for all the polymers and according to the XRD results; ^b According to the DSC results; G: glassy state; SmA_s: smectic A phase with single layer; SmA_d: smectic A phase with double layer; SmB: smectic B phase; SmE: smectic E phase; Iso: isotropic state; ^c Minimized layer spacing of the periodic arrangement; ^d The data of P-1 and P-6 referenced as P-4 and PMMS-*X*_{chol}-1.00 in Refs. [20] and [36], respectively, and listed here for comparison only.^[20,36]

pansion in layer spacing. A pronounced leap in the measured c from 3.17 nm to 6.48 nm is observed as the chiral molar ratio increases from 0.6 to 0.8.

Assuming an all-trans conformation for the alkyl tails, the theoretical lengths of the side chains are calculated to be 2.50 nm (L_2) for the achiral side chain and 3.09 nm (L_1) for the chiral side chains. A comparative analysis between the measured c and the respective side chain lengths yields valuable insights. For P-2, the measured c exceeds L_2 by 0.46 nm and falls short of L_1 by 0.13 nm. In the case of P-3, the measured c closely approximates L_1 . In contrast, for P-4 and P-5, the measured c surpasses L_1 by 0.08 nm and $2L_1$ by 0.30 nm, respectively. These observations suggest that the self-assembly structure of these polymers is influenced by the dimensions of the side chains.

In essence, the side chains from adjacent backbone units in the smectic structures are substantially interdigitated, ensuring a parallel and tightly packed alignment of the mesogen units. It is plausible that in P-2, the *n*-alkyl tails of the chiral side chains engage in a partial interdigitation, whereas a fully extended packing is observed in P-3, P-4 and P-5. Notably, the chiral side groups play an increasingly crucial role in the formation of the self-assembly structure as the chiral molar ratio increases. Upon reaching a chiral molar ratio of 0.8, the periodic smectic arrangement of the structure is predominantly governed by chiral monomer, resulting in a marked alteration in the measured layer spacing (Fig. 9).

In contrast to the series of SCLC polymers constructed from a poly(3-mercaptopropylmethylsiloxane) (PMMS) backbone decorated with uniform chiral side chains and *p*-methoxybenzene-terminated achiral side chains (PMMS-*OCH*₃-based polymers),^[36] the transition in the measured c is triggered by a chiral molar ratio of 0.8 rather than 0.5. This phenomenon implies that the emergence of the liquid crystalline phase is a synergistic outcome of the two distinct side chains. The *p*-biphenyl-terminated achiral side chains, which exhibit increased rigidity in this study, can partially offset the effects imparted by the chiral side chains, which occupy a larger spatial volume and present greater steric hindrance, thus delaying the change in the measured c .

**Fig. 9** Composition dependence of phase transition temperatures and minimized layer spacings of for polymers.

Our meticulous examination and interpretation of DSC, POM, 1D-WAXD, SAXS and 2D-WAXD data revealed three distinct liquid crystalline (LC) phases and four unique molecular configurations within this polymer series (Fig. 10). These findings are dependent upon the two LC building blocks, highlighting the delicate interplay among structural elements and their influence on the collective phase behavior.

CONCLUSIONS

In summary, a series of novel SCLC copolymers bearing both chiral cholesteryl-based and achiral biphenyl-based mesogenic units attached to a poly(3-mercaptopropylmethylsiloxane) (PMMS) backbone *via* thiol-ene click chemistry was synthesized and characterized. Three distinct liquid crystalline (LC) phases and four unique molecular configurations was observed depending on molar ratio of chiral monomers with a larger spatial volume and greater steric hindrance. Our research highlights the critical influence of side chain dimensions, rigidity, and spatial volume on the self-assembly structures and phase characteristics of liquid crystalline polymers. The chiral molar ratio and the diversity of side chains present play a crucial role in shaping the organization of mesogenic units within the polymer matrix.

