# Influence of Different Linkage Groups in Biphenyl Mesogenic Core on Phase Behaviors of Mesogen-Jacketed Liquid Crystalline Polymers

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ABSTRACT: The work focuses on the design, synthesis, and characterization of a series of mesogen-jacketed liquid crystalline polymers (MJLCPs) based on the octyl substituted biphenyl mesogenic core through different linkage groups. The molecular characterizations of the polymers obtained by conventional free radical polymerization were performed with <sup>1</sup>H NMR, gel permeation chromatography, and thermogravimetric analysis. Their thermotropic liquid crystalline (LC) behaviors were investigated in detail by a combination of various techniques, such as polarized light microscopy, differential scanning calorimetry, and 1D and 2D wide-angle X-ray diffraction. Our results showed that all the polymers were thermally stable, and their LC phases were greatly dependent on the linking groups between the biphenyl mesogenic core and terminal

**INTRODUCTION** The relationships between the molecular structures and phase structures or transitions of thermotropic liquid-crystalline polymers (LCPs) have been one of the most important topics for the fundamental research in polymer chemistry and physics for their applications in the past several decades.<sup>1</sup> Through designed synthetic strategies, rigid mesogenic groups (rod, disks, or bent-core) can be incorporated in LCPs and results in several different molecular architectures combining with various mesomorphic structures and phase behaviors. According to the location of the mesogenic groups in polymers, LCPs can be mainly classified into two categories: main-chain LCPs with mesogenic units located in the main chain and side-chain LCPs (SCLCPs) with mesogens as side groups.<sup>2</sup> For both of these two types of LCPs, to promote the formation of liquid crystalline (LC) phase and improve the mobility of the mesogenic groups, flexible spacers were often introduced into their structures.<sup>3</sup> Moreover, in the SCLCPs with mesogenic groups either laterally or terminally attached to the backbones, the insertion of flexible spacers with reasonable length are needed to decouple the motions between the main chain and the mesogenic side groups based on Finkelmann's principle.<sup>4</sup>

alkyl group substituent. Polymers with ether/ester or ether linkage group exhibited an unusual phase behavior with temperature increasing, tetragonal columnar nematic LC phase, or columnar nematic phase developed at high temperatures for the polymers transformed into amorphous phase during cooling process, showing a re-entrant phase behaviors. However, polymers with ester linkage group were not LC with temperature varied. It is illustrated that subtle changes in the molecular structure brought about tremendous variation of the LC phase properties for MJLCPs. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 2545–2554

**KEYWORDS**: biphenyl core; different linkage group; glass transition; liquid-crystalline polymers (LCP); phase behavior

In the past few decades, researchers in Zhou's group have focused on the design and synthesis of SCLCPs with the gravity centers of mesogen units attached to the backbones via a very short linkage or only a single covalent carbon-carbon bond, named mesogen-jacketed LC polymers (MJLCPs).<sup>5,6</sup> Different from Finkelmann's principle, the bulky and rigid mesogenic units directly linking to the polymer backbone force the main chain of the MJLCPs to take an extended chain conformation, thus the flexible spacers to decouple the dynamics of main chain and side groups seemed not necessary.<sup>7</sup> The concept of MJLCPs has been confirmed by experimental results via X-ray diffraction<sup>8</sup> and small-angle neutron scattering.<sup>9,10</sup> Since the first publication of MJLPCs, up to date, a rich variety of MJLCPs with different structures and unique properties have been designed, synthesized, and investigated in detail. Abundant phase structures such as columnar nematic  $(\Phi_N)$ ,<sup>5,6</sup> hexagonal columnar  $(\Phi_{\rm H})$ ,<sup>11</sup> hexatic columnar nematic  $(\Phi_{\rm HN})$ <sup>12</sup> rectangular columnar  $(\Phi_{\rm R})$ <sup>13</sup> smectic A (SmA),<sup>14,15</sup> and C  $(SmC)^{16}$  phase have been reported. Additionally, adjusting the phase structures and phase behaviors of MJLCPs by trying to change some variables such as the molecular weight, rigidity or shape of the mesogens, terminal

