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# Mesogen-Jacketed Liquid Crystalline Polymers with a Polynorbornene Main Chain: Green Synthesis and Phase Behaviors

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**ABSTRACT:** We synthesized a new series of MJLCPs with a polynorbornene main chain, PNb*n*PT (n = 8, 10, 12, 14, 16, 18, which is the number of carbons in the side-chain alkyl tails), through ring-opening metathesis polymerization and investigated their phase behaviors. The monomers were facilely synthesized in satisfactory yields through a key intermediate, N-(2,5-dicarboxylphenyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide. Differential scanning calorimetry, polarized light microscopy, and wide-angle X-ray diffraction results



demonstrate that the phase behavior of PNb*n*PT is strongly dependent on the alkyl-tail length. Polymers with relatively short alkyl tails, PNb8PT and PNb10PT, are amorphous in the whole temperature range before degradation. When the alkyl-tail length increases, PNb*n*PTs (n = 12, 14, 16, 18) develop into the smectic A phase, and the degree of order increases with increasing alkyl-tail length. The synthetic pathway for MJLCPs with a polynorbornene main chain in this work is more robust and greener than those reported to the best of our knowledge. And MJLCPs with a polynorbornene main chain show quite different phase behaviors compared with those with a polyethylene backbone, and they may be used to create fascinating functional materials.

# INTRODUCTION

The decoupling concept, in which flexible spacers are used to decouple the motion of the ordered arrangement of side-chain mesogens from that of the random-coiled main chain, is undoubtedly a landmark for the development of side-chain liquid crystalline polymers (LCPs).<sup>1</sup> To hinder the rotational motion around the long axis of the side-chain mesogen, Finkelmann et al. synthesized a side-chain LCP with mesogens laterally attached to the polymer backbone.<sup>2</sup> Mesogen-jacketed liquid crystalline polymer (MJLCP), proposed by Zhou et al. in the late 1980s,<sup>3,4</sup> is an LCP with bulky side groups (often mesogens) laterally attached to the main chain through a short spacer or a single covalent bond.<sup>5</sup> Although MJLCPs have molecular structures like side-chain LCPs, they exhibit properties similar to those of main-chain LCPs, such as forming banded textures by shearing in the liquid crystalline (LC) state and having large persistence lengths in solutions,<sup>6–8</sup> because the backbones of MJLCPs are forced to take the extended-chain conformation owing to the steric effect of the crowded side chains, the "jacketing" effect.9 Many LC phases of MJLCPs have been reported, including columnar nematic  $(\Phi_{\rm N})$ ,<sup>10–12</sup> hexatic columnar nematic  $(\Phi_{\rm HN})$ ,<sup>11,13</sup> hexagonal columnar  $(\Phi_{\rm H})$ ,<sup>11,14</sup> rectangular columnar,<sup>12,15</sup> smectic A (SmA),<sup>14,16</sup> and smectic C<sup>17</sup> phases, in which the MJLCP chain behaves like a cylinder or tablet to form the LC phases.

With the development of the structural library of MJLCPs, many efforts have been put on the molecular engineering of the MJLCP main chains. The first reported series of MJLCPs are based on polyacrylates and polymethacrylates.<sup>3,4</sup> Compared to polyacrylates, the polymethacrylate backbone tends to depress

the LC phase formation, indicating the influence of the polymer backbone on liquid crystallinity. The most studied MJLCPs are those with a polystyrene main chain, which can be synthesized by controlled radical polymerizations.<sup>18</sup> A series of MJLCPs with side-chain cores based on 2-vinylhydroquinone,<sup>19</sup> 2-vinyl-1,4-phenylenediamine,<sup>8</sup> 2-vinylterephthalic acid (VTA),<sup>20–25</sup> vinylbiphenyl,<sup>16,26–28</sup> vinylterphenyl,<sup>29,30</sup> and oxadiazole-containing conjugated structure<sup>14,31</sup> have been successfully synthesized.<sup>18</sup> By hydrosilylation of polymethylhydrosiloxane with the styrenic monomers, MJLCPs with a polysiloxane main chain were synthesized.<sup>32</sup>