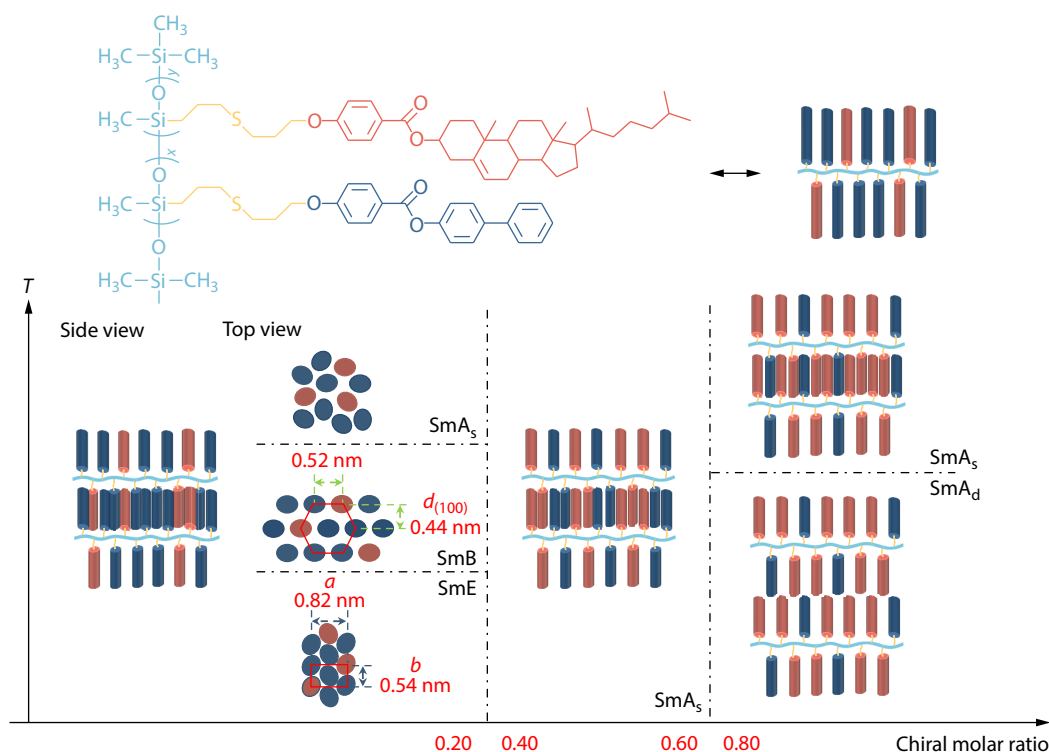


Fig. 10 Schematic drawing of the proposed model for the self-assembly of all the polymers with different chiral molar ratios and temperatures.

Understanding the complexities of these interactions and their impact on structural formation is essential for the rational design and innovative development of advanced functional materials with tailored properties.

Conflict of Interests

The authors declare no interest conflict.

Data Availability Statement

The related data (DOI: <https://doi.org/10.1007/s10118-024-3167-8>) for this paper is available in the (Tunable Phase Structure of Side-chain Liquid Crystalline Polymers Enable by Molecular Engineering of Dual Mesogenic Cores) database (<https://www.scidb.cn/c/cjps>).

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 52263033 and 52202081), China Postdoctoral Science Foundation Funded Project (No. 2021M690954), Natural Science Foundation of Gansu Province (No. 20JR10RA105), the Natural Science Foundation of Hunan Province (No. 2022JJ30152), the graduate research funding project of Northwest Normal University (No. 2023KYZZ-S157) and Natural Science Foundation of Jiangxi Province, China (No. 20232BAB204030).