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alkyl length, and the molecular architectures have also been widely investigated, and some interesting results were found. Other work about jacketed polymers from V. Percec laboratory was also widely investigated and reported. A variety of polymers where the backbones were jacketed with functionally modified bulky dendritic or taper-shaped side groups were designed and synthesized,<sup>17–22</sup> and interesting self-assembly structures<sup>23–32</sup> and unusual molecular conformations<sup>33,34</sup> were discovered and descripted in detail. Reviews on the self-organization of polymers jacketed with self-assembling dendrons are also available.<sup>35,36</sup>

In our previous article,<sup>37</sup> we have reported the design, synthesis, and characterization of a series of MJLCPs based on biphenyl mesogen with asymmetric alkyl substitutions, poly(alkyl 4'-(octyloxy)-2-vinylbiphenyl-4-carboxylate) (pVBP(*m*,8), m = 1, 2, 4, 6, 8, 10, and 12) in detail. Unusual LC phase behaviors and columnar LC phase structure were found for most of the polymers, and their phase transformations and phase structures were greatly dependent on the relative length of the asymmetric terminal alkyl substitutions. Here, in this article, based on the above research work studied, we tried to change another variable-the linkage groups in the mesogenic core so as to further investigate the relationship between a single structural change of the monomers and the variable in the phase behaviors of MJLCPs. The monomer structures designed are shown in Scheme 1, we simply chose the commonly used linkage units such as ether and ester groups between the biphenyl mesogenic core and the terminal flexible alkyl substituent. To the best of our knowledge, the first time that the linkage group as a structural variable was studied in MJLCPs.

# **EXPERIMENTAL**

#### Materials

Methyl 4-bromo-3-methylbenzoate (98%, Alfa Aesar), 4-bromo-3-methylphenol (98%, Alfa Aesar), 4-(octyloxy)phenylboronic acid (99.6%, Alfa Aesar), triphenylphosphine (99%, Alfa Aesar), 40% formaldehyde (AR, Beijing Yi Li Chemical), N,N'-dicyclohexyl carbodiimide (95%, Sinopharm Chemical Reagent), 4-dimethylaminopyridine (99%, ACRO), and N-bromosuccinimide (NBS, 99%, Aldrich) were used as received without further purification. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol before use. Benzoyl peroxide (BPO) was recrystallized from chloroform and methanol. The catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> was synthesized according to the procedure in the literature.<sup>38</sup> The compound of 2(3)-vinylbiphenyl-4,4'-dicarboxylic acid was synthesized using the method previously reported.<sup>39</sup> Chlorobenzene was washed with H<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub>, and distilled water and then distilled from calcium hydride. Tetrahydrofuran (THF, AR, Beijing Chemical) was refluxed over sodium and distilled before use. Dichloromethane (AR, Beijing Chemical) was dried over magnesium sulfate anhydrous. All other reagents and solvents were used as received from commercial sources.

# **Equipments and Measurements**

<sup>1</sup>H/<sup>13</sup>C NMR spectra, mass spectra (MS), gel permeation chromatographic (GPC) measurements, thermogravimetric analyses (TGAs), differential scanning calorimetry (DSC), polarized light microscopy (PLM), and wide-angle X-ray diffraction (WAXD) (1D and 2D) experiments were performed according to the procedures described previously.<sup>37</sup>

# Synthesis of the Monomers

The synthetic routes of the monomers are shown in Scheme 2, the experimental details are described as follows.