Besides MJLCPs with flexible backbones, the jacketed structure has also been applied to polymers with rigid backbones, such as polyalkynes<sup>33,34</sup> and polythiophenes.<sup>35,36</sup> In addition, MJLCPs with a polynorbornene backbone and laterally attached 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy] mesogens in side chains display enantiotropic nematic mesophases.<sup>37</sup> Terminating the hydrocarbon substituents of the mesogen with immiscible components, such as fluorocarbon segments or oligodimethylsiloxane segments, can induce smectic layering in these polymers with a polynorbornene backbone.<sup>38,39</sup> Very recently, Yang et al. reported a new series of MJLCPs with a polynorbornene backbone.<sup>40</sup> The polymers are liquid crystalline when the number of carbon atoms in the alkoxy terminal chains of the side-chain mesogen is more than nine.

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In the past two decades, Percec and co-workers have intensively investigated and synthesized the other type of jacketed polymers, namely dendron-jacketed polymers, a set of living polymerization methods, such as living cationic polymerization,<sup>44,45</sup> living polymerization of acetylenes,<sup>46</sup> and living metathesis polymerization.<sup>47</sup> With the consideration of the high tolerance of functional groups like fullerene, the convenient synthesis by ring-opening metathesis polymerization (ROMP),<sup>48,49</sup> and the excellent properties of polynorbornenes,<sup>50,51</sup> the exploration of MJLCPs with a polynorbornene main chain is of great interest. The reported procedures for synthesizing MJLCPs with a polynorbornene main chain are either too complicated or using heavy metal catalysts, which is not environmentally friendly. In addition, they are not robust enough to create various MJLCPs. Herein, we designed and synthesized a new series of MJLCPs with a which is the number of carbons in the side-chain alkyl tails. Chart 1), via a green and robust pathway. The phase behaviors

### Chart 1. Chemical Structure of PNbnPT



PNbnPT, n = 8, 10, 12, 14, 16, 18

of PNb*n*PTs are strongly dependent on the length of the alkyl tail. PNb*n*PTs with long alkyl tails (n = 12, 14, 16, 18) develop into the SmA phase, and those with short alkyl tails (n = 8, 10) are amorphous.

## EXPERIMENTAL SECTION

Materials and Characterization Methods. Dichloromethane  $(CH_2Cl_2)$  was pretreated by the Braun solvent purification system. *cis*-S-Norbornene-*exo*-2,3-dicarboxylic anhydride (96%) and *N*,*N*-dimethylformamide (DMF, HPLC) were purchased from J&K Chemical. Grubbs catalyst (second generation) was purchased from Sigma-Aldrich. All other reagents were obtained from commercial sources and used as received unless otherwise noted. <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz), high-resolution mass spectrometry (MS), elemental analysis, gel permeation chromatographic (GPC) measurements, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized light microscopy (PLM), and one-

Scheme 1. Synthetic Pathway of the Polymers (PNbnPTs)

dimensional (1D) wide-angle X-ray diffraction (WAXD) experiments were performed according to the procedures described previously.<sup>12,52</sup> For 1D WAXD experiments, about 35 mg of the powder sample was dissolved in tetrahydrofuran (THF,  $\sim 1 \text{ mL}$ ) and cast into a film on a copper substrate. Solvent was then allowed to evaporate at ambient temperature for hours, and the sample was dried overnight at 35 °C in vacuum before characterization. To avoid thermal degradation, the sample chamber was charged with nitrogen during measurements. Two-dimensional (2D) WAXD experiments were performed using a Bruker D8Discover diffractometer with VANTEC 500 as a 2D detector. Corundum was used for calibration of the reflection peak positions. The diffraction patterns were recorded in the transmission mode at ambient temperature using uniaxially oriented fiber samples. Macroscopically oriented fiber samples of all polymers were drawn with a pair of tweezers at 190-230 °C for 2D WAXD experiments. All fiber samples were annealed at 100 °C overnight before characterization.

**Synthetic Procedures.** The *p*-(*n*-alkoxyl)phenols (C*n*-OH, n = 8, 10, 12, 14, 16, 18) were prepared as described in the literature.<sup>53</sup> The chemical structures and synthetic procedures of all the monomers and polymers are illustrated in Scheme 1. The experimental details are described as follows.