REFERENCES

- Shibaev, V. P.; Bobrovsky, A. Y. Liquid crystalline polymers: development trends and photocontrollable materials. *Russ. Chem. Rev.* **2017**, *86*, 1024–1072.
- Siva Mohan Reddy, G.; Jayaramudu, J.; Ray, S. S.; Varaprasad, K.; Rotimi Sadiku, E., Side Chain Liquid Crystalline Polymers: Advances and Applications. In *Liquid Crystalline Polymers: Volume 2—Processing and Applications*, Thakur, V. K.; Kessler, M. R., Eds. Springer International Publishing: Cham, **2015**; pp. 389–415.
- Hsu, C. S. The application of side-chain liquid-crystalline polymers. *Prog. Polym. Sci.* **1997**, *22*, 829–871.
- White, T. J.; Broer, D. J. Programmable and adaptive mechanics with liquid crystal polymer networks and elastomers. *Nat. Mater.* **2015**, *14*, 1087–1098.
- Imrie, C. T.; Karasz, F. E.; Attard, G. S. Effect of backbone flexibility on the transitional properties of side-chain liquid-crystalline polymers. *Macromolecules* **1993**, *26*, 3803–3810.
- He, E. J.; Tu, K.; Cheng, J. N.; Wang, Y. X.; Lu, H. J.; Zhang, L. F.; Cheng, Z. P. Synthesis and phase behavior of (semifluorinated alkane)-based side-chain liquid crystalline copolymers. *Macromol. Rapid Commun.* **2022**, *43*, 2200266.
- Tanaka, D.; Nagashima, Y.; Hara, M.; Nagano, S.; Seki, T. Alternation of side-chain mesogen orientation caused by the backbone structure in liquid-crystalline polymer thin films. *Langmuir* **2015**, *31*, 11379–11383.
- Percec, V.; Tomazos, D. Can the rigidity of a side-chain liquid-crystalline polymer backbone influence the mechanism of distortion of its random-coil conformation. *Polymer* **1990**, *31*, 1658–1662.
- Craig, A. A.; Imrie, C. T. Side chain liquid crystal copolymers containing electron rich and electron deficient mesogenic groups. The synthesis and characterization of the poly[ω -(4-cyanobiphenyl-4'-oxy)alkyl methacrylate]s-co-poly[6-(4-butyl-