### Synthesis of Mono-1

The experimental details of mono-1 synthesis are in accordance with the literature.<sup>37</sup> <sup>1</sup>H NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 0.869–0.910 (m, 6H, terminal CH<sub>3</sub>), 1.255–1.357, 1.459–1.478, 1.770–1.807 (m, 24H, CH<sub>2</sub>), 3.984–4.017 (t, 2H, OCH<sub>2</sub>), 4.327–4.460 (t, 2H, COOCH<sub>2</sub>), 5.246–5.274, 5.775–5.818 (d, 2H, =CH<sub>2</sub>), 6.701–6.773 (q, 1H, CH=), 6.941–6.963 (m, 2H, Ar–H), 7.255–7.282 (m, 2H, Ar–H), 7.329–7.349 (m, 1H, Ar–H), 7.939–7.964 (m, 1H, Ar–H), 8.287–8.291 (d, 1H, Ar–H), <sup>13</sup>C NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 166.449, 158.736, 144.670, 135.864, 135.372, 131.817, 130.643, 130.049, 129.080, 128.333, 127.207, 115.446, 114.035, 67.918, 65.053, 31.762, 31.731, 29.314, 29.219, 29.199, 29.151, 28.689, 26.018, 25.988, 22.600, 22.586, 14.027. MS: 464 (m/e).

# Synthesis of 1-Bromo-2-methyl-4-(octyloxy)benzene

4-Bromo-3-methylphenol (5.3 g, 0.0283 mol),  $K_2CO_3$  (7.821 g, 0.0567 mol), KI (catalytic amount), and acetonitrile (160 mL) were charged in a 250-mL three-necked flask. Then, a solution of 1-bromo-octane (6.021 g, 0.0312 mol) in acetonitrile (10 mL) was added dropwise, and the mixture was refluxed overnight. Thin-layer chromatography monitored the reaction process until the raw material was completely consumed. The mixture was cooled to ambient temperature and filtrated to remove the floating substance. After it was filtered, the filtrate was concentrated by a rotary evaporator to give the crude product. The purified product was obtained by silica gel column chromatography with petroleum ether

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SCHEME 2 Synthetic routes of the monomers.

as the eluent to yield 8.270 g (98%). <sup>1</sup>H NMR (300 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 7.360–7.389 (d, 1H, Ar—H), 6.775–6.785 (d, 1H, Ar—H), 6.547–6.617 (m, 1H, Ar—H), 3.877–3.921 (t, 2H, -OCH<sub>2</sub>), 2.334–2.350 (s, 3H, -CH<sub>3</sub>), 1.729–1.779, 1.286–1.434, 0.862–0.907 (m, 15H, aliphatic chain). MS m/z (M<sup>+</sup>): 298.

# Synthesis of 2-Methyl-4,4'-bis(octyloxy)biphenyl

In this step, a typical Suzuki cross-coupling reaction was used. 1-Bromo-2-methyl-4-(octyloxy)benzene (4.520 g, 0.015 mol), 4-(octyloxy)phenylboronic acid (4.168 g, 0.017 mol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.062 g, 0.546 mmol), and potassium carbonate ( $K_2CO_3$ , 4.183 g, 0.030 mol) were mixed in a 250-mL three-

necked flask under an argon atmosphere. Then, 160 mL of acetonitrile/water (3/1) mixture was added and refluxed at 80°C for 40 h. The mixture was cooled to ambient temperature and filtrated to remove the floating substance. After evaporation of the solvent, a colorless liquid was obtained by passing through a silica gel column with dichloromethane and petroleum ether (v:v, 1:12) as eluent to yield 6.436 g (91.8%). <sup>1</sup>H NMR (300 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 7.210–7.234 (m, 2H, Ar—H), 7.120–7.188 (d, 1H, Ar—H), 6.896–6.925 (m, 3H, Ar—H), 6.793–6.802(m, 1H, Ar—H), 3.942–3.999(m, 4H, -OCH<sub>2</sub>), 2.245 (s, 1H, -ArCH<sub>3</sub>), 1.762–1.823, 1.296–1.515, 0.831–0.956 (m, 30H, aliphatic chain). MS m/z (M<sup>+</sup>): 424.



SCHEME 3 Chemical structures and the synthesis of the polymers.





FIGURE 1  $^{1}$ H (a) and  $^{13}$ C (b) NMR spectra of mono-1 and  $^{1}$ H NMR spectrum of poly-1 (c).

