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Polymer Chemistry

PAPER

Side Chain Liquid Crystalline Polymers with an Optically Active Polynorbornene Backbone and Achiral Mesogenic Side Groups

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Most of traditional chiral side-chain liquid crystalline polymers (SCLCP) depend on pendant chiral mesogenic units to introduce chirality in their structure, with the polymer backbones being usually achiral. In this work, we asymmetrically synthesize several enantiomerically pure norbornene monomers
10 functionalized with achiral mesogenic units, and further apply ring-opening metathesis polymerization technique to prepare series of side-on and end-on SCLCPs with an optically active polynorbornene main chain and achiral mesogens. Their physical properties are fully characterized by NMR, UV, CD, GPC, TGA, DSC, polarimetry, polarized optical microscopy and small-angle X-ray scattering. The obtained side-on SCLCPs display the tendency of forming nematic, i.e. achiral mesophases, in strong contrast with
15 the chiral nematic (cholesteric) mesophase exhibited by their comparative end-on analogues. The proposed explanation for this phenomenon is that the chiral backbones and the laterally attached mesogens of side-on SCLCPs can concurrently exist in a parallel arrangement so that the mesogenic directors might not be affected by the chirality information, while the mesogenic directors of end-on SCLCPs always tilt to the backbone orientation so that the twisting power of chiral main chains might
20 force the terminally attached mesogens to form helical structures.

Introduction

Chiral liquid crystalline polymers (LCPs) possess many fascinating optical and electro-optic properties, such as chiral mesophases,[1] helical pitches,[2] selective light reflection[3] and
25 ferroelectricity,[4,5] and thus have broad application prospects[6] in electronic-controlled elastomer materials,[7,8] light reflection materials,[9] chiral recognition,[10,11] chiral separation,[12] etc. The introduction of chirality in LCPs derives from building delicately designed chiral centers on the molecular structures, which
30 markedly influence the mesomorphic properties of LCPs. Among chiral LCPs, most of previously reported side-chain LCPs (SCLCPs)[13-17] depend on pendant chiral mesogenic units to induce chirality while the polymer backbones are achiral. Herein comes a fascinating and particularly interesting question: if the
35 pendant mesogens are optically inactive, can chiral macromolecular backbones alone generate chiral mesophases (blue phase, N*, SmA*, SmC*, etc.)?

However, literature reports related to SCLCPs having chiral backbones and achiral mesogens are scarce. The few known
40 chiral backbone examples are limited to LC polypeptides and LC polycarbonates (Figure 1). Watanabe pioneered in studying thermotropic poly(glutamates) bearing terminally attached (end-on) achiral mesogens and found these samples could form cholesteric LC phases.[18-21] Gallot synthesized a series of
45 mesomorphic poly(lysines) containing end-on mesogenic azobenzene units and characterized them as exhibiting smectic A (SmA) and hexagonal phases, although no further electric-optic experiments were performed to determine whether a chiral smectic phase existed.[22,23] Deming first employed laterally
50 attached (side-on) mesogens onto poly(lysine) main chains and demonstrated that mesogens and polypeptide helices could concurrently exist in an achiral nematic-hexagonal structure.[24] Recently, Muge et al. developed a supercritical carbon dioxide technique to copolymerize mesogenic chiral epoxides and CO_2 to
55 yield optically active end-on side-chain LC polycarbonates, which presented chiral nematic (cholesteric) phase under polarized optical microscope (POM) observations.[25]

These previous works demonstrated that chiral macromolecular backbones could arrange the pendant achiral
60 mesogens into either chiral or achiral order packing. In order to further elucidate the relationship between the molecular structures of this type of SCLCPs containing chiral backbones and achiral mesogens, and the possibly induced chiral or achiral mesomorphic properties, we report in this manuscript on series of
65 SCLCPs with a novel optically active polynorbornene backbone (Figure 1). For comparison purpose, both end-on and side-on achiral mesogenic units are grafted onto the chiral polynorbornene main chain, respectively. The mesomorphic properties of the corresponding SCLCPs are characterized and
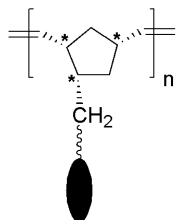70 discussed herein.