*N*-(2,5-*Dicarboxylphenyl)-cis-5-norbornene-exo-2,3-dicarboximide (<i>NbTA*). *cis*-5-Norbornene-*exo-2*,3-dicarboxylic anhydride (2.00 g, 12.2 mmol) and glacial acetic acid (30.0 mL) were charged in a 100 mL three-necked flask. 2-Aminoterephthalic acid (2.21 g, 12.2 mmol) was added stepwise to the reaction mixture at 120 °C in 30 min. Then the reaction mixture was stirred for 12 h. After cooling to ambient temperature, the mixture was poured into cold water (~150 mL) and vigorously stirred for 2 h. After filtration and drying under an infrared lamp, the product was obtained as a white powder. Yield: 80%. <sup>1</sup>H NMR (400 MHz, DMSO, δ, ppm): 13.53 (s, 2H), 7.77–8.11 (m, 3H), 6.37 (s, 2H), 3.19–3.26 (d, 2H), 2.85–2.89 (d, 2H), 1.36–2.02 (m, 2H). MS (HR-ESI):  $[M - H]^{-}/z$ , Calcd 326.0670; Found 326.0662. Anal. Calcd for C<sub>17</sub>H<sub>13</sub>O<sub>6</sub>N: C, 62.39; H, 4.00; N, 4.28. Found: C, 62.40; H, 4.22; N, 4.28.

*Monomers (NbnPTs).* The synthetic procedures for the monomers with different alkyl-tail lengths are similar. The details are described below with Nb8PT as an example.

C8-OH (1.36 g, 6.12 mmol), NbTA (1.00 g, 3.06 mmol), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 3.15 g, 15.3 mmol), 4-(dimethylamino)pyridine (DMAP, 0.17 g, 1.53 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (50.0 mL) were loaded in a 100 mL round-bottomed flask and stirred for 24 h at ambient temperature. The floating solid was filtered off, and the solvent was evaporated. The crude product was purified by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub> and subsequent recrystallization from ethanol. Yield of Nb8PT: 70%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.00–8.50 (m, 3H), 7.00–7.18 (m, 4H), 6.85–6.99 (m, 4H), 6.32 (s, 2H), 3.88–4.04 (q, 4H), 3.40 (s, 2H), 2.87 (s, 2H), 1.73–1.85 (m, 4H), 1.53–1.71 (s, 2H), 1.17–1.53 (m, 20H), 0.88 (t, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 176.9, 176.4, 163.6, 163.2, 157.3, 143.9, 143.6, 138.0, 134.6, 132.8, 132.2, 131.5, 130.7,



122.2, 115.2, 68.5, 68.4, 48.5, 45.6, 43.5, 31.6, 29.3, 25.7, 22.6, 14.0. MS (HR-ESI):  $[M + H]^+/z$ , Calcd 736.3849; Found, 736.3836. Anal. Calcd for  $C_{45}H_{53}O_8N$ : C, 73.44; H, 7.26; N, 1.90. Found: C, 73.17; H, 7.16; N, 2.12.

Nb10PT was prepared starting from C10-OH. Yield: 74%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.00–8.50 (m, 3H), 7.00–7.18 (m, 4H), 6.85–6.99 (m, 4H), 6.32 (s, 2H), 3.88–4.04 (q, 4H), 3.40 (s, 2H), 2.87 (s, 2H), 1.73–1.85 (m, 4H), 1.53–1.71 (s, 2H), 1.17–1.53 (m, 28H), 0.88 (t, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 176.9, 176.4, 163.6, 163.2, 157.3, 143.9, 143.6, 138.0, 134.6, 132.8, 132.2, 131.5, 130.7, 122.2, 115.2, 68.5, 68.4, 48.5, 45.6, 43.5, 31.9, 29.6, 29.4, 29.3, 26.1, 22.7, 14.1. MS (HR-ESI): [M + H]<sup>+</sup>/z, Calcd 814.4295; Found, 814.4293. Anal. Calcd for C<sub>49</sub>H<sub>61</sub>O<sub>8</sub>N: C, 74.31; H, 7.76; N, 1.77. Found: C, 73.95; H, 7.63; N, 1.95.