- azobenzene-4'-oxy)hexyl methacrylate)s. *Polymer* **1997**, *38*, 4951–4957.
- 10 Imrie, C. T.; Karasz, F. E.; Attard, G. S. Side-chain liquid-crystalline copolymers containing spacers of differing lengths. *Macromolecules* **1992**, *25*, 1278–1283.
- 11 Han, X. H.; Yang, X. W.; Chen, S.; Luo, H.; Zhang, D.; Zhang, H. L. Multiple effects tailoring the self-organization behaviors of triphenylene side-chain liquid crystalline polymers via changing the spacer length. *Chinese J. Polym. Sci.* **2018**, *36*, 960–969.
- 12 Ji, L. L.; Chen, X. F.; Wu, Y. H.; Yang, X. M.; Tu, Y. F. Influence of liquid crystalline formation on the phase behavior of side-chain liquid crystalline block copolymers. *Polymer* **2015**, *61*, 147–154.
- 13 Orodepo, G. O.; Gowd, E. B.; Ramakrishnan, S. Periodically spaced side-chain liquid crystalline polymers. *Macromolecules* **2020**, *53*, 8775–8786.
- 14 Takeshita, H.; Kanazawa, A.; Tokumitsu, K. Effects of copolymer composition on phase transition behavior and mobility of mesogenic group for side-chain liquid crystalline-amorphous random copolymers. *Nihon Reoroji Gakkaishi* **2022**, *50*, 189–195.
- 15 Michinobu, T.; Fujii, N.; Tokita, M.; Watanabe, J.; Shigehara, K. Thermoreversible contraction and extension of layer spacing in smectic phase of side chain liquid crystal poly(fumarate)s. *Macromol. Rapid Commun.* **2008**, *29*, 1593–1597.
- 16 Chen, S.; Luo, H. B.; Xie, H. L.; Zhang, H. L. Influence of molecular weight on the phase behaviors of comb-like polymers with longn-alkyl side chains based on mesogen-jacketed liquid crystalline polymers. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 924–935.
- 17 Ye, C.; Zhang, H. L.; Huang, Y.; Chen, E. Q.; Lu, Y. L.; Shen, D. Y.; Wan, X. H.; Shen, Z. H.; Cheng, S. Z. D.; Zhou, Q. F. Molecular weight dependence of phase structures and transitions of mesogen-jacketed liquid crystalline polymers based on 2-vinylterephthalic acids. *Macromolecules* **2004**, *37*, 7188–7196.
- 18 Xu, Y.; Dupont, R. L.; Yao, Y. X.; Zhang, M.; Fang, J. C.; Wang, X. G. Random liquid crystalline copolymers consisting of prolate and oblate liquid crystal monomers. *Macromolecules* **2021**, *54*, 5376–5387.
- 19 Pei, J. W.; Wei, W. J.; Li, B.; Huang, J. D.; Chen, X. F. Composition-dependent phase transformation in side-chain liquid crystalline copolymers with mesogenic groups at different substituent positions. *Soft Matter* **2021**, *17*, 4594–4603.
- 20 Yao, W. H.; Wang, Y. X.; Liu, L. S.; Ma, A. Z.; Zhao, J.; Ma, Z. R.; Zhang, L. Y.; Lan, R. C. Finely tuning the self-assembled architectures of liquid crystal polymers by molecular engineering: phase transitions derived from terminal group variations. *Mater. Adv.* **2024**, *5*, 3450–3458.
- 21 Liu, Y.; Yang, S. C.; Shen, Z. H.; Fan, X. H.; Zhou, Q. F. Design, synthesis, and self-assembly of mesogen-jacketed liquid crystalline polymers constructed by hydrogen bonding. *Acta Polymerica Sinica* (in Chinese) **2023**, *54*, 1555–1567.
- 22 Zheng, J. F.; Ge, Y. C.; Cheng, X. F.; Wu, Y. T.; Xu, P.; Chen, E. Q. Manipulating molecular shapes and phase structures of mesogen-jacketed liquid crystalline polymers: from sheet-like to rod-like molecule and from smectic to columnar phase. *Acta Polymerica Sinica* (in Chinese) **2023**, *54*, 1343–1354.
- 23 Zhu, Y. F.; Zhang, Z. Y.; Zhang, Q. K.; Hou, P. P.; Hao, D. Z.; Qiao, Y. Y.; Shen, Z. H.; Fan, X. H.; Zhou, Q. F. Mesogen-jacketed liquid crystalline polymers with a polynorbornene main chain: green synthesis and phase behaviors. *Macromolecules* **2014**, *47*, 2803–2810.
- 24 Chen, S.; Zhang, L. Y.; Gao, L. C.; Chen, X. F.; Fan, X. H.; Shen, Z. H.; Zhou, Q. F. Influence of alkoxy tail length and unbalanced mesogenic core on phase behavior of mesogen-jacketed liquid crystalline polymers. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 505–514.