Previous works
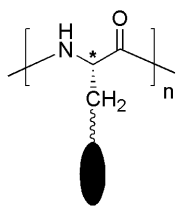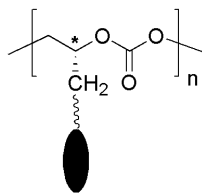
LC Polypeptide   LC Polycarbonate

This work

End-on or Side-on
Achiral Mesogens

Optically Active Polynorbornene

Fig. 1 Schematic illustration of side chain liquid crystalline polymers with chiral backbones and achiral mesogens reported in literatures and from this manuscript.

Experimental Section

The instrumentation descriptions, starting materials, the detailed synthetic procedures and ^{1}H NMR spectra of compounds **3**, **4**, **5**, **7**, **10**, **11a**, **11b**, **12a**, **12b**, **14a**, **14b**, **15a**, **15b**, **17a**, **17b**, **18a**, **18b** are listed in the supporting information.

Synthesis of LCPs *via* ROMP. Typical procedure to prepare **PNSM3**: **NSM3** (100 mg, 0.146 mmol), Hoveyda-Grubbs 2nd generation catalyst (1.83 mg, 0.003 mmol), and 1,2-dichloroethane (1.5 mL) were added into a Schlenk-type flask. The flask was degassed and exchanged with nitrogen gas. The reaction mixture was stirred at 50 ℃ for 2 h and then poured into methanol to precipitate the polymer. The resulting polymer was further purified by redissolving in THF, reprecipitating from methanol several times, and drying under the reduced pressure, which gave the desired polymer **PNSM3** (80 mg, Yield: 80%) as a brownish solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.10 (s, 4H), 7.84 (s, 1H), 7.40 (s, 1H), 7.22 (s, 1H), 6.94 (s, 4H), 5.36 – 5.03 (m, 2H), 4.16 (s, 2H), 4.00 (s, 4H), 3.73 (s, 2H), 3.05 (s, 1H), 2.77 (s, 2H), 1.80 – 1.50 (m, 7H), 1.56 – 1.43 (s, 4H), 1.32 – 1.22 (s, 2H), 1.21 – 1.06 (s, 1H), 0.97 (s, 6H).

Results and Discussion

Polynorbornenes are a class of cyclic olefin polymers which are used mainly in rubber industry for anti-vibration, anti-impact, grip improvement, etc.[26] and usually prepared by ring-opening metathesis polymerization (ROMP)[27-29] of norbornene-based monomers. Most of commercially available norbornene derivatives although consisting of chiral carbons, are racemic compounds and optically inactive. Thus in order to prepare optically active LC polynorbornenes, enantiomerically pure norbornene-based mesogens should be stereoselectively synthesized.

Scientists have previously developed various chiral catalysts or chiral auxiliaries to promote asymmetric Diels-Alder reactions[30,31] to synthesize enantiomerically pure norbornene derivatives. After a careful literature exploration, we chose Helmchen's method to prepare the key intermediate, (-)-(1S, 2S)-5-norbornene-2-carboxylic acid.[32] As illustrated in scheme 1, acryloyl chloride (**1**) was first decorated with the chiral auxiliary, D-pantolactone (**2**) and the resulting chiral ester underwent a TiCl$_4$-catalyzed high endo-selective Diels-Alder addition to cyclopentadiene. As shown in Fig. S2, the ^{1}H NMR spectrum of compound **4** presents only the endo isomer's olefinic protons which appear at δ ~5.92 and ~6.25 ppm while the exo isomer's olefinic protons appearing at δ ~5.95 and ~6.45 ppm[33] are absent. Thus the ratio of endo-adduct to exo-adduct is almost 100/0 after a two recrystallizations process. After removal of the chiral auxiliary, (-)-(1S, 2S)-5-norbornene-2-carboxylic acid (**5**) was obtained in high optical purity. The measured optical rotation, $[\alpha]_D^{20}$ (deg·dm^{-1}·g^{-1}·cm^3) of compound **5** (c = 3.0 g·L^{-1}, 95% EtOH) is -137.8° which is very close to literature data ($[\alpha]_D^{20}$ = -137°).[33]
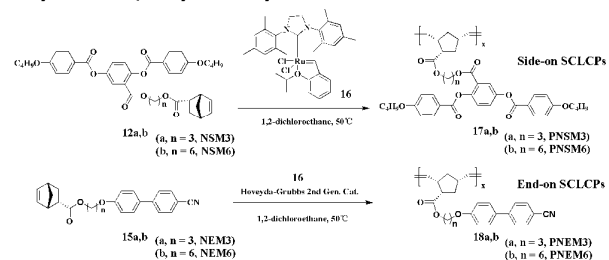
1. Synthesis of (-)-(1S,2S)-5-norbornene-2-carboxylic acid
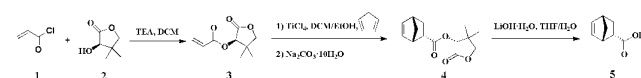
2. Synthesis of Mesogenic Monomers
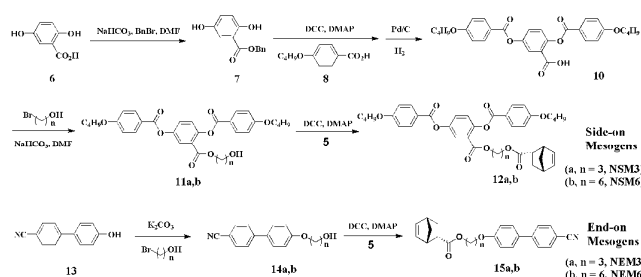
3. Synthesis of Liquid Crystalline Polymers