Nb12PT was prepared starting from C12-OH. Yield: 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.00–8.50 (m, 3H), 7.00–7.18 (m, 4H), 6.85–6.99 (m, 4H), 6.32 (s, 2H), 3.88–4.04 (q, 4H), 3.40 (s, 2H), 2.87 (s, 2H), 1.73–1.85 (m, 4H), 1.53–1.71 (s, 2H), 1.17–1.53 (m, 36H), 0.88 (t, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 176.9, 176.6, 163.6, 163.0, 157.2, 143.7, 143.6, 138.0, 134.6, 132.8, 132.2, 131.5, 130.7, 122.2, 115.2, 68.4, 48.5, 45.6, 43.5, 31.9, 29.7, 29.6, 29.4, 26.0, 22.7, 14.1. MS (HR-ESI): [M + H]<sup>+</sup>/z, Calcd 848.5101; Found, 848.5075. Anal. Calcd for C<sub>53</sub>H<sub>69</sub>O<sub>8</sub>N: C, 75.06; H, 8.20; N, 1.65. Found: C, 75.12; H, 7.95; N, 1.63.

Nb14PT was prepared starting from C14-OH. Yield: 72%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.00–8.50 (m, 3H), 7.00–7.18 (m, 4H), 6.85–6.99 (m, 4H), 6.32 (s, 2H), 3.88–4.04 (q, 4H), 3.40 (s, 2H), 2.87 (s, 2H), 1.73–1.85 (m, 4H), 1.53–1.71 (s, 2H), 1.17–1.53 (m, 44H), 0.88 (t, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 176.9, 176.6, 163.6, 163.0, 157.2, 143.7, 143.6, 138.0, 134.6, 132.8, 132.2, 131.5, 130.7, 122.2, 115.2, 68.4, 48.5, 45.6, 43.5, 31.9, 29.7, 29.6, 29.4, 26.0, 22.7, 14.1. MS (HR-ESI): [M + H]<sup>+</sup>/z, Calcd 904.5727; Found, 904.5724. Anal. Calcd for C<sub>57</sub>H<sub>77</sub>O<sub>8</sub>N: C, 75.71; H, 8.58; N, 1.55. Found: C, 75.71; H, 8.64; N, 1.53.

Nb16PT was prepared starting from C16-OH. Yield: 68%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.00–8.50 (m, 3H), 7.00–7.18 (m, 4H), 6.85–6.99 (m, 4H), 6.32 (s, 2H), 3.88–4.04 (q, 4H), 3.40 (s, 2H), 2.87 (s, 2H), 1.73–1.85 (m, 4H), 1.53–1.71 (s, 2H), 1.17–1.53 (m, 52H), 0.88 (t, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 176.9, 176.6, 163.6, 163.0, 157.2, 143.7, 143.6, 138.0, 134.6, 132.8, 132.2, 131.5, 130.7, 122.2, 115.2, 68.4, 48.5, 45.6, 43.5, 31.9, 29.7, 29.6, 29.4, 26.0, 22.7, 14.1. MS (HR-ESI): [M + H]<sup>+</sup>/z, Calcd 960.6353; Found, 960.6362. Anal. Calcd for C<sub>61</sub>H<sub>85</sub>O<sub>8</sub>N: C, 76.29; H, 8.92; N, 1.46. Found: C, 76.31; H, 8.87; N, 1.37.

Nb18PT was prepared starting from C18-OH. Yield: 75%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.00–8.50 (m, 3H), 7.00–7.18 (m, 4H), 6.85–6.99 (m, 4H), 6.32 (s, 2H), 3.88–4.04 (q, 4H), 3.40 (s, 2H), 2.87 (s, 2H), 1.73–1.85 (m, 4H), 1.53–1.71 (s, 2H), 1.17–1.53 (m, 60H), 0.88 (t, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 176.9, 176.6, 163.6, 163.0, 157.2, 143.7, 143.6, 138.0, 134.6, 132.8, 132.2, 131.5, 130.7, 122.2, 115.2, 68.4, 48.5, 45.6, 43.5, 31.9, 29.7, 29.6, 29.4, 26.0, 22.7, 14.1. MS (HR-ESI): [M + NH<sub>4</sub>]<sup>+</sup>/z, Calcd 1033.7245; Found, 1033.7263. Anal. Calcd for C<sub>65</sub>H<sub>93</sub>O<sub>8</sub>N: C, 76.81; H, 9.22; N, 1.38. Found: C, 76.81; H, 9.19; N, 1.28.