- 25 Yuan, Q. L.; Liu, W. J.; Deng, Y.; Ling, Y.; Tang, H. Y. Synthesis, characterization and phase behaviors of polypeptides bearing biphenyl mesogens and oligo-ethylene-glycol tails. *Chinese J. Polym. Sci.* **2015**, *33*, 1150–1161.
- 26 Dai, S. Q.; Li, J. X.; Kougo, J. C.; Lei, H. Y.; Aya, S.; Huang, M. J. Polar liquid crystalline polymers bearing mesogenic side chains with large dipole moment. *Macromolecules* **2021**, *54*, 6045–6051.
- 27 Mei, X.; Zhang, J.; Shen, Z. H.; Wan, X. H. Synthesis, liquid crystalline properties, and lithium complexes of vinyl polymers with cyclic pendants containing ethylene oxide units. *Polym. Chem.* **2012**, *3*, 2857–2866.
- 28 Mei, X.; Chu, Y.; Cui, J. X.; Shen, Z. H.; Wan, X. H. Steric interaction between flexible main chain and nonmesogenic cyclic pendants leading to thermotropic liquid crystalline property. *Macromolecules* **2010**, *43*, 8942–8949.
- 29 Guan, Y.; Chen, X. F.; Shen, Z. H.; Wan, X. H.; Zhou, Q. F. Structure-property relationship of thermotropic liquid-crystalline vinyl polymers containing no traditional mesogen. *Polymer* **2009**, *50*, 936–944.
- 30 Kosaka, Y.; Kato, T.; Uryu, T. Synthesis and the smectic mesophase of copolymers containing a mesogenic (carbazolyl-methylene)aniline group as the electron donor and a (4'-nitrobenzylidene)aniline group as the electron acceptor. *Macromolecules* **1994**, *27*, 2658–2663.
- 31 Schlee, T.; Imrie, C. T.; Rice, D. M.; Karasz, F. E.; Attard, G. S. Ultrastructure studies of polystyrene-based side-chain liquid-crystalline copolymers containing charge transfer groups. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1859–1869.
- 32 Imanishi, R.; Nagashima, Y.; Takishima, K.; Hara, M.; Nagano, S.; Seki, T. Induction of highly ordered smectic phases in side chain liquid crystalline polymers by means of random copolymerization. *Macromolecules* **2020**, *53*, 1942–1949.
- 33 Imrie, C. T.; Attard, G. S.; Karasz, F. E. Role of specific interactions in determining the mesogenic behavior of side-chain liquid crystal polymers. *Macromolecules* **1996**, *29*, 1031–1035.
- 34 Wei, W.; Liu, Y.; Xiong, H. M. Interplay of liquid crystalline ordering in double side-chain liquid crystalline diblock copolymer. *Polymer* **2013**, *54*, 6793–6800.
- 35 Cheng, Z. H.; Cao, H.; Zhao, D. Y.; Hu, W.; He, W. L.; Yuan, X. T.; Xiao, J. M.; Zhang, H. Q.; Yang, H. Liquid crystalline and thermo-optical properties of cyclic siloxane tetramers containing cholesteryl-4-allyloxy-benzoate and biphenyl-4-yl 4-allyloxybenzoate. *Liq. Cryst.* **2011**, *38*, 9–15.
- 36 Yao, W. H.; Gao, Y. Z.; Yuan, X.; He, B. F.; Yu, H. F.; Zhang, L. Y.; Shen, Z. H.; He, W. L.; Yang, Z.; Yang, H.; Yang, D. K. Synthesis and self-assembly behaviours of side-chain smectic thiol-ene polymers based on the polysiloxane backbone. *J. Mater. Chem. C* **2016**, *4*, 1425–1440.
- 37 Gao, S.; Liu, Z. P.; Cong, Y. H.; He, X. Z.; Zhang, B. Y.; Meng, F. B.; Jia, Y. G. Cholesteric fluorescent liquid crystal polysiloxanes with different liquid crystal side chain lengths-synthesis and properties. *Dyes Pigm.* **2020**, *181*, 108520.
- 38 Zheng, X. L.; Zhan, Y. J.; Liu, Y. C.; Lu, M. P.; Jiao, E. X.; Zhang, H. Z.; Shi, J.; Lu, M. G.; Wu, K. High intrinsic thermally conductivity side-chain liquid crystalline polysiloxane films grafted with pendent difunctional mesogenic groups. *Polym. Chem.* **2022**, *13*, 3915–3929.
- 39 Zhang, M. T.; Liu, G. Q.; Du, S. H.; Chen, R.; Chen, P.; Weng, Q.; Gao, A. A.; Chen, X. B.; An, Z. W. Preparation and properties of novel liquid crystal ionomers bearing benzoxazole-based mesogenic side-chains and their membranes. *J. Mol. Liq.* **2024**, *394*.
- 40 Wang, X. T.; Chen, Z. F.; Huang, Y. W.; Ye, X. T.; Wang, J. C.; Yang, Y. Y.; Li, X. F.; Liu, Z. F. Liquid crystallinity and thermal properties of polyhedral oligomeric silsesquioxane/side-chain azobenzene hybrid copolymer. *Nanotechnol. Rev.* **2020**, *9*, 886–895.