Scheme 1 Synthetic procedures of (-)-(1S, 2S)-5-norbornene-2-carboxylic acid, side-on or end-on mesogenic monomers and liquid crystalline polynorbornenes.

With the optically active norbornene precursor **5** in hand, we consequently designed and synthesized two side-on and two end-on mesogenic monomers with different alkyl lengths (n = 3, 6) respectively. As described in Scheme 1, the starting material, 2,5-dihydroxybenzoic acid (**6**) underwent benzyl-protection, DCC coupling, hydrogenation-deprotection and esterification reactions to give the key intermediates **11a** and **11b** which were DCC-coupled with (-)-(1S, 2S)-5-norbornene-2-carboxylic acid (**5**) to provide two side-on mesogens **NSM3** and **NSM6**. The synthetic protocol for the two end-on mesogenic monomers **NEM3** and **NEM6** is straightforward, *via* a two steps process using

etherification and DCC coupling reactions successively.

ROMP of the two side-on mesogens (**NSM3**, **NSM6**) and **the** two end-on mesogens (**NEM3**, **NEM6**) were carried out using Hoveyda-Grubbs 2nd generation catalyst **16**. For comparison purpose, the initial concentration ratios of four monomers and olefin metathesis catalyst **16** were all set as 50/1 (Table 1), the reaction temperatures (50 ℃) and the reaction times (2 h) also

kept constant. As shown in Figure 2, the cyclic olefin protons of these monomers appear at δ ~5.7 and ~6.2 ppm. After ROMP reactions, the original cyclic olefin protons become acyclic olefin protons which move upfield to ~5.2 ppm. These NMR spectra demonstrate that our desired LCPs have been successfully polymerized.
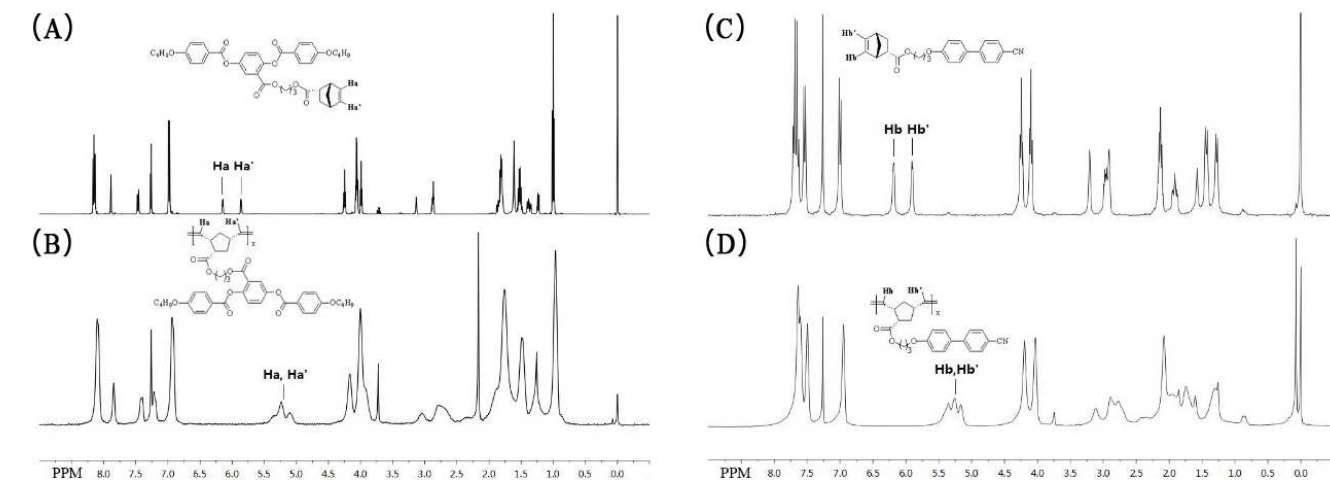