*Polymers (PNbnPTs).* The synthetic procedures for the polymers with different alkyl-tail lengths are similar. The details are described below with PNb8PT as an example.

Nb8PT (200 mg) and Grubbs second-generation catalyst (4.61 mg) were loaded in a dry Schlenk tube with a magnetic stirring bar. After three pump-purge cycles with high purity nitrogen,  $CH_2Cl_2$  (~2 mL) was injected to the mixture under vigorous stirring to initiate polymerization. After the reaction mixture was stirred at ambient temperature for 1 h, a few drops of vinyl ethyl ether were added to the reaction mixture using a syringe. Then polymerization was stopped after an additional hour. The viscous liquid was diluted with 5 mL of  $CH_2Cl_2$  and passed through a short alumina column to separate the catalyst, and then the polymer was precipitated out in 100 mL of methanol. By filtration and drying in vacuum at 35 °C for 24 h, the target polymer PNb8PT was obtained as a white solid. Yield: 95%.

PNb10PT, PNb12PT, PNb14PT, PNb16PT, and PNb18PT were similarly prepared starting from corresponding monomers as white solids with yields of 93, 92, 94, 95, and 92%, respectively.

# RESULTS AND DISCUSSION

Synthesis of Monomers and Polymers. As shown in Scheme 1, the monomers can be prepared in three very efficient steps with commercially available starting materials. The key intermediate for the synthesis of this kind of MJLCPs with a polynorbornene main chain was NbTA, which can be facilely synthesized by the imidization of cis-5-norbornene-exo-2,3dicarboxylic anhydride and 2-aminoterephthalic acid with a yield of 80%. This key intermediate NbTA may open a new avenue for the synthesis of MJLCPs containing a polynorbornene main chain, which is similar to VTA for the synthesis of MJLCPs with a polyethylene backbone.<sup>5</sup> Cn-OH was synthesized by Williamson etherification of hydroquinone and the corresponding 1-bromoalkane. Then Steglich esterification of NbTA and Cn-OH gave the monomers NbnPTs in satisfactory yields. The chemical structures of the monomers were verified by the combination of <sup>1</sup>H/<sup>13</sup>C NMR, highresolution MS, and elemental analysis.

High-molecular-weight (MW) polymers with relatively narrow MW distributions were obtained through ROMP in dichloromethane with Grubbs second-generation catalyst. The molecular characteristics of the polymers are summarized in Table 1. GPC results show that  $M_n$ 's of PNbnPTs are 3.5 ×

 Table 1. Molecular Characteristics and Thermal Properties

 of the Polymers

polymer	$M_n^a$ (×10 <sup>5</sup> Da)	PDI	$T_{d}^{b}$ (°C)	T <sub>transition</sub> (°C) (and corresponding enthalpy change, <sup>c</sup> kJ/mol)
PNb8PT	3.86	1.24	401	
PNb10PT	3.74	1.30	404	
PNb12PT	3.64	1.29	394	
PNb14PT	3.65	1.35	408	
PNb16PT	3.50	1.34	399	1 (13.44), 143 (1.92)
PNb18PT	3.45	1.32	402	25 (25.10), 147 (3.05)

<sup>a</sup>Determined by GPC in THF using polystyrene standards. <sup>b</sup>5% weight loss temperature evaluated by TGA under a nitrogen atmosphere at a heating rate of 10  $^{\circ}$ C/min. <sup>c</sup>Evaluated by DSC during the second heating cycle at a rate of 20  $^{\circ}$ C/min.