#### Synthesis of Mono-2

Samples of methyl 4-bromo-3-methylbenzoate (5.907 g, 0.014 mol), NBS (3.714 g, 0.021 mol), and BPO (0.067 g, 0.277 mmol) were dissolved in  $CCl_4$  (160 mL) and refluxed for 6 h. The floating succinimide was filtrated off, and the solvent was evaporated. Then, the residue was boiled with triphenylphosphine (3.648 g, 0.014 mol) in acetone (180 mL) overnight, and the obtained phosphonium salt was purified by silica gel column chromatography with dichloromethane and methanol, respectively.

Then, 5 M NaOH aqueous solution (100 mL) was added slowly to formaldehyde (40%, 200 mL) containing (10.06 g, 0.0146 mmol) of the phosphonium salt. The mixture was

stirred for 48 h at room temperature. After the floating substance was filtrated off, the filtrate was washed by dichloromethane for several times. Combined the organic phase, evaporated and purified by column chromatography with petroleum and dichloromethane (v:v, 2:1) as the eluent, a colorless oily liquid product was obtained. Yield: 65%. <sup>1</sup>H NMR (300 MHz, δ, ppm, CDCl<sub>3</sub>): 7.228-7.253 (m, 3H, Ar-H), 7.206-7.221 (m, 1H, Ar-H), 7.170-7.191 (m, 2H, Ar-H), 7.135-7.142 (m, 1H, Ar-H), 6.869-6.926 (m, 1H, =CH), 5.648-5.695 (d, 1H, =CHH), 5.160-5.190 (d, 1H, =CHH), 3.969-4.026 (m, 4H, -OCH<sub>2</sub>), 1.784-1.826, 1.460-1.492, 1.297–1.355, 0.875–0.909 (m, 30H, aliphatic chain). <sup>13</sup>C NMR (δ, ppm, CDCl<sub>3</sub>): 163.315, 158.291, 138.611, 136.098, 131.003, 129.711, 128.314, 122.614, 114.911, 114.113, 111.112, 68.790, 31.897, 29.612, 29.311, 25.899, 22.703, 14.111. MS m/z (M<sup>+</sup>): 436.

# Synthesis of Mono-3

The synthesis of mono-3 used the same method as described for the preparation of mono-1. Yield: 45%. <sup>1</sup>H NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 8.328 (s, 1H, Ar—H), 8.122–8.317 (m, 2H, Ar—H), 8.090–8.101 (m, 1H, Ar—H), 7.457–7.526 (m, 2H, Ar—H), 7.266–7.423 (m, 1H, Ar—H), 6.637–6.659 (m, 1H, =CH), 5.791–5.853 (d, 1H, =CHH), 5.270–5.310 (d, 1H, =CHH), 4.327–4.381 (m, 4H, -OCH<sub>2</sub>), 1.743–1.813, 1.177–1.669, 0.866–0.910 (m, 30H, aliphatic chain). <sup>13</sup>C NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 165.809, 146.605, 143.735, 138.587, 135.401, 130.100, 127.713, 127.100, 126.789, 126.310, 114.239, 65.210, 31.910, 31.713, 29.234, 25.809, 22.713, 14.098. MS m/z (M<sup>+</sup>): 492.

#### Synthesis of Mono-4

The synthesis of mono-1 used the same method as described for the preparation of mono-3. Yield: 48%. <sup>1</sup>H NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 8.127–8.148 (d, 2H, Ar—H), 7.983–8.003 (d, 1H, Ar—H), 7.794–7.798 (s, 1H, Ar—H), 7.685–7.707 (m, 2H, Ar—H), 7.507–7.579 (d, 2H, Ar—H, =CH), 5.700–5.747 (d, 1H, =CHH), 5.398–5.428 (d, 1H, =CHH), 4.312–4.363 (m, 4H, -OCH<sub>2</sub>), 1.760–1.808, 1.439–1.473, 1.293–1.380, 0.872–0.906 (m, 30H, aliphatic

**TABLE 1** Molecular Weights, Polydispersity Indexes, 5%

 Weight Loss Temperatures, Glass Transition Temperatures, and Liquid Crystallinity of the Polymers