Fig. 2 ^{1}H NMR spectra of (A) the side-on mesogenic monomer **NSM3** and (B) the corresponding polymer **PNSM3**, (C) the end-on mesogenic monomer **NEM3** and (D) the corresponding polymer **PNEM3**.

The polymerization results were further examined by gel permeation chromatography (GPC). As illustrated in Table 1, all four LCPs exhibit very narrow average molecular weight

distributions, indicated by polydispersity index (PDI) values ranging from 1.07 to 1.26, which are in good agreements with the living character of ROMP.

Table 1 Molecular weights and thermal properties of the polymers

Polymer	[M]/[C]^a	M_n (g/mol)^b	M_n (× 10^4 g/mol)^c	M_w (× 10^4 g/mol)^c	M_w/M_n	T_g (℃)^d	T_d (℃)^e
PNSM3	50:1	34230	4.4	4.7	1.07	50	238
PNSM6	50:1	36340	3.9	4.9	1.26	35	336
PNEM3	50:1	18670	3.7	4.6	1.23	80	368
PNEM6	50:1	20770	4.2	4.7	1.12	37	370

^{a} Initial monomer/catalyst molar ratio. ^{b} Calculated according to a polymerization degree of 50. ^{c} Measured by GPC based on calibration using polystyrene standards. ^{d} Evaluated by DSC at a rate of 10 ℃/min. ^{e} The temperature at which 5% weight loss of the sample determined by TGA under nitrogen atmosphere at a heating rate of 10 ℃/min.
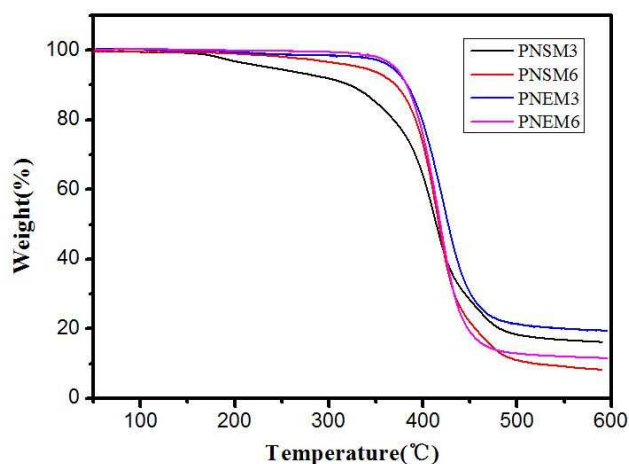

Fig. 3 Thermogravimetric analysis of four chiral polynorbornene liquid crystalline polymers.

The thermal properties of the four polynorbornene-based LCPs were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As presented in Figure 3, the temperatures at 5% weight loss (T_d) of two end-on LCP samples under N$_2$ are over 360 ℃, implying excellent thermal stabilities, while the two side-on LCP samples, in particular **PNSM3**, show a relatively lower T_d which can be ascribed to the three thermal-labile ester bonds packed on one central benzene ring.

The DSC curves of these four novel LCPs all present one obvious glass transition (T_g) during the first cooling and the subsequent heating scans. The LCPs (**PNSM3**, **PNEM3**) having shorter spacers (n = 3) connecting polynorbornene backbone and mesogens, compared with their longer spacer analogues (**PNSM6**, **PNEM6**), posses higher T_g temperatures. Besides glass transitions, DSC spectra of all four LCPs except **PNEM3**, exhibit another apparent first order phase transition, which is the LC-to-isotropic phase transition. As to **PNEM3**, since the flexible alkyl spacer linking polymer backbone and mesogens is too short (n =