 $10^5-3.9 \times 10^5$  Da, with polydispersity indexes (PDIs) of 1.24– 1.35. Figure 1 gives <sup>1</sup>H NMR spectra of Nb16PT and PNb16PT in CDCl<sub>3</sub>. The characteristic resonance of vinyl H appearing at  $\delta = 6.32$  ppm completely disappears after polymerization, and the resonance peaks of PNb16PT are rather broad and consistent with the expected polymer structure, indicating the successful polymerization as well.

**Thermal Properties of PNb***n***PTs.** TGA and DSC were used to investigate the thermal properties of PNb*n***PTs.** TGA results show that all the polymers exhibit excellent thermal stabilities with the 5% weight loss temperatures above 390 °C in nitrogen atmosphere, as shown in Table 1.

Figure 2 shows the DSC traces of all polymers on the first cooling and subsequent heating processes at a rate of 20  $^{\circ}C/$ min under nitrogen. All the samples were heated to 280  $^{\circ}C$  first to eliminate thermal history. Glass transitions occur at 100–120  $^{\circ}C$  with small changes in heat flow possibly due to the rigidity of the polymer chains that renders quite slow glass-transition kinetics. As shown in Figure 2, the DSC traces of the



Figure 1. <sup>1</sup>H NMR spectra of PNb16PT (top) and Nb16PT (bottom) in  $\text{CDCl}_3$ .



Figure 2. DSC traces of PNbnPTs at a rate of 20 °C/min under a nitrogen atmosphere.

polymers are different depending on alkyl-tail length. Upon heating, an endothermic peak is observed at the temperature range of 140-150 °C during heating for PNb16PT and PNb18PT. The enthalpy values of these transitions are relatively small (1.92-3.05 kJ/mol), and no more transitions are observed at even higher temperatures. These results suggest that the transitions at the temperature range of 140-150 °C may be related to the isotropization of the polymers from a possible LC phase. The increasing enthalpy change with increasing alkyl-tail length indicates that a more ordered structure may be generated in polymers with longer alkyl tails. For PNb16PT and PNb18PT, an additional peak is observed at 1 and 25 °C, respectively, during heating. This transition corresponds to melting of the crystals formed by the long alkyl tails. In the cooling cycles, one or two exothermic peaks appear, consistent with the endothermic peaks during heating,

indicating the enantiotropic phase behaviors of PNb16PT and PNb18PT.

**Phase Structures of PNb***n***PTs.** Phase behaviors of PNb*n*PTs were then examined by PLM observation of samples cast from THF solutions and slowly dried at ambient temperature. Properties of PNb*n*PTs with long alkyl tails (n = 12, 14, 16, 18) are similar. For example, PNb18PT shows strong birefringence at 80 °C, which implies a possible LC phase, as shown in Figure 3a. However, these four samples only





Figure 3. PLM micrographs of PNb18PT (a) and PNb8PT (b) at 80  $^\circ\text{C}.$ 

exhibit noncharacteristic textures. On the other hand, PNb8PT (Figure 3b) and PNb10PT do not show any birefringence in the whole temperature range even when the samples are sheared, indicating that these two samples with relatively short alkyl tails are amorphous.

Because DSC and PLM results do not provide enough structural information on the polymers, variable-temperature 1D WAXD experiments were conducted to further identify the phase structures of the polymers. In agreement with the PLM results, two kinds of 1D WAXD patterns are observed for the polymers, as shown in Figures 4 and 5 for PNb18PT and PNb10PT, respectively, as examples. For PNb18PT, two diffraction peaks with a scattering vector ratio of 1:2 are observed in the low-angle region during the first heating process, demonstrating a long-range ordered smectic phase. The broad halo in the wide-angle region is characteristic of the disordered packing of the side chains. After heating to higher temperatures, the diffraction pattern remains the same until isotropization at about 150 °C when the sharp diffraction peak in the low-angle region becomes broad. The isotropization temperature of 150 °C for PNb18PT from 1D WAXD results is consistent with DSC results. Upon cooling, the two diffraction peaks originating from the smectic phase develop again, indicating the enantiotropic phase behavior of PNb18PT.



Figure 4. 1D WAXD patterns of PNb18PT during the first heating (a) and subsequent cooling (b) processes.