Sample	<i>M</i> <sub>n</sub> (×10 <sup>4</sup> g/mol) <sup>a</sup>	PDI <sup>a</sup>	7 <sub>d</sub> (°C) <sup>b</sup>	T <sub>g</sub> (°C) <sup>c</sup>	Liquid Crystallinity <sup>d</sup>
Poly-1 <sup>37</sup>	9.2	1.46	369	64	Yes
Poly-2	9.7	1.78	378	68	Yes
Poly-3	7.8	1.87	387	75	No
Poly-4	16.6	1.97	394	78	No

 $^{\rm a}$  The apparent  ${\it M}_{\rm n}$  and PDI values were measured by GPC using PS standards.

 $^{\rm b}$  The temperatures at 5% weight loss of the samples under nitrogen were measured by TGA heating experiments at a rate of 20°C/min.

 $^{\rm c}$  The glass transition temperatures of the samples under a nitrogen atmosphere were measured by DSC at a scanning rate of 10°C/min.

<sup>d</sup> Determined by the combination of PLM and 1-D WAXD observations.



FIGURE 2 Typical polarized light microscope images of solution-cast films of poly-1 taken at 180°C (a) and poly-2 taken at 220°C (b).

chain). <sup>13</sup>C NMR ( $\delta$ , ppm, CDCl<sub>3</sub>): 167.891, 165.345, 146.615, 145.801, 145.103, 138.218, 134.541, 130.312, 127.819, 127.098, 127.001, 114.312, 64.819, 31.901, 31.718, 29.314, 25.819, 22.713, 14.123. MS *m/z* (M<sup>+</sup>): 492 (*m/e*).

# Polymerization

As shown in Scheme 3, the polymers were obtained by typical conventional free-radical polymerization in solution. Taking the polymerization of poly-2 as an example, the detailed procedure was carried out as follows. About 0.538 g of mono-2, 15  $\mu$ L of 0.106 M AIBN/chlorobenzene solution, and 1.244 g of chlorobenzene were transferred into a polymerization tube with a magnetic stir bar. The reaction mixture was purged with nitrogen and subjected to three freeze-pump-thaw cycles and sealed under vacuum. Polymerization was performed at 60°C for 48 h. Subsequently, the

polymerization was stopped by dipping the tube in ice/ water. After the tube was broken, the solution was diluted with THF (10 mL) and then added dropwise to vigorously stirred methanol (300 mL). To eliminate the unreacted monomer completely, we repeated the precipitation process three times. After purification, the polymer was dried under vacuum for 2 d.

# **RESULTS AND DISCUSSION**

# Synthesis and Characterizations of the Monomers and Polymers

As shown in Scheme 2, the monomers could be successfully prepared through a few simple and effective reaction such as typical Witting reaction, Suzuki coupling reaction, etherification, and esterification reaction. The chemical structures of



FIGURE 3 1D WAXD powder patterns of poly-2 during the first cooling (a) and the second heating (b) process under a nitrogen atmosphere.



**FIGURE 4** 2D WAXD patterns of a sheared poly-2 sample recorded with the X-ray incident beam along *Z* (a), *Y* (b), and *X* (c) directions at 200°C; the shearing geometry (d).

the monomers were confirmed by  ${\rm ^{1}H}/{\rm ^{13}C}$  NMR and mass spectrometry.

Figure 1 shows the <sup>1</sup>H (a) and <sup>13</sup>C (b) NMR spectra of mono-1 and the <sup>1</sup>H NMR spectrum (c) of the corresponding polymer poly-1. The mono-1 displays the representative resonances of the vinyl group at 5.246-5.818 and 6.701-6.773 ppm. After polymerization, the signals disappeared completely and the chemical shifts of the polymer became quite broad, indicating the successful polymerization. Other monomers and polymers were characterized in a similar manner, and the results were in accordance with the desired structures.