3), it cannot effectively decouple the dynamics of the bulky and rigid polynorbornene main chain and longitudinally attached mesogenic units. Thus, the random-coil chain motions of polymer backbones dramatically disturb the mesomorphic organization of
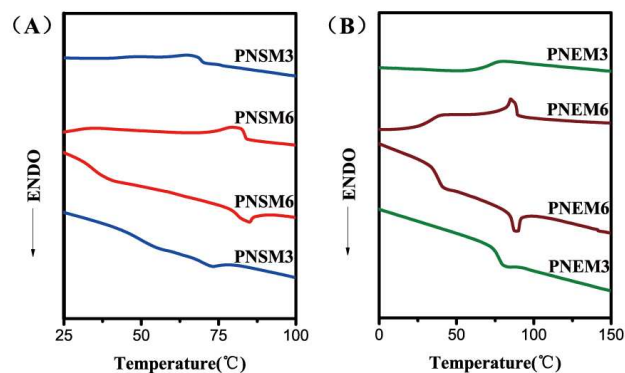5 mesogenic side groups and prevent the apparition of liquid crystallinity.[34-38]

Fig. 4 DSC curves of (A) two side-on SCLCPs: **PNSM3**, **PNSM6** and (B) two end-on SCLCPs: **PNEM3**, **PNEM6** during the first cooling scan
10 and the second heating scan at a rate of 10 ℃/min under nitrogen atmosphere.

The chiroptical properties of the intermediates, the mesogenic monomers and the corresponding LCPs are summarized in Table 2. The specific optical rotations ($[\alpha]_D^{20}$) of norbornene
15 intermediates **3**, **4** and **5** match literature values perfectly. After decorating (-)-(1S, 2S)-5-norbornene-2-carboxylic acid with mesogenic units, large decreases in optical rotation magnitude happen for all the four monomers. Most interestingly, ring opening polymerizations of these four chiral norbornene
20 mesogens all result in opposite sign of optical rotations and diminished magnitudes for the polymers.

Table 2 Specific Rotations of the Monomers and Polymers[a]

Compound	$[\alpha]_D^{20}$ (deg·dm^{-1}·g^{-1}·cm^3)	Polymer	$[\alpha]_D^{20}$ (deg·dm^{-1}·g^{-1}·cm^3)
3[b]	+6.5° (lit.[32] +6.5°)		
4[b]	-106.2° (lit.[33] -106°)		
5[c]	-137.8° (lit.[33] -137°)		
NSM3[d]	-12.5°	**PNSM3**[d]	+15.2°
NSM6[d]	-22.3°	**PNSM6**[d]	+24.8°
NEM3[d]	-72.4°	**PNEM3**[d]	+35.0°
NEM6[d]	-43.9°	**PNEM6**[d]	+25.0°

[a] Specific optical rotation was measured in a 1 dm cell at a concentration of [b] 17.0 g·L^{-1} in CH$_2$Cl$_2$, or [c] 3.0 g·L^{-1} in 95% EtOH, or [d] 1.0 g·L^{-1} in THF
25 at 20 ℃.

Figure 5 illustrates the UV-vis absorption and circular dichroism (CD) spectra of four polynorbornene-based polymers dissolved in THF solvent at a polymer (D.P. assumed as 50) concentration of ca. 4 × 10^{-7} mol/L. The UV-vis spectra of
30 **PNSM3** and **PNSM6** reveal two absorption peaks centered at ca. 225 nm and 270 nm, which are assigned as the electronic transitions of carbonyl groups and aromatic groups respectively. **PNEM3** and **PNEM6** possess similar UV-vis spectra although the absorption peak of aromatic rings blue-shift to ca. 292 nm due

35 to the long-range conjugation with nitrile groups. However, the CD spectra of all four polymers exhibit almost no signals in the same UV absorption regions, indicating that the grafted mesogens are not affected by the chirality information of the polymer main chains and arrange in a fully disordered way in solution.
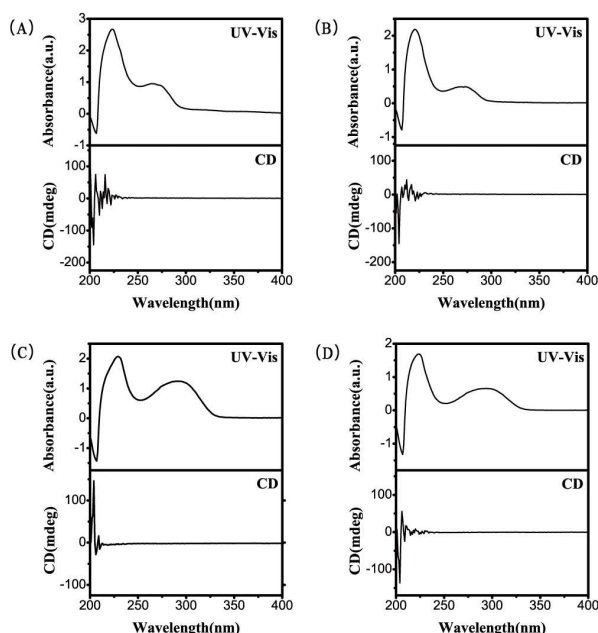