Because the temperature was not low enough during cooling, the crystallization process of the side-chain alkyl tails indicated by DSC results was not observed. However, for PNb10PT, the as-cast sample only gives two broad halos in the low- and wideangle regions. And the diffraction pattern remains almost unchanged in the whole temperature range during heating and cooling processes, indicating the amorphous nature of PNb10PT.

PNb8PT and PNb*n*PT (n = 12, 14, 16) have very similar diffraction patterns as PNb10PT and PNb18PT, respectively. The 1D WAXD patterns of the as-cast PNb*n*PTs at ambient temperature are summarized in Figure 6a. This set of diffraction profiles demonstrates clearly that the phase behaviors of PNb*n*PTs strongly depend on the alkyl-tail length. For the diffraction in the low-angle region, namely the (100) diffraction of the smectic phase, the intensity decreases, and the peak becomes broader with decreasing alkyl-tail length until the polymer becomes amorphous (for PNb10PT and PNb8PT). And the (200) diffraction can hardly be observed when *n* is 14



Figure 5. 1D WAXD patterns of PNb10PT during the first heating (a) and subsequent cooling (b) processes.

or less. These results show that the longer alkyl tail can induce the smecticity of the polymers. This inducing effect should stem from the nanophase separation of the benzoate core and alkyl tails in the side chains. Hence, our results show that increasing the alkyl tails of the side-chain mesogens in these polymers is also an effective way to induce smectic phases, in addition to the incorporation of immiscible segments at the side-chain terminals reported by Pugh et al.<sup>38,39,54</sup> In comparison to the amorphous polymers (n = 8, 10), the scattering halo in the high-angle region, which represents the average lateral distance between side chains, slightly shifts to lower angles for the LCPs (n = 12, 14, 16, 18) with *d*-spacing values changing from 0.43 to 0.46 nm. This slight shift indicates that the formation of LC phases may be accompanied by the conformational change of the side chains.<sup>55</sup> Figure 6b shows the plot of the *d*-spacing values of the (100) peak for the LCPs (n = 12, 14, 16, 18) and the low-angle halo of the amorphous polymers (n = 8, 10) in Figure 6a against number of carbons in the alkyl tails. The dspacing values of the (100) peak for the LCPs (n = 12, 14, 16,

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Figure 6. 1D WAXD patterns of the as-cast PNbnPTs at ambient temperature (a) and *d*-spacing values of the (100) peak or the low-angle halo in (a) as a function of the number of carbons in the alkyl tails (b).

18) changes approximately linearly with n following an equation of d = 2.48 + 0.07n. The intercept of 2.48 nm, which indicates the diameter of the rigid core of the polymer, is slightly larger than the estimated length of  $\sim 2$  nm for the benzoate core in the side chain,<sup>11</sup> possibly owing to the offcenter arrangement of the side chains relative to the rigid polynorbornene backbone. In addition, the slope of 0.07 nm is the projected length of two methylene units along the sidechain axis in the SmA phase. The theoretical value can be estimated to be ~0.25 nm assuming an all-trans conformation. The great inconsistency between these two values may suggest a significant interdigitation between the polymer side chains in the smectic layers. On the other hand, the *d*-spacing values of the low-angle halo of the amorphous polymers (n = 8, 10)deviate from the line, which can be immediately attributed to their different states from the LC phases of the polymers with longer alkyl tails.

To determine the alignment of the mesogens relative to the polymer main chain in the smectic layer, 2D WAXD experiments were then carried out. Figure 7a shows the 2D



Figure 7. 2D WAXD pattern of PNb18PT at ambient temperature with the X-ray beam perpendicular to the fiber direction (a) and azimuthal scan (b) of (a) in the low- and high-angle regions.

