





Multiple Phase Structures and Enhanced Dielectric Properties of Side-Chain Liquid Crystalline Polymer Containing Unique Biaxial Mesogen with Large Dipole Moment

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To achieve all-organic polymer with high dielectric performances, we have designed a novel side-chain liquid crystalline polymer (**P7**) with strong polar mesogen of (*Z*)-4-(2-cyano-2-phenylvinyl)benzonitrile (CSCN) attached to polycyclooctene backbone. The bis-cyano-substituted CSCN is board-shaped and exhibits a large dipole moment (8.54 D) which tilts ~34.2° away from its molecular long axis. Consequently, CSCN shows unique dual molecular anisotropy: one from biaxial shape anisotropy and the other from polarization anisotropy. The complex phase behaviors of **P7** were investigated employing mainly the techniques of differential scanning calorimetry and X-ray diffraction. Four liquid crystal (LC) phases are identified as K0, K1, K2 and K3, which are SmA, highly-ordered biaxial SmA, B5-like and B7-like, respectively, with the thermal stability increased in sequence. The experimental results indicate that the different LC phases are arisen from the competition and balance between π - π stacking and dipole-dipole interaction. While the face-to-face π - π stacking is dominant in K0 and K1, optimizing the dipole-dipole interaction causes the CSCN mesogens within the smectic layer to tilt and rotate, resulting in K2 and K3. We further investigated the dielectric properties of **P7** films using polarization-electric field

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loops test. The dielectric constant (ε_r) of **P7** is found to be LC structure dependent, which is increased when the LC phase is varied from K0 to K3. With an average ε_r of 9.7 achieved in K3 and the low dielectric loss (tan $\delta = 0.001$), **P7** film offers a promising material in advanced applications like energy storage and electronic devices.

1 Introduction

The fast development of advanced electronic devices and electrical power systems draws forth higher requirements for energy storage dielectric materials, especially those materials satisfying both higher dielectric constant (ε_r) and lower dielectric loss (tan δ) [1-4]. Considering the fundamental polarization mechanism of organic polymers, the utilization of dipolar polarization has been proved to be the most effective strategy to enhance the material's intrinsic dielectric permittivity [2,5]. The regulation of dipolar polarization includes two major parts, one is the incorporation of strong polar groups such as -CN (~4.0 D), -NO2 (~3.6 D), - SO_2 - (~4.3 D) [6–9] and the other one is controlling the structures of dipolar domains [2]. Simple dipolar glass polymers consisting of isolated small polar groups usually exhibit linear dielectric behavior, while some crystalline polymers such as PVDF in β phase and nylon-11 in γ - or δ -phase can show strong ferroelectric behavior due to the existence of large domains with many dipoles [10-15]. To achieve novel polymers with better dielectric performances or even ferroelectric properties, both the dipole moment and the assembly of polar groups matter.

In consideration of tailoring the dipole moment and the domain structure simultaneously, side-chain liquid crystalline polymer (SCLCP) is an attractive option. SCLCPs often contain polar groups, e.g., cyanobiphenyls or aromatic esters and amides, to assist the formation of liquid crystal (LC) phases. Through simple chemical synthesis, common strong polar groups can also be modified on traditional rod-like mesogens to form a polar mesogen with larger dipole moment [16-21]. It turns out that the shape anisotropy of rod-like mesogens may significantly help to orient the dipoles and generate anisotropic dipolar domains. Albeit that the SCLCPs usually exhibit linear dielectric due to possible antiparallel packing of dipoles, the uniform orientation can still boost the polymer's ε_r . In a sulforylated mesogen-jacketed liquid crystalline polymer, a large ε_r of 20.8 and a discharge energy density of 6.2 J/m³ at 270 MV/m at room temperature was achieved [16]. In recent years, Zhu and his co-workers have reported several mesogen-free SCLCPs with stable LC phases formed through strong dipolar interactions between -SO₂- groups [22-24]. Since the -SO₂- groups are aligned in the same direction to form ordered LC phases, the ε_r of these SCLCPs can reach above 20. Recently in a new series of Smectic C (SmC) polymers, paraelectric behavior has been observed [25], which indicates a step closer to novel ferroelectric SCLCP. However, it still remains great challenging in constructing large LC domains with net dipoles.

In order to obtain domains with net dipoles to further enhance the dielectric performance or to obtain ferroelectricity in SCLCPs, we consider increasing complexity in the shape of mesogens to be the key point. Conventional rod-like mesogens such as cyanobiphenyl all bear C_{2h} symmetry and tend to form smectic A (SmA) phase in end-on SCLCPs, where mesogens usually align

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antiparallelly, leading to cancellation of dipoles and macroscopic polarization. To break the C_{2h} symmetry, more complexed mesogens with biaxial anisotropy are potential candidates. The most widely known biaxial anisotropic LC molecules are bentcore (banana-shaped) molecules, which often include a rather rigid bent aromatic core and flexible alkyl chain as tail groups, rendering its polar order pointing out from the rigid bent-core [26]. When assembling into LC phases, the bent-core molecules tend to avoid formation of macroscopic polarization through the packing schemes such as layer modulation or helical formation, thus giving sophisticated LC phases that can be identified with B-nomenclatures [26,27]. It should be stressed that sometimes at certain temperatures, these LC phases can be ferroelectric, although at ground state they are usually antiferroelectric due to the escape of macroscopic polarization. Most SCLCPs containing such bent-core molecules only show antiferroelectric switching [28,29], while ferroelectricity was once reported in a polysiloxane polymer by Tschierske, where they suggested the microsegregation of backbone from the bent-core side-chain mesogens into distinct sublayers to be the main reason for the ferroelectric phase [30].