40 **Fig. 5** UV-vis and CD absorption spectra of (A) **PNSM3**, (B) **PNSM6**, (C) **PNEM3** and (D) **PNEM6** in THF at a polymer (D.P. assumed as 50) concentration of ca. 4 x 10^{-7} mol/L.

The mesomorphic properties of the monomers and polymers
45 were investigated by POM and one-dimensional wide-angle X-ray scattering (WAXS) experiments. As shown in Table 3 and Figure 6, the two side-on monomers **NSM3** and **NSM6** show typical cholesteric oily streaks textures (Figure 6A,B), while the two end-on monomers **NEM3** and **NEM6** present crystalline
50 spherulite textures (Figure 6C,D) and have no LC phases.

Table 3 Mesomorphic Properties of the Monomers and Polymers[a]

Monomer	Phase transitions (℃)	Polymer	Phase transitions (℃)
NSM3	K 35 N* 100 I I 99 N* 24 K	**PNSM3**	G 50 N 73 I I 68 N 43 G
NSM6	N* 48 I I 43 N*	**PNSM6**	G 35 N 85 I I 81 N 28 G
NEM3	K 68 I I 35 K	**PNEM3**	G 80 I I 71 G
NEM6	K 49 I I 37 K	**PNEM6**	G 37 N* 88 I I 85 N* 32 G

[a] Detected by polarized optical microscopy. Glass phase are determined by DSC. K = crystalline, G = glass phase, N = nematic phase, N* = cholesteric phase. First line obtained on heating, second line obtained on
55 cooling.

Evaluated by WAXS experiments (Figure 7), the two side-on SCLCPs **PNSM3** and **PNSM6** present two diffuse scattering peaks in low-angle and high-angle regions respectively, which is similar to the scattering characteristics of mesogen-jacketed
60 liquid crystalline polymers (MJLCP),[39-43] whereas the end-on SCLCP **PNEM6** shows only one diffuse peak in high angles and

no signals in low angles. These WAXS patterns indicate that these three polymers possess no lamellar layer structures or columnar mesophases, and only nematic phase or cholesteric phase can exist in these samples.
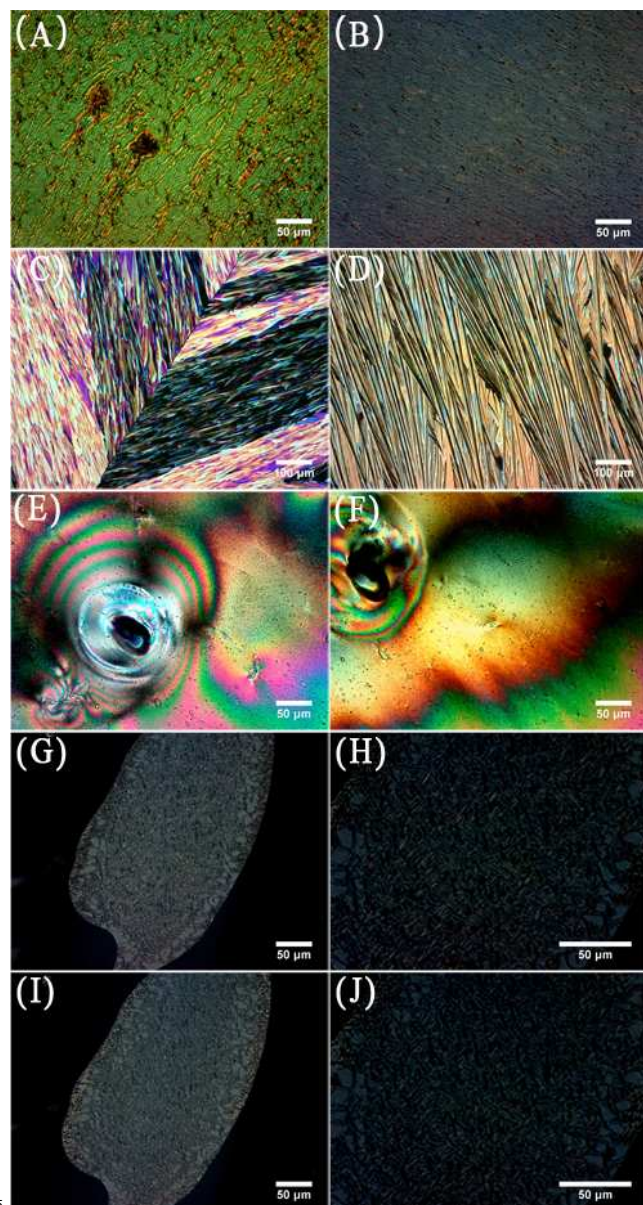