WAXD pattern of PNb18PT at ambient temperature. A pair of diffraction arcs with a *d*-spacing value of 3.74 nm originating from the layer structure are located on the equator. In addition, a pair of diffused halos at  $2\theta \approx 20^{\circ}$  (d-spacing of ~0.45 nm) corresponding to the average distance between neighboring mesogens are more or less concentrated on the meridian with rather broad azimuthal distributions. As shown in Figure 7b, the azimuthal scans of the diffraction arc and the diffused halo in the low- and high-angle regions, respectively, have an offset of 90°, indicating an SmA phase of PNb18PT. The estimated length of the benzoate core in the side chains of PNb18PT is  $\sim 2$  nm according to the literature,<sup>11</sup> and the simulated length of the C18 alkyl tail with the *all-trans* conformation is  $\sim 2$  nm. Therefore, the side chain of PNb18PT should be about 6 nm. However, the *d*-spacing values of the low-angle peak in the 1D WAXD pattern at ambient temperature is 3.74 nm, which is much smaller than the calculated side-chain length of about 6 nm. The inconsistency may be attributed to two reasons. First, the side chains may not be in an ideally all-trans conformation. Second, the alkyl tails may adopt an interdigitated packing. Other LC PNbnPTs (n = 12, 14, 16) have similar 2D WAXD patterns as PNb18PT. Therefore, on the basis of 1D and 2D WAXD results, we can conclude that the phase behavior of

PNb*n*PT is greatly dependent on the alkyl-tail length. When n is more than 10, the polymer is induced to develop an SmA phase, and the degree of order increases with increasing alkyltail length. The polymer is amorphous when n is no more than 10. Figure 8 depicts the molecular packing of PNb*n*PTs at ambient temperature.



**Figure 8.** Schematic drawing of the molecular packing of PNb*n*PTs at ambient temperature.

Comparison of MJLCPs with Polynorbornene and Polyethylene Main Chains. From a synthetic point of view, this work describes a new method by introducing a key intermediate, NbTA, for facilely synthesizing varieties of MJLCPs with a polynorbornene main chain. Compared with the reported pathways,<sup>37–40,47</sup> the method in this work is more robust and greener, with elimination of complicated synthetic procedures and polluting heavy metal catalysts. From a molecular point of view, polynorbornene is a more rigid main chain than polyethylene because of the double bonds and fivemembered rings in the backbone. More flexible units are needed in these polymers to balance the rigidity of the backbone for the formation of LC phases. On the other hand, the length of the repeating unit of polyethylene is  $\sim 0.25$  nm compared with  $\sim 0.5$  nm for that of polynorbornene.<sup>24,56</sup> In other words, the mesogen density in a polynorbonene-based MJLCP is only about one-half of that in a polyethylene-based MJLCP. Therefore, longer alkyl tails are required in the side chains for the polymers to become liquid crystalline. Compared to MJLCPs with a polystyrene backbone, the entropy change of the main chain and side chains in polynorbornenes cannot compensate for the enthalpy increase at high temperatures.<sup>13,57</sup> Hence, MJLCPs with a polynorbornene main chain have lower isotropization temperatures than those of MJLCPs with a polystyrene main chain and can go into the isotropic state during heating. To prove this hypothesis, molecular engineering of the side chains, such as introducing more bulky biphenyl or terphenyl groups to the side chains, is currently ongoing in our laboratory.

# CONCLUSIONS

We synthesized a new series of MJLCPs, PNbnPT (n = 8, 10, 12, 14, 16, 18), with a polynorbornene main chain through a robust and green pathway. ROMP was used to obtain these polymers with high MWs and relatively narrow MW distributions. The phase behavior of PNbnPT strongly depends

on the alkyl-tail length. PNb8PT and PNb10PT are amorphous in the whole temperature range before degradation. When the alkyl tail becomes longer, PNbnPTs (n = 12, 14, 16, 18) develop into the SmA phase, and the LC phase becomes more ordered with increasing alkyl-tail length. Compared with polyethylene-based MJLCPs, MJLCPs with a polynorbornene main chain exhibit different phase behaviors resulting from their specific structural characteristics. Such MJLCPs with a very high MW ( $M_{\rm p} > 10^5$  Da) may be fabricated into polymer films and fibers to be used as structural materials. In addition, controllable stereoregularity and high functional group tolerance of polynorbornenes render these MJLCPs to be potential functional materials, such as photovoltaic materials. With the new development of organic metal catalysts and ROMP reactions, polynorbornene-based MJLCPs with welldefined composition, topology, stereoregularity, and functionality will be prepared to explore new functional materials with fascinating ordered structures and properties.

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# Notes

The authors declare no competing financial interest.

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