Here we propose a new design concept of mesogen. Away from the bent-core molecules in geometric shape but retaining the biaxial anisotropy, we pick up a special board-shaped mesogen, (Z)-4-(2-cyano-2-phenylvinyl)benzonitrile (CSCN), with bissubstituted cyano groups and large dipole moment (Fig. 1). CSCN is biaxially shape anisotropic: the end-on cyano group guarantees the aspect ratio required for the LC phase, while the cyano substitution on the carbon-carbon double bond introduces unique rotation hindrance because of specific intermolecular interactions from the polar groups. In this case, the C_{2h} symmetry of traditional rod-like mesogens is broken [31]. In addition to the unique biaxial anisotropy of CSCN, the mesogen also exhibits a large dipole moment (μ) of 8.54 Debye (D) with a tilt angle of ca. 34° from the molecular long axial. Consequently, strong dipolar interactions can form between CSCNs laterally to stabilize the formation of biaxial LC phase and to prevent total cancellation of net dipoles. CSCN has been used as a fluorescent mesogen in SCLCP [32], yet the effect of biaxial anisotropy and strong polarity of CSCN on the formation of LC phases has not been investigated. We assume that the biaxial CSCN mesogen could be of huge potential to form polar LC phases and thus enhance the dielectric performance of the polymer.

In this study, we attach the unique CSCN mesogen to polycyclooctene main-chain and obtain a novel dipolar SCLCP denoted as **P7**. Similar to bent-core molecules, **P7** relies on both the shape anisotropy and strong dipole-dipole interactions to determine the molecular assemblies. Consequently, **P7** exhibits sophisticated phase behavior. Here we investigate the phase structure and transition processes of **P7** in detail. Through delicate differential scanning calorimetry (DSC) and X-ray diffraction (XRD) experiments, four different LC phases are revealed: K0, K1,



Chemical structure and schematic assembly of dipolar SCLCP P7.

K2 and K3 (listed in the order of thermal stability from low to high), which can be identified as smectic A (SmA), highly-ordered biaxial SmA, B5-like and B7-like phase, respectively. The strong dipole-dipole interaction between CSCNs accounts most for the high thermal stability of K2 and K3 phase, while the competition between π - π stacking and the dipolar interaction is found to be the driving force of phase transition in **P7**. We also inspected the dielectric property of hot-pressed **P7** thin films in each LC phase through polarization-electric (P-E) loops. Albeit linear dielectric for all the films, their dielectric performances are eye-catching, as they can be regulated by LC phases with the highest average ε_r of 9.7 achieved in K3 film. Additionally, the observation of B5- and B7-like phases suggests the potential of **P7** to assemble into polar LC domains through optimization of dipolar interactions.

2 Experimental section

2.1 Materials

4-Hydroxyphenylacetonitrile (98 %, Aladdin), 3,4-dihydro-2*H*-pyran (98 %, Aladdin), pyridinium *p*-toluenesulfonate (PPTS, 98 %, OKA), 4-cyanobenzaldehyde (98 %, Aladdin), *p*-toluenesulfonic acid (TsOH, AR, Aladdin), cyclooct-4-enol (97 %, Aladdin), 8-bromooctanoic acid (97 %, Aladdin), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 99 %, Aladdin), 4dimethylaminopyridine (DMAP, 99 %, Aladdin), potassium carbonate (K₂CO₃, Xilong), potassium iodide (KI, Xilong), sodium hydroxide (NaOH, Xilong), acetone (HPLC, Xilong), methanol (HPLC, Fisher), dichloromethane (DCM, anhydrous, Acros Organics) were used as received.

2.2 Instrumentation and characterization methods

NMR data were acquired on a Bruker AVANCE III 400M spectrometer. Proton signals were quoted to TMS ($\delta = 0.00$ ppm) and ¹³C signals were referenced to the recommended shift values of the used solvents (δ (CDCl₃) = 77.16 ppm, δ (CDCl₂) = 53.84 ppm). High-resolution ESI mass spectra were acquired on a Waters Vion Quadrupole-TOF LC-MS/MS spectrometer. Gel permeation chromatography (GPC) was carried out on a Waters 515 GPC instrument using THF as an eluent at a flow rate of 1.0 mL/min at 35 °C. The GPC calibration curve was obtained with linear polystyrene standards. DSC curves were measured using a TA DSC

250 instrument. One- and two-dimensional (1D and 2D) XRD experiments were performed with the Ganesha system (SAXSLAB, USA) equipped with a multilayer focused Cu K α radiation as the X-ray source (Genix3D Cu ULD) and a 2D semiconductor detector (Pilatus 300K, DECTRIS, Swiss). The scattering peak positions were calibrated with LaB₆ for the wide-angle region and silver behenate for the small-angle region, respectively. A Linkam HFSX350-GI stage attached to Ganesha was utilized to study the structure evolution as a function of temperature. The LC phase texture was obtained with Nikon LV100N polarized optical microscope (POM). Ag circular electrodes (diameter = 2 mm) were sputtered onto **P7** films by a JCP-600M3 ion source assisted three-target magnetron sputtering system. The dielectric property of unipolar P-E loops at 10 Hz was measured by a Polarization Loop & Dielectric Breakdown Test System (PolyK Technologies, State College, USA). The dielectric properties of the films were measured using a Keysight E4980A precision LCR meter, the frequency ranges from 20 Hz to 2 MHz.

The molecular features of CSCN were calculated through Density Functional Theory (DFT) method. In order to achieve accurate results, we used B3LYP method and the basis set of 6-311+G(d,p). Parameter "geom = connectivity" was added for maintaining the continuity of the original bond relationship and geometric structure of the molecule. Parameter "empiricaldispersion = gd3" was added for correcting the calculation of dispersion force.