Fig. 6 POM images of (A) **NSM3** recorded at 36 ℃, (B) **NSM6** recorded at 38 ℃, (C) **NEM3** recorded at 25 ℃, (D) **NEM6** recorded at 25 ℃, (E) **PNSM3** recorded at 59 ℃, (F) **PNSM6** recorded at 67 ℃, and **PNEM6** recorded at (G, H) 58 ℃, (I, J) 68 ℃ respectively.

However, the initial POM examinations of all the polymers except **PNEM3**, provided ambiguous and noncharacteristic birefringent textures. We also found it was extremely difficult to fill these polymer samples into anti-parallel or homeotropic aligned LC cells even at temperatures much higher than the clearing points due to polymers' high viscosities. Alternatively, we heated up these LCP samples to the isotropic melts in between microscope slides, constantly applied shear stress on the cover glass to force the viscous samples to develop into as thinner as possible films, slowly cooled these samples at a rate of - 0.1

℃/min to the LC phases, and then kept them at LC phases annealing for 24~72 h. Fortunately, these three LCP samples eventually grew in characteristic textures. As shown in Figure 6E-F, two side-on SCLCPs **PNSM3** and **PNSM6** present marble textures of nematic phase, while a fingerprint texture can be observed in Figure 6G-J, indicating that the end-on SCLCP **PNEM6** contrarily possesses a chiral nematic (N*, cholesteric) phase.
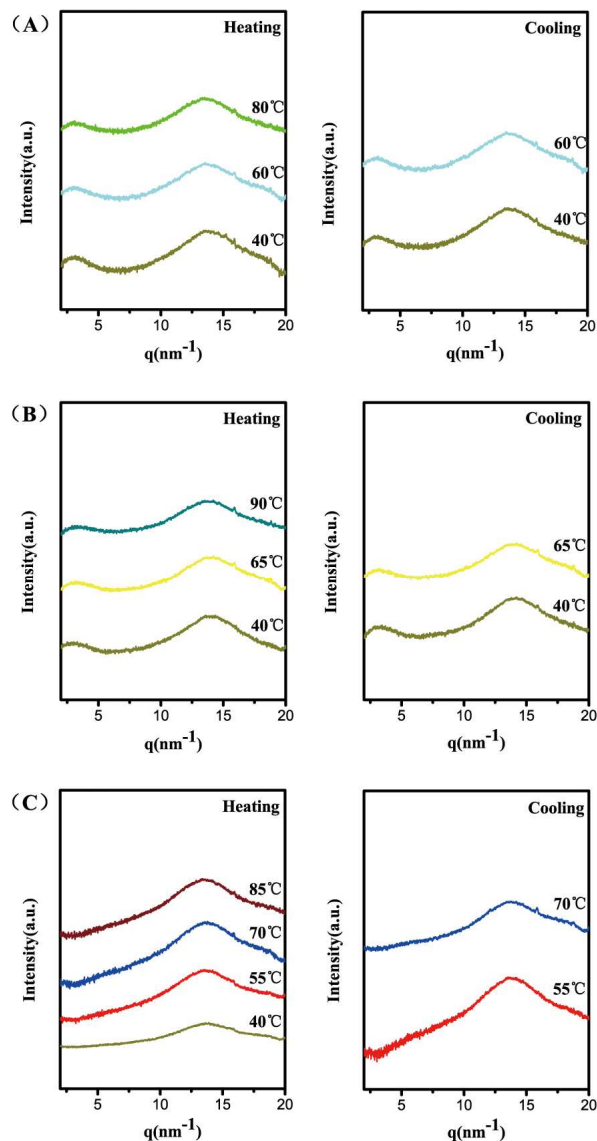

Fig. 7 One-dimensional WAXS patterns of (A) **PNSM3**, (B) **PNSM6** and (C) **PNEM6**.