All the polymers were obtained with high yield by conventional free radical polymerization in chlorobenzene with AIBN as an initiator. The polymers were easily soluble in common organic solvents such as THF, acetone, chloroform, dichloromethane, and chlorobenzene. Their preliminary molecular characterizations are summarized in Table 1. GPC analysis of the polymers shows that the apparent molecular weights are about  $8 \times 10^4$  g/mol or more, with molecular distribution below 2, confirming their polymeric nature. TGA results shows that all the polymers were quite thermally stable under nitrogen atmosphere and their 5% weight loss temperatures ( $T_d$ 's) were above 369°C as shown in Table 1.

# Phase Transitions and Phase Structures of the Monomers and Polymers

Similar to mono-1, all other monomers were also pale yellow liquid at ambient temperature, and no mesophases were observed in any of the monomers in PLM experiments at higher temperatures. The phase behaviors of all the polymers were investigated by DSC, PLM, and WAXD. Their thermal properties are listed in Table 1. First, DSC experiments were conducted. With the consideration of the effect of thermal history generated during solvent evaporation and drying, the second heating traces were used to determine the  $T_{\rm g}$  values, all the DSC profiles showed only glass transitions (the data are listed in Table 1), and no other transition processes were observed, as found for most other MILCPs reported previously.<sup>16,37</sup> The glass transition temperatures of all the polymers were relatively low compared to most other MJLCPs synthesized previously that have large molecules rigidity, we believe that the relatively weak rigid biphenyl mesogenic core and the long flexible terminal alkyl contribute to the result. In addition, the glass transition temperatures of the polymers with ester linkage group are about 10°C higher than that of the polymers with ether linkage group, which is in accordance with the higher polarity of the ester groups. Due to the insensitivity of the DSC method to determine the phase transitions of these polymers except for glass transitions, PLM and WAXD techniques were utilized to further investigate their LC phase behavior.



**FIGURE 5** 1D WAXD powder patterns of poly-3 during the first cooling (a) and the second heating (b) process under a nitrogen atmosphere and the *d*-spacing of the low-angle peak/halo as a function of temperature (c) during the first cooling and the second heating as shown in (a) and (b).

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**FIGURE 6** 1D WAXD powder patterns of poly-4 during the first cooling (a) and the second heating (b) process under a nitrogen atmosphere and the *d*-spacing of the low-angle peak/halo as a function of temperature (c) during the first cooling and the second heating as shown in (a) and (b).

Birefringence of the polymers was observed with PLM. The polymers were cast from CDCl<sub>3</sub> solution and dried at room temperature. At ambient temperature, all the polymers exhibited only very weak birefringence, probably due to the existence of certain alignment of the polymer chains during the sample preparation. Upon heating, the polymers behaved quite differently depending on the different linkage groups between the biphenyl and terminal alkyl in the side chain. Poly-1, which had the ester linkage as one side and ether linkage group as another, exhibited distinct birefringent texture [as shown in Fig. 2(a)] when the temperature was much higher than  $T_{\rm g}$ , as reported in our article previously.<sup>37</sup> When cooled to room temperature from 250°C, the birefringence of the sample remained unchanged. For poly-2 that had ether bond as the linkage group, obvious birefringence could be observed when the sample heated to a temperature higher than  $T_{g}$ , but not a typical texture developed during further heating process [as displayed in Fig. 2(b)]. While for the poly-3 and poly-4 that used ester bond as the connecting group, no discernible change was displayed even heated to up to 250°C, indicating probably no LC properties developed during the whole process.

Because the PLM textures were ambiguous for the phase structure identification of the polymers, variable-temperature 1D and 2D WAXD experiments were performed to further verify their phase transitions.