2.3 Synthesis of monomer M7 and polymer P7

The synthetic route of **P7** is shown in Scheme 1. The boardshaped mesogen unit, (*Z*)-4-(2-cyano-2-(4-hydroxyphenyl)vinyl)benzonitrile (compound **3**) was synthesized through Knoevenagel condensation between 4-cyanomethylphenol and 4-cyanobenzaldehyde. The backbone motif, (*Z*)-cyclooct-4-en-1-yl 3-bromopropanoate (compound **4**) with a flexible spacer of seven methylene groups was easily synthesized through esterification between 4-cyclooctene and 8-bromooctanoic acid. Finally, through Williamson etherfication of the mesogen and the backbone motif, the monomer **M7** was achieved with high yield. Detailed synthetic procedure and characterizations of all intermediate compounds can be found in Supplementary



Scheme 1

Synthesis of monomer M7 and polymer P7.

Information. Here we only describe the synthesis of monomer **M7** and the polymerization procedure.

Compound **4** (1.67 g, 5.50 mmol), compound **3** (1.31 g, 5.00 mmol), anhydrous potassium carbonate (3.45 g, 25.0 mmol) and 50 mL acetone were combined in a 150 mL round-bottomed flask and the mixture was refluxed overnight. Upon completion of the reaction, the mixture was allowed to cool to room temperature and the solvent was removed on a rotary evaporator. After the residue was dissolved in DCM, the insoluble components were discarded and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography (V(PE):V(DCM) = 3:7) and the collected fraction was recrystallized with MeOH, furnishing the pure monomer **M7** as a yellow-greenish powder in 68 % yield.

P7 was then polymerized from **M7** by ring-opening metathesis polymerization (ROMP) with the second-generation Grubbs catalyst. **M7** (250 mg, 500 μ mol) and the second-generation Grubbs catalyst (1.50 mg, 1.78 μ mol) was added into the schlenk tube under a nitrogen atmosphere. Then 0.3 mL dry DCM was injected and the tube was sealed. The polymerization was allowed to proceed at 50 °C for 2 h, few drops of dry DCM were added when the system became too sticky. After polymerization, 0.5 mL dry DCM and 0.3 mL ethyl vinyl ether was added to quench the reaction. The final product **P7** was isolated by repeating the processes of precipitation from methanol (25 mL × 4) and centrifugation for four times. The pure polymer was obtained as light-yellow solid in 80% yield. Determined using GPC, the apparent number-average molecular weight (M_n) of **P7** is 8.8 × 10⁴ g/mol and the polydisperse index (D) is 1.80.

3 Results and discussion

3.1 Structural features of biaxial mesogen CSCN

The mesogen CSCN is designed with a unique geometric shape referred to as board-shaped. For clear illustration, using the model compound with the end group of methoxy (Fig. 2), essential molecular features of CSCN were calculated with DFT method [33]. Fig. 2 shows the resulting geometrical properties of CSCN.

single molecular state, rendering geometrically board-shaped. The molecular length of CSCN is ca. 1.30 nm and the width is ca. 0.52 nm. Due to the significant planarization of CSCN, the face-toface π - π stacking is enforced, thus hindering the fast rotation of CSCN around its long axis. As a result, CSCN exhibits inherent biaxiality. Despite the geometric biaxiality, the polarization of CSCN is also biaxial because of the bis-substitution of cyano groups. The total dipole moment (P) of CSCN is 8.54 D and it tilts about 34.2° away from its molecular long axis (Fig. 2A). The *x*-component (parallel to **n**, **n** is the molecular direction) of **P** is 7.06 D; the z-component (perpendicular to **n**) reaches 4.80 D, which is comparable to the commonly used polar groups. As a result, the dipole-dipole interactions between CSCNs will generate both parallel and perpendicular to the molecular long axis. On the perspective of molecular alignment, such biaxial dipole-dipole interaction will reenforce the biaxial packing of CSCNs. In total, the formation of LC phases in P7 will be dominated by the two types of intermolecular interactions, i.e., the π - π stacking and the dipole-dipole interaction between the CSCN mesogens, respectively. The competition and the balance of these two actuation forces can lead to novel assemblies.

As can be seen from Fig. 2B, CSCN is highly planarized in

3.2 Phase transitions of P7

The phase transition of **P7** was first studied by DSC. Fig. 3 shows the DSC results of **P7** measured with varied ramping rates (first cycle (red line): 20 °C/min; second cycle (blue line): 10 °C/min; third cycle (yellow line): 1 °C/min). To be noticed, here we used the precipitated **P7** pristine to perform the first heating; the subsequential measurements were carried out with the same sample and thus the previous thermal history had been removed. For the precipitated **P7** pristine, there is only one huge melting peak at 85.1 °C with its fusion enthalpy (ΔH_m) of 33.07 J/g. No clear glass transition can be observed. This demonstrates that the precipitated **P7** pristine possesses an ordered structure with little amorphous fraction. In the first cooling process, a strong exothermal peak appears at around 40 °C, indicating that a fast



Structural features of CSCN calculated by DFT. **A**, 3D view of CSCN showing the relationship between molecular direction (**n**) and dipole moment (**P**). **B**, Side-view (yz plane) of CSCN. Note that the molecule used in calculation is the model compound with methoxy end group.