In order to further verify the existence of N* phase, we mixed **PNEM6** sample with 5 wt% THF solvent to lower the viscosity, filled the mixture into a 4 μm thick anti-parallel surface-rubbed LC cell above the clearing point, and slowly cooled the sample at a rate of - 0.1 ℃/min from the isotropic melts to the LC phase. Under POM observation as presented in Figure 8, **PNEM6** sample shows fairly uniform birefringence indicating that the mesogenic directors are anchored under planar conditions at the substrates,[2] and contains plenty of isotropic regions possibly due

to the evaporation or microphase separation of THF solvent. Most importantly, a characteristic oily streaks texture of N* phase is clearly visualized, proving that the end-on SCLCP **PNEM6** has a chiral nematic phase.
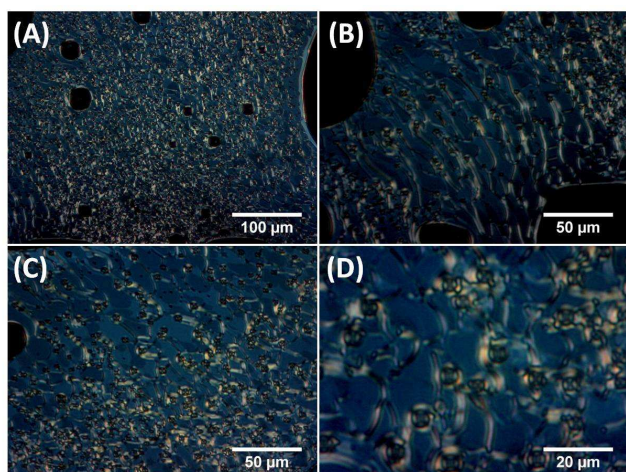

Fig. 8 POM images of **PNEM6** recorded at 68 ℃.

The proposed explanation for this phenomenon is schematically illustrated in Figure 9. Our hypothesis is that the chiral backbones and the laterally attached mesogens of side-on SCLCPs can concurrently exist in a parallel arrangement so that the mesogenic directors might be less likely affected by the backbones' chirality information and spontaneously obtain long-range orientational orders to form achiral mesophases, while the mesogenic directors of end-on SCLCPs will always tilt to the backbone orientation so that the twisting power of chiral main chains might force the terminally attached mesogens to form helical structures, resulting in chiral mesophases. This hypothesis can be used to explain why Watanabe's end-on mesogenic polypeptides[18-21] and end-on LC polycarbonates[25] showed cholesteric phases while Deming's side-on mesogenic polypeptides[24] presented achiral nematic phase.
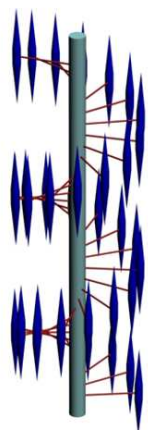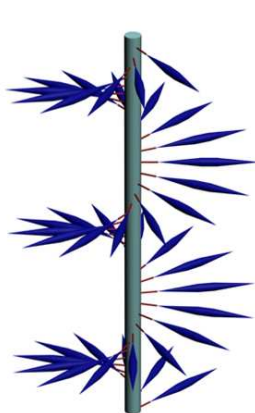

Fig. 9 Schematic illustration of the proposed mesogenic directors and backbone orientations of side-on SCLCPs and end-on SCLCPs.

Conclusions

In this work, we asymmetrically synthesized several enantiomerically pure norbornene monomers attached with achiral mesogenic units, and further applied ROMP technique to prepare a series of side-on or end-on SCLCPs with an optically active polynorbornene main chain and achiral mesogens. Through investigation, we found that the obtained side-on SCLCPs displayed the tendency of forming nematic phases, in strong contrast with the chiral nematic (cholesteric) phase of their comparative end-on analogue. A hypothesis about the orientational arrangements of mesogenic directors and chiral backbones is described. Developments of novel terminally attached mesogens to explore chiral smectic structures derived from this basic strategy are under investigation.

Acknowledgement

Notes and references

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