# Poly-1

The phase transition and phase structure of poly-1 sample has been detailed investigated and reported in our paper previously, a more ordered tetragonal columnar nematic ( $\Phi_{\rm TN}$ ) phase with a local square lattice (a = 1.92 nm) developed at high temperatures, and the LC phase transformed into the amorphous state upon cooling.<sup>37</sup>

# Poly-2

The phase transition of as-cast poly-2 sample was evidenced by variable-temperature 1D WAXD patterns. Sets of 1D WAXD patterns of the sample obtained during the first heating and the subsequent cooling are shown in Figure 3(a,b), respectively. The sample prepared by solution casting from a THF solution was amorphous due to the fast solvent evaporation that froze the chain motion. Upon the first heating in Figure 3(a), a diffraction peak at the lower angle  $(2\theta = 2 - 7.5^{\circ})$  rapidly developed after 140°C, which was much higher than the  $T_{\rm g}$  of the polymer, and the peak slightly shifted to a higher angle, indicating the development of an ordered phase, probably a LC phase. Combining with the PLM results, we could conclude that it was truly a LC phase. On the other hand, the scattering halo in the wideangle region remained as a halo which moved to lower angles with increasing temperature possibly due to the close molecular arrangement. No higher-order diffractions of the low-angle peak could be observed in the 1D WAXD experiments, even when we attempted with more sample amounts or longer exposure times. Upon cooling, the sharp peak which originated from the LC phase disappeared at temperatures below 120°C, and the low-angle scattering halo reappeared [as shown in Fig. 3(b)], which suggested that the ordered structure formed at high temperatures transformed into the low-temperature amorphous phase. Therefore, similar to the poly-1, poly-2 also exhibited an enantiotropic, reentrant phase behavior.

Owing to the dimensionality limit of 1D WAXD and the properties of the re-entrant phase behavior, varied-temperature 2D WAXD experiments were conducted with mechanically sheared samples at 135°C. Figure 4(a-c) shows 2D WAXD patterns of the oriented, annealed sample with the X-ray incident beam perpendicular (along Y or Z direction, with the X direction as the equatorial direction) and parallel (along X direction) to the shear direction at 200°C. The patterns were virtually identical when the shearing direction was along the equatorial direction [in Fig. 4(a,b)]. A pair of sharp arcs could be observed in the low-angle region on the meridian, indicating the existence of an ordered structure on the nanometer scale with lattice planes oriented primarily parallel to the equatorial direction. In addition, the scattering halo at a  $2\theta$  of about  $20^{\circ}$  in the high-angle region was more or less concentrated on the equator with rather broad





FIGURE 7 Schematic drawing of the whole phase evolution diagram for all the polymers at different temperatures.

azimuthal distributions, indicative of subnanometer structures with a short-range order existing mainly along the meridian direction. On the other hand, a sharp low-angle ring and a diffuse ring-like high-angle halo are shown in Figure 4(c) with the X-ray beam parallel to the shearing direction, demonstrating a rotational isotropy with the shear direction as the axis. The 2D WAXD patterns combining the results of PLM and 1D WAXD support that the high-temperature LC phase of poly-2 was a  $\Phi_{\rm N}$  just like the polymers reported previously.<sup>37</sup>

### Poly-3

The phase transitions of the poly-3 were further verified by variable-temperature, 1D WAXD experiments. Sets of 1D WAXD profiles of the as-cast sample of poly-3 recorded during the first heating and subsequent cooling processes are presented in Figure 5. Upon the first heating, as shown in Figure 5(a), the as-cast amorphous sample demonstrated two scattering halos in a low-angle region of  $2-7.5^{\circ}$  and a high-angle region of  $15-25^{\circ}$  at low temperatures. The scattering halo in the low-angle region increased a little in intensity with increasing temperature, but still kept as a broad scattering for the whole temperature region. As shown in Figure 5(b), upon cooling, a reverse trend was observed. Due to the lack of sharp changes in either the breadth of the low-angle peak/halo or the intensity, it was very difficult to judge from the figures whether there were phase transitions during the heating and cooling process. Figure 5(c) presents

the quantitative changes in the *d*-spacing of the low-angle peak/halo with respect to the temperature during the first heating and first cooling for poly-3 on the basis of the results in Figure 5(a,b). For the first heating curve, the *d*-spacing increased a little with the increasing temperature, the inflection point at about  $80-100^{\circ}$ C represents the glass transition and no other sharp changes or jump occurred during the whole process, indicating the as-cast sample poly-3 is amorphous during the whole process<sup>40</sup> combining the results of PLM and 1D WAXD.