Fig. 3

DSC (**A**, **B**) and XRD (**C**) results of **P7** with different thermal treatments. **A**, Red lines: the first heating/cooling cycle with ramping rate of 20 °C/min; blue lines: second heating/cooling cycle with ramping rate of 10 °C/min. Inset: the exothermal peak of "cold-crystallization" process. The heat flow of each curve has been normalized. **B**, The third heating/cooling cycle with ramping rate of 1 °C/min. The insets show the two exotherms detected during heating. **C**, 1D XRD profiles for different **P7** samples. The light-blue box indicates major shifts of diffraction peaks. Inset: middle-angle 1D XRD profiles and the *q* values of the peak positions.

ordering process can occur when the supercooling becomes larger than 40 °C. The second heating process reveals that the glass transition of **P7** appears at 29.0 °C, which is followed by a "coldcrystallization" process with a small exotherm at around 50 °C (the inset figure in Fig. 3A). It can be deduced that during the fast-cooling process with 20 °C/min, amorphous domains were formed. Once polymer chains are activated at temperatures higher than the glass transition temperature (T_g), they start to reorganize into a more thermal-stable phase. This phase exhibits the melting temperature (T_m) of 70.7 °C, nearly 15 °C lower than the T_m of precipitated **P7** pristine.

After cooling at 10 °C/min which generates a large exotherm peaked at 41.8 °C, a small exotherm at ca. 50 °C can still be detected in the following heating process with the rate of 1 °C/min, indicating a rather weak "cold-crystallization" (see the lower inset figure in Fig. 3B). Both of these two exothermic processes result in the ordered structure melted at 70.6 °C, same as the one observed on the heating curve with 10 °C/min (Fig. 3B). Interestingly, the slow heating at 1 °C/min unveils that a partial reorganization could soon take place after the major melting, evidenced by a tiny exothermal peak (see the upper inset figure in Fig. 3B). Afterwards, two melting peaks appear at higher temperatures, one at 74.7 °C and the other at 80.2 °C, respectively.

Fig. 3C compares the 1D XRD results of **P7** with different thermal histories. The precipitated **P7** pristine exhibits multiple diffractions, featuring with the two notably strong peaks at ca. q (= $4\pi \sin\theta/\lambda$, with 2θ the scattering angle and λ the wavelength)

of 1.4 and 10 nm⁻¹, respectively. After cooling from melt, it is observed that the first diffraction in the low angle region (marked by the red dash-line box) shifts to a lower angle; on the other hand, the peak at ca. $q = 10 \text{ nm}^{-1}$ (marked by the blue dash-line box) reduced remarkably. However, once P7 was slowly re-heated to 70 °C, both the first diffraction and the higher-angle peak largely recover. This result suggests that after the major melting process at 70 °C, **P7** could partially reorganize into another LC phase, which is similar to P7 pristine. The DSC and XRD results shown in Fig. 3 indicate the complex phase behaviors of **P7**. Particularly, the multiple transition peaks in the slow ramping DSC curve are evidence for the melting of different LC structures and the melt-reorganization process as well. Since the $\Delta H_{\rm m}$ of the highest melting peak (80.2 °C, Fig. 3B) is too much smaller than the one of precipitated P7 pristine (85.1°C, Fig. 3A), the meltreorganization process upon continuous heating is insufficient. To make the LC phase with higher thermal stability well developed, additional thermal treatment is required.

To further investigate into the multiple LC phases of **P7**, conditions of thermal treatments were selected delicately. We employed in-situ DSC to examine different isothermal conditions by changing the pathway and annealing temperature. Before each thermal treatment session, the sample was kept at 100 °C for 5 min to totally remove the thermal history. In this way, the temperature and enthalpy of the transition peak measured from each thermal treatment condition will be compared quantitively with as little error as possible. Fig. 4A and 4B illustrate two pathways for the



Schematic illustration of two thermal treatment pathways and the resulting DSC curves recorded in the final heating process after different thermal treatments. **A**, the "cold-crystallization" process. **B**, the "isothermal-crystallization" process. **C**, DSC curves recorded after "cold-crystallization". **D**, DSC curves recorded after "isothermal-crystallization".

thermal treatments. The first pathway is referred to as "coldcrystallization" (Fig. 4A), where the sample quenched from 100 °C was heated from room temperature (RT, below T_g) to the target annealing temperature (T_a). The second one is called "isothermalcrystallization" (Fig. 4B), where the sample was cooled from the quiescent melt at 100 °C directly to T_a . In both experiments, the sample was annealed at T_a for 1 h and then it was directly cooling to RT followed by re-heating to 100 °C. These cooling and heating processes were recorded by DSC for analyzing the phase behavior of each product of the thermal treatments. For each annealing product, the highest endothermal peak temperature shown in DSC heating curve is indexed as the T_m for convenience. The T_m and the total ΔH_m (calculated by integrating all endothermal peaks) were used for comparison.

For "cold-crystallization", we tested three different T_a s, which were 60, 70 and 75 °C, respectively. Fig. 4C shows the DSC heating curves recorded with the ramping rate of 10 °C/min. As can be seen clearly, the exothermal peak at ca. 50 °C in Fig. 3A disappears in all products and the T_m increases with increasing T_a . Annealing at 60 °C gives a LC phase with the sharp melting peak at 72.3 °C (blue line). Here we denote this LC phase as K1. After **P7** was annealed at 70 or 75 °C, a complex melting process is detected. The major melting peaks, which might reflect a size distribution of LC domains or the domains with varied perfection. It should be stressed that the selected T_a s of either 70 or 75 °C are within the melting range of K1. Considering that K1 can form readily upon cooling and heating (see Fig. 3A, blue line), we presume that during annealing at 70 and 75 °C using the "coldcrystallization" protocol, **P7** undergoes the melt-reorganization process *via* the previously grown K1 phase. However, the LC phase developed through the simple tempering contains lots of defects. Using the "step-wise annealing" method, where **P7** was annealed step-wisely at 60, 70, and then 75 °C for 1 h sequentially, can lead defects to be effectively removed and thus raise the perfection degree of LC phase (Fig. 4C, red line), as evidenced by the narrowing of the major melting process. Finally, we can obtain the LC phase with a T_m of 85.4 °C, which we denote as K2.