- 41 Wu, Y.; Zhang, Q.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Nagase, Y. Photoinduced alignment of polymer liquid crystals containing azobenzene moieties in the side chain. 5. Effect of the azo contents on alignment behavior and enhanced response. *Macromolecules* **1999**, *32*, 3951–3956.
- 42 Younis, O.; Tsutsumi, O. Single-component white-color photoluminescence from liquid crystal polymers: color tuning by a combination of luminescence thermo- and mechanochromism. *Dyes Pigm.* **2021**, *188*, 109189.
- 43 Liu, Y. Y.; Wu, W.; Wei, J.; Yu, Y. L. Visible light responsive liquid crystal polymers containing reactive moieties with good processability. *ACS Appl. Mater. Interfaces* **2017**, *9*, 782–789.
- 44 Bisoyi, H. K.; Li, Q. Liquid crystals: versatile self-organized smart soft materials. *Chem. Rev.* **2022**, *122*, 4887–4926.
- 45 da Cunha, M. P.; Debije, M. G.; Schenning, A. Bioinspired light-driven soft robots based on liquid crystal polymers. *Chem. Soc. Rev.* **2020**, *49*, 6568–6578.
- 46 Lan, R. C.; Shen, W. B.; Yao, W. H.; Chen, J. Y.; Chen, X. Y.; Yang, H. Bioinspired humidity-responsive liquid crystalline materials: from adaptive soft actuators to visualized sensors and detectors. *Mater. Horiz.* **2023**, *10*, 2824–2844.
- 47 Yang, H.; Liu, M. X.; Yao, Y. W.; Tao, P. Y.; Lin, B. P.; Keller, P.; Zhang, X. Q.; Sun, Y.; Guo, L. X. Polysiloxane-based liquid crystalline polymers and elastomers prepared by thiol-ene chemistry. *Macromolecules* **2013**, *46*, 3406–3416.
- 48 Yao, W. H.; Gao, Y. Z.; Zhang, C. H.; Li, C. Y.; Li, F. S.; Yang, Z.; Zhang, L. Y. 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. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 1765–1772.
- 49 Xie, H. L.; Hu, T. H.; Zhang, X. F.; Zhang, H. L.; Chen, E. Q.; Zhou, Q. F. Design, synthesis, and characterization of a combined main-chain/side-chain liquid crystalline polymer based on mesogen-jacketed liquid crystal polymer via atom transfer radical polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 7310–7320.
- 50 Nardele, C. G.; Asha, S. K. Photoresponsive smectic liquid crystalline multipods and hyperbranched azo polymers. *J. Phys. Chem. B* **2014**, *118*, 1670–84.
- 51 Hida, N.; Nakajima, T.; Hara, M.; Seki, T.; Nagano, S. Induced smectic e phase in a binary blend of side-chain liquid crystalline polymers. *Macromol. Rapid Commun.* **2023**, *44*, 2200761.
- 52 Chen, S.; Gao, L. C.; Zhao, X. D.; Chen, X. F.; Fan, X. H.; Xie, P. Y.; Zhou, Q. F. Synthesis and properties of mesogen-jacketed liquid crystalline polymers with asymmetry mesogenic core. *Macromolecules* **2007**, *40*, 5718–5725.
- 53 Cheng, Y. H.; Chen, W. P.; Shen, Z. H.; Fan, X. H.; Zhu, M. F.; Zhou, Q. F. Influences of hydrogen bonding and peripheral chain length on mesophase structures of mesogen-jacketed liquid crystalline polymers with amide side-chain linkages. *Macromolecules* **2011**, *44*, 1429–1437.