### Poly-4

The phase behavior of the sample poly-4 was verified by 1D WAXD experiment at various temperatures. Figure 6(a,b) presents the changes of the structurally sensitive 1D WAXD patterns of poly-4 during heating and subsequent cooling. Similar to the 1D WAXD result of the sample poly-3, the ascast amorphous sample demonstrated two scattering halos in a low-angle region of  $2-5^{\circ}$  and a high-angle region of 15-25° at low temperatures. Upon the first heating and subsequent cooling, the scattering halo in the low-angle region changed a little in intensity and breadth with temperature varied. The *d*-spacing changes as shown in Figure 6(c) of the low-angle peak/halo as a function of the temperature during the first heating and first cooling for poly-4 decreased slowly below 100°C at first, then deceased sharply after that, indicating that there was no phase transition except glass transition. Combining the results of PLM, we can conclude that the sample poly-4 was amorphous during the whole variable-temperature process.

# Dependence of the Mesophase Behaviors of the Polymers on Molecular Structures

Since the first evolution of MILCPs reported by Zhou and coworker, many kinds of MJLCPs with various structures, molecular weight, and properties have been designed and investigated. Furthermore, dependence of the phase behaviors on the chemical structures of the polymer repeated unit<sup>40</sup> and rigidity of the side chain<sup>41</sup> has been investigated in detail. Reports have shown that the phase behaviors of the MJLCPs can be modulated by a few factors such as the shape of the mesogens,<sup>13</sup> the molecular weight,<sup>40</sup> and the terminal alkyl length in the side chain,<sup>15,16</sup>. But from this work, we can elucidate that by tuning the linkage groups between biphenyl mesogenic core and terminal alkyl in the side chain, their phase behaviors can also be changed greatly. In this series of four polymers, two different types of LC phase and three types of phase structures were found, depending on the different linkage groups in the side chain, as shown in Figure 7. The poly-1 sample with ether linkage as one side and ester linkage as the other exhibited unusual LC phase behaviors with temperature varying, a more ordered tetragonal columnar nematic ( $\Phi_{TN}$ ) phase with a local square lattice (a = 1.92 nm) developed at high temperatures, and the LC phase transformed into the amorphous state upon cooling. For poly-2 polymer with ether bond as the connecting group, it also showed unusual LC transformation, but only nematic phase ( $\Phi_{TN}$ ) developed in the high temperatures. While poly-3 and poly-4 with ester bond linkage group was not LC even at high temperatures. Thus, we can conclude that subtle changes in the molecular structure brought about tremendous variation of the LC phase properties for MJLCPs. Compared with the similar work reported by Yin,<sup>42</sup> who designed and synthesized a series of MJLCPs with one benzene ring modifying by different length of alkyl through different linkage group as the mesogenic core. Results revealed that ester bond was more beneficial to stabilize the LC phase than ether bond. While for our biphenyl system, polymers with ether linkage group were easier to develop a LC phase. Therefore, we believe that the relationship of complex MJLCPs system between chemical structures and properties still need further deep investigation.

# CONCLUSIONS

In summary, a series of new MJLCPs based on biphenyl mesogenic core with terminal alkyl through different connecting linkage groups were successfully designed and synthesized via conventional free radical polymerization. The chemical structures of the monomers and polymers were confirmed by various characterization techniques. The resulting polymers were highly thermal stable, and their glass transition values were dependent on the linkage groups in the side chain, the higher polarity of the side chain, and the higher glass transition for the polymers. Phase transitions and phase structures of the polymers were investigated by DSC, PLM, and WAXD, and dependence of the phase transformations on their structures was visually found. Polymers with ether linkage group in the side chain were easier to develop a LC phase, and poly-1 with ether linkage as one side and ester linkage as the other exhibited a more ordered tetragonal columnar nematic ( $\Phi_{TN}$ ) phase at high temperatures. While polymers with ester bond linkage group was not LC even at high temperatures. We expect that these MJLCPs with biphenyl mesogenic core will possess more interesting properties and have potential applications, and our work will provide more guidance in designing new MJLCPs and investigating their structure–property relationships.

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