For "isothermal-crystallization", we tested $T_{a}s$ as 65, 60 and 50 °C, respectively (Fig. 4D). Higher T_as were ignored because the ordering of P7 from isotropic melt becomes severely slow. We picked up the T_a s according to the DSC results of slow cooling of **P7** from melt. As shown in Fig. 3B, the cooling curve recorded at 1 °C/min presents two exothermic processes. Namely, the high temperature one starting from ca. 60 °C is broad and relatively weak, and the low temperature one that peaks at 49.4 °C is sharp and strong. These two exotherms may be associated with different intermolecular interactions, thus the formation of different LC phases. For "isothermal-crystallization" at $T_a = 50$ °C, the low temperature exothermic process governs P7 ordering, and the resulting LC phase renders T_m of 72 °C that should be the K1 phase (Fig. 4D, the yellow line). On the contrary, isothermal annealing P7 at 60 or 65 °C (the green and blue lines), where the high temperature exothermic process becomes dominant, facilitates the development of LC domains with higher thermal stability. To improve the perfection of LC phase, we used again the stepwise annealing strategy. Firstly, P7 was cooled straightforwardly to 60 °C, allowing the LC phase to grow fast at a relatively large



XRD results of K0. A, 1D XRD integration and scheme of side-chain packing. B, 2D XRD pattern. The arrow indicates the stretch direction.

supercooling. Afterwards, the T_a was increased to 70 and then 75 °C to remove the defects. Finally, a uniformed LC phase with T_m of 85.6 °C is successfully obtained (Fig. 4D, red line), which is denoted as K3.

According to the results shown in Fig. 3 and 4, as well as the measured $T_{\rm m}$ s and $\Delta H_{\rm m}$ s (Table s1 and s2), three LC phases, i.e., K1, K2, and K3, can be speculated for **P7**. Namely, K1 with $T_{\rm m}$ of 72.3 °C develops from quenched **P7** through "coldcrystallization" or from "isothermal-crystallization" at $T_{\rm a} < 60$ °C; K2 evolves through melt-reorganization of K1, which has a $T_{\rm m}$ of 85.4 °C; K3 forms directly from quiescent **P7** melt at $T_{\rm a} \ge 60$ °C, which melts at 85.6 °C. In addition, we should be aware that the quenched **P7** stands for an independent phase. Although it can easily transform into K1, the quenched **P7** at below $T_{\rm g}$ can remain the structure unchanged for long time. So here we denote the LC phase of quenched **P7** as K0, which is supposed to be less ordered. In the order of thermal stability, these four phases rank as K0 < K1 < K2 ~ K3.

3.3 Liquid crystalline phase identification of P7

Table 1

In order to understand the LC structures associating with the sophisticated phase transitions of **P7**, well-oriented **P7** samples were prepared for 2D XRD experiments. Firstly, the precipitated **P7** pristine was hot-pressed at 90 °C to get a 150 μ m-thick film. The film was then cut into rectangular strips of 4 mm × 3 mm. To get well-oriented **P7** samples with K0 phase, the **P7** strips were softened at ca. 85 °C and were then quickly uni-axially

stretched and quenched to RT. Samples with K1 and K2 phases were achieved by thermal annealing, following the procedure mentioned in Section 3.2. During annealing, the oriented **P7** strips were pinned strictly to a stainless-steel plate to maintain orientation. To obtain the oriented K3 strip, a rectangular strip was annealed at 100 °C for 5 min and then uni-axially stretched when cooling to 60 °C. After that, the stretched strip was then pinned to the stainless-steep plate (pre-heated in hot stage) and step-wisely annealed to give oriented K3 sample. Specifically, in order to achieve fully developed LC phases, the isothermal time was elongated to 4 h for each sample. Fig. s1 shows the DSC curves of the uni-axially oriented **P7** films after thermal treatments. The sharp melting peaks exhibit the T_m s agreeing well with the results acquired in the in-situ DSC experiments, confirming the well-developed, uniformed LC phases.

1D and 2D XRD patterns for each phase are presented in Fig. 5 to Fig. 8. From the results, we consider that K0, K1, K2 and K3 phase individually belong to SmA, highly-ordered biaxial SmA, B5-like and B7-like phase, respectively. Especially, the B5- and B7like phases are suggested for K2 and K3 because they present some common diffraction features with the B5 and B7 phases of bentcore LC molecules [26,27]. Table 1 lists the T_m , ΔH_m and LC phase details of these four mesophases. It should be emphasized that while the diffractions of **P7** are diffused and limited in number, the structure identification could be lack of accuracy. In this paper, we simply attempt to give some reasonable explanation of the molecular packing in different LC phases of **P7**. Besides the low

Information for K0, K1, K2 and K3 phases in P7.				
Nomenclature	T _m (°C)/ ΔH _m (J/g)	Mesophase type	Organization of mesogens	Phase
КО	_	Smectic without in-plane order	Non-tilted	SmA
K1	72.34/	Smectic bilayer with partial in-plane	Slightly tilted	Highly ordered
	28.37	order		biaxial SmA
K2	85.23/	Undulated smectic bilayer with	Tilted	B5-like
	28.57	partial in-plane order		
K3	85.60/	Undulated modulated smectic	Tilted	B7-like
	29.25			



Fig. 6

XRD results of K1. A, 1D XRD profile and scheme of side-chain packing. B, 2D XRD pattern. The arrow indicates the stretch direction.

angle diffractions, particularly attentions have been paid to the diffractions at 0.35 nm and around 0.6 nm, which are tightly relevant to the packing of the board-like CSCN.

The 2D XRD pattern of K0 recorded at RT shows a typical SmA phase. Layer diffractions with q ratio of 1:3 appears clearly along the stretching direction (SD, the meridian) (Fig. 5A). The layer spacing in K0 is 4.48 nm and is slightly smaller than double of the side-chain length with extended methylene segments of **P7** (2.36 nm, as calculated by Chem 3D, Fig. s2), indicating the partially interdigited packing of side-chains. Since the smectic layer normal is parallel to the meridian and the high angle scattering concentrates on the equator, we can deduce that the CSCN mesogens are oriented along SD during melt-stretching at 85 °C, thus forming a bilayer structure where a sublayer consisted of main-chains separates the two layers of CSCN mesogens (inset figure in Fig. 5A).

After "cold-crystallization" at 60 °C, P7 transformed from K0 into K1 phase. As can be seen from Fig. 6, K1 maintains the basic bilayer structure, yet exhibiting much higher molecular ordering. Firstly, multiple diffractions with the *q* ratio of 1:3:4:5:6 appear in the meridian (i.e., SD), representing a highly-ordered layer structure with layer spacing of 4.87 nm. Secondly, on the equator, a clear spot at $q = 17.86 \text{ nm}^{-1}$ (indicated as 1 in Fig. 6B) stands out from the diffused high-angle scattering. With the *d*-spacing (*d*) of 0.35 nm, this reflection shall originate from the face-to-face π - π stacking of aryl rings of CSCN moieties. Meanwhile, a short streak in the quadrant (2 in Fig. 6B) tilts 9° from the equator (Fig. s3A), of which the d of 0.58 nm that can be attributed to the distance of the slightly tilted CSCN mesogens in the packing fashion of edgeto-edge. Given the board-like shape of CSCN, the diffractions 1 and 2 indicate the molecular ordering in two directions within the smectic layer, which are perpendicular and nearly parallel to the molecular plane, respectively. Schematic illustration of the molecular packing is depicted in the inset figure of Fig. 6A. Albeit tilting in the molecular plane, the CSCN mesogens are still parallel to the smectic layer normal when viewing along the edge of boardlike CSCN. In this case, we tentatively assign K1 a highly-ordered biaxial SmA phase. The tilt of CSCN mesogens could be ascribed to the adjustment of lateral dipole-dipole interactions as the dipole moment of CSCN deviates from the molecular long axis.

8

Tilting of CSCNs helps to reduce possible contradiction between dipoles.

K2 also exhibits smectic-like structure, yet the layer is slightly undulated. Along the SD, five layer diffractions can be observed; however, careful examination reveals an incommensurate q-ratio of 1:2.1:3.2:4.1:5.2 (Fig. 7A). The deviated q values as well as the diffused diffractions indicate density fluctuations in the smectic layer [34]. Additionally, the third order diffraction is rather weak, showing similarity to that of SmA_d phase with mesogens partially overlapping in the bilayer [35,36]. The significant differences between K1 and K2 are evidenced by the high-angle diffractions corresponding to the arrangement of CSCNs. At ca. $q = 10 \text{ nm}^{-1}$, diffraction 2 in quadrants tilts more away from the equator and moves to a lower q (Fig. s3B), resulting in an eyebrowlike streak with a larger d of 0.66 nm. On the other hand, it is surprising to note that spot 1 (d = 0.35 nm) greatly shifts 45° into quadrants. Speculated from the positional changes of 1 and 2, CSCN mesogens should have significantly tilt and rotate themselves in smectic layers. Possible molecular alignment is depicted in Fig. 7A. In the front view of the board-like CSCN, the mesogens tilt 16° from the SD, and enlarge the edge-to-edge distance (2 in Fig. 7B). On the other hand, in the side view, the CSCN plane rotates away from the layer normal and leads to 45° shift of the π - π stacking reflection spot from equator to quadrants (1 in Fig. 7B). Consequently, the layer distance significantly shortens to 4.27 nm and the positional change of mesogens creates fluctuation of smectic layers. The 2D XRD pattern of K2 phase is highly similar to the B5 phase that has been found in banana-shaped LC molecules [37-39]. To our knowledge, this is the first time that a B5-like phase is discovered in a non-typical bent-core SCLCP. Worthy of remark is that the distance of 0.66 nm given by 2 is fairly the value of a face-to-face dimer of aromatics. Nevertheless, diffractions 2 and 1 are well separated in azimuthal angle, thus rather than the dimer, the two diffractions shall be more likely associated with the in-plane and out-of-plane packings of CSCN, respectively.

Different from that K2 is developed based on the process of melt-reorganization of K1, K3 grows directly from isotropic melt. Although sharing almost the same $T_{\rm m}$ (Table 1, Fig. s1), K3 is totally different from K2 as indicated by XRD results. Fig. 8B







Fig. 8

XRD results of K3. A, 1D XRD integration and scheme of side-chain packing, P and the blue arrows indicate for polarization. B, 2D XRD pattern. The arrow indicates the stretch direction.

of K3 shows that while the SD is along the meridian, the layer diffractions with *q*-ratio of 1:2:4 are observed on the equator, giving the layer distance of 4.24 nm. In comparison with K1 and K2, the layer structure in K3 looks much less ordered as the high order diffractions are rather weak. Since layer diffractions are on the equator, the normal direction of smectic layer is perpendicular to SD. In the high-angle region, the weak π - π stacking reflection (*1* in Fig. 8B, *d* = 0.35 nm) appears on the equator, demonstrating that the CSCN plane should also pack parallel to the layer normal direction. Meanwhile, the very strong diffraction arc at *d* = 0.67 nm (*2* in Fig. 8B), which corresponds to edge-to-edge packing of CSCN mesogens, distributes in a wide range of azimuth angle (0°-30°), meaning that the densely packed CSCNs vary their tilt angle in the smectic layer.

Interestingly, except the smectic layer scattering, another lowangle scattering can be found on the meridian (i.e., SD), giving an additional periodicity with a spacing of 4.39 nm. The orthogonal low-angle scatterings indicate that K3 exhibits a unique 2D order. In bent-core LC molecules, such 2D order is often noticed in structures with layer modulation, which is usually driven by the escape from a macroscopic polar order by means of antiparallel or splay packing of molecules [26]. In combination with the high-angle scatterings, we conclude that in K3, CSCN mesogens pack in a splay mode in the smectic layer in order to optimize their densely aggregated dipoles and avoid formation of net dipole (inset figure in Fig. 8A). Such splay packing of CSCNs also disturbs the layer order and weakens the face-to-face π - π stacking between mesogens. According to previous work on banana-shaped LC molecules, the 1D XRD profile of K3 is similar to the B7 phase (Fig. 8A) [40,41]. Nevertheless, while typical LC phase textures of B7 such as helical filaments, striped focal conics, banana-leaf shape domains and checkerboard textures have not been discovered in K3, we have observed ring-banded spherulites that could have grown with twisting domains in K3 (Fig. s4).

3.4 Competition and balance between π - π stacking and dipole-dipole interaction in LC phase assembly

According to the investigations into the structures of K0, K1, K2 and K3 phases, it can be now concluded that there are two major characteristics in the assemblies of **P7**, one is the face-to-face π - π stacking between CSCN planes, and the other is the edge-to-edge ordered tilting of CSCN mesogens. In K0 that quenched from isotropic melt, CSCNs just uni-axially aligned parallel to smectic layer normal. Without optimize the molecular interactions, the mesogen packing only leads to diffuse scattering





In-situ XRD results recorded during K1-to-K2 transition. **A**, 2D XRD pattern evolution. Reflection spot 1 stands for face-to-face π - π stacking between CSCN mesogens and spot 2 is relevant to the edge-to-edge order of CSCN mesogens. The white arrows indicate the low-angle scattering originates from smectic layer modulation. **B**, 2D low-angle scatterings of the Col_{rec} phase. **C**, Possible molecular packing in the Col_{rec} phase, where the first layer modulates with the second one by shifting a/4.

in high-angle region. In K1, strong π - π stacking appears as the board-like CSCNs adjust themselves to strengthen face-to-face packing. The face-to-face packing remains strong in K2, however it looks disturbed more in K3 due to tilt of CSCN planes to avoid dipole contradiction. As for the edge-to-edge packing of CSCN, we find that the corresponding diffraction at ca. q of 10 nm⁻¹ intensifies from K1 to K2 to K3, together with increasing the d value and tilt angle. This implies that when tending to assemble into more stable structure, CSCNs keep adjusting their edge-to-edge positions to optimize the dipole-dipole interactions, since that the dipole moment of CSCN lies in the molecular plane and deviates 34° from the molecular long axis.

To further understand the relationship between π - π stacking and dipole-dipole interaction in the LC phase transition, we investigated the K1-to-K2 transition in detail through in-situ varied temperature XRD measurements (Fig. 9). During the experiment, a well-oriented K1 strip was fixed on the hot-stage by sticking both ends of the sample to the hot-stage with Kapton tape, and the middle part of the strip was exposed to X-ray beam. The ramping rate was set as 1 °C/min from 60 to 80 °C and at each measure point, the sample was isothermal for 30 min before measurement. Fig. 9A presents the 2D XRD patterns recorded during heating, indicating that the K1-to-K2 transition takes place right before 75 °C. The 1D integration also confirms this process

(Fig. s5B). As can be seen clearly, the smectic layer structure as well as the orientation maintain throughout the whole process. As a result, during the transition the well-annealed K1 should just undergo partial melting, and the molecular reorganization into K2 is restricted by the smectic layers. On the other hand, we notice the dramatic change of high-angle reflections when passing the transition point. At 75 °C, reflection 1 of π - π stacking that is striking on the meridian (the direction perpendicular to SD) at below 75 °C almost vanish; meanwhile, reflection 2 relevant to the edge-to-edge ordering tilts greater and shifts to higher angles. Therefore, the formation of K2 requires the relaxation of faceto-face stacking between CSCN planes, which in turn allows the tilting and rotating of mesogens to accommodate their dipoledipole interactions. Seemingly, the polarization orientation of CSCN dominates the K1-to-K2 transition. Once the dipole-dipole interaction has been optimized, CSCNs adjust again their position to maximize the π - π stacking to stabilize the phase structure. As a result, spot 1 reappears in the quadrants and both 1 and 2 gain in intensity at higher temperatures.

It is also worth noting that before the K1-to-K2 transition, diffraction 2 of K1 gradually moves to larger azimuth angle with increasing temperature, making the diffraction streak split more clearly (Fig. s5A). More interestingly, as indicated by the white arrow in Fig. 9A, a new low-angle scattering can be explicitly



Apparent dielectric properties of **P7** films. **A**, Average ε_r of different **P7** films calculated from 10 samples for each phase. **B**, ε_r and tan δ of **P7** films measured by broadband dielectric spectroscopy (BDS) from 100 to 1 MHz.

detected at 4.39 nm in the quadrants from 62.5 to 72.5 °C (Fig, 9A only shows the results at 65 and 70 °C as representative), which is shown more clearly in Fig. 9B. The co-appearance of the new one and the layer scattering on the equator (i.e., SD), which can be indexed as (11) and (20) with q value of 1.88 nm^{-1} and 1.28 nm⁻¹, respectively, implies a mesophase of rectangular columnar (Colrec) phase [42]. According to the studies of banana-shaped molecules [26,43,44], the Col_{rec} mesophase can be explained by the modulation of SmA layers, which is driven by the growing of dipole-dipole interactions and the accumulating of net dipoles in an individual layer. For P7, we consider that the CSCN mesogens also tend to tilt themselves to larger angles and cause the intercalation between adjacent smectic layers to escape from the macroscopic polar order. According to the XRD result shown in Fig.9B, we calculate the lattice parameter of the Col_{rec} phase as a = 9.81 nm and b = 5.19 nm and give a possible way of frustrated molecular packing into Col_{rec} phase [45]. The schematic illustration of the possible SmA modulation and Col_{rec} phase is shown in Fig. 9C. When the K1-to-K2 transition completes, the layer modulation disappears.

In short, π - π stacking plays a key role in the formation of basic SmA structure, while the dipole-dipole interaction between CSCNs drives the phase transition of **P7** in the way of escaping macroscopic polarization. The dipole-dipole interaction also helps stabilize the LC assembly at high temperatures due to its stronger force generated by the permanent dipole of CSCNs.

3.5 Dielectric property study

Given the large dipole moment of CSCN (8.54 D), we anticipate that **P7** film would exhibit good dielectric properties. P-E loops of **P7** thin films with the four different phases were tested at room temperature with the frequency of 10 Hz. **P7** thin films were processed through hot-pressing method. In order to obtain as thin a film as possible, the bulk **P7** was pressed under a pressure of 10 MPa at 90 °C without a spacer. The thickness of resulting **P7** film ranges from 30 to 50 μ m. Then the films were annealed according to the aforementioned procedures to obtain samples with K0, K1, K2 and K3 phases. Silver electrodes with diameter of 2 mm were then sputtered on the both sides of the thin film by magnetron

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sputtering. The exact thickness of the film (including the thickness of electrodes) was individually measured before experiments.

Linear P-E loops were achieved for all **P7** films, with the poling electric field up to 250 MV/m (Fig. s6). It is interesting to find that rather high apparent ε_r is achieved in **P7**. We averaged 10 samples for each phase, and the resulting average ε_{rs} from K0 to K3 are 6.9, 7.2, 8.7 and 9.7 (K0 < K1 < K2 < K3), respectively (Fig. 10A). Since CSCN possesses positive dipolar anisotropy (μ_{\parallel} > μ_{\perp}), possibly CSCN is also dielectrically positive ($\varepsilon_{r\parallel} > \varepsilon_{r\perp}$). We presume the change in ε_r relative to the alignment of CSCN dipoles in the hot-pressed films. As shown in Fig. s7 of 2D XRD results, K0, K1 and K2 thin films are shear-oriented after in hotprocessing, giving diffraction patterns more or less similar to that observed from the melt-stretched samples. For the K3 thin film, due to the relaxation of molecular orientation after annealing at 100 °C, no preferential orientation of the K3 domains would be detected. Within the K0 and K1 films, the CSCN mesogens tend to lie parallelly with the film surface and the $\varepsilon_{r\perp}$ contributes most to ε_r . For K2 and K3 films, as discussed in Section 3.3, the CSCN mesogens tilt and rotate after annealing and make $\varepsilon_{r\parallel}$ more dominant. In this case, the ε_r of K2 and K3 films is higher than that of K0 and K1 films. On the other hand, the aggregation of CSCN may also play a role. In the SmA layers of K0 the dipoles of CSCNs are counteracted to a large extent, while K3 contains the most densely packed CSCN domains with their dipoles wellorganized to give the maximized dipole moment in the thickness direction of the film. Consequently, K3 presents the highest ε_r . The schematic illustration of the molecular alignments in different thin films are shown in Fig. s8. The dielectric constant of K1, K2 and K3 also shows good stability under varied frequencies and the dielectric loss is rather low, as the tan δ of K2 and K3 films is smaller than 0.002 (Fig. 10B). In consideration of practical application, the breakdown strength of each film was also calculated according to Weibull distribution (Fig. s9). P7 films all show the high dielectric breakdown voltage (> 270 MV/m).

4 Conclusions

In conclusion, we have designed a biaxial board-shaped mesogen CSCN with bis-substituted polar cyano groups. With remarkably

large dipole moment (8.54 D), CSCN performs as a novel mesogen with dual orientation force: one from molecular shape $(\pi - \pi \text{ stacking})$ and the other from polarization (dipole-dipole interactions). We investigated the LC phase transition of the CSCN-contained SCLCP named P7 in detail. We have identified four LC phases in total: 1, K0 of SmA phase; 2, K1 of highlyordered biaxial SmA phase; 3, K2 of B5-like phase; 4, K3 of B7like phase. The most important discovery is the effect of the competition and balance between intermolecular dipole-dipole interaction and π - π stacking on the assembly of LC phases, which can influence greatly the films' dielectric properties. It has been revealed that strong dipole-dipole interaction is essential for the formation of LC phases with high thermal stability; and the dielectric anisotropy of CSCN mesogens can be used to regulate the dielectric performance of P7 films. Simply by thermal annealing, the polarization orientation of CSCN mesogens not only facilitates the formation of thermal-stable K2 and K3 phases, but also leads to the thin film with high ε_r of 9.7 in average for K3. Overall, this study provides a deeper understanding of the peculiar molecular assembly of the polymers bearing biaxial polar side-chains, and marks a step forward in the field of dielectric materials. The incorporation of the strong polar CSCN mesogen into the SCLCP structure has successfully resulted in a material with enhanced dielectric properties, which can open new avenues for the development of advanced materials in energy storage and electronic applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Supplementary material associated with this article can be found in the online version.

CRediT authorship contribution statement

Zi-Fan Yang: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. Le Zhou: Investigation. Wei Xia: Investigation. Lan-Ying Zhang: Funding acquisition. Huai Yang: Funding acquisition. Yang Shen: Supervision. Shuang Yang: Supervision. Er-Qiang Chen: Conceptualization, Supervision, Writing – review & editing.

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Supplementary materials

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