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Synthesis and Properties of Mesogen-Jacketed Liquid Crystalline Polymers with Asymmetry Mesogenic Core

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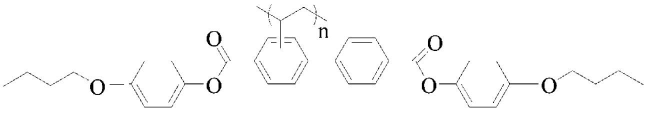
ABSTRACT: Smectic A (S_A) liquid crystalline phase developed from a new kind of mesogen-jacketed liquid crystalline polymer (MJLCP) whose mesogenic side groups are asymmetrically bonded to the main-chain was first reported. Two series of MJLCPs, poly[4,4′-bis(4-butoxyphenyloxycarbonyl)-2-vinylbiphenyl] (PBP2VBP) and poly[4,4′-bis(4-butoxyphenyloxycarbonyl)-3-vinylbiphenyl] (PBP3VBP) with different molecular weights were designed and synthesized *via* atom transfer radical polymerization successfully. The chemical structures of the monomers were confirmed by elemental analysis, mass spectrometry and ^{1}H NMR. The molecular characterization of the polymers was performed with ^{1}H NMR, gel permeation chromatography, and thermogravimetric analysis. Their phase structures and transitions were investigated by differential scanning calorimetry, wide-angle X-ray diffraction and polarized light microscopy experiments. The experimental results suggest that the polymer (PBP2VBP and PBP3VBP) with asymmetry mesogenic core can develop into a well-defined smectic A (S_A) phase. This implies that the polymer molecules in the LC phase can be more ribbonlike rather than rodlike.

Introduction

Liquid crystalline polymers (LCPs) have attracted long-standing attention for their outstanding applications in engineering plastics and optic, electroptic, nonlinear optic devices and so on.[1] According to the positions of mesogens, LCPs can be divided into two categories: the main-chain ones whose mesogens are present as part of the molecular backbones and the side-chain ones whose mesogens as side groups.[2] For side-chain LCPs, Finkelmann pointed out that the flexible spacers are needed to decouple motions between the main chain and the mesogenic side groups.[3] However, a new class of “mesogen-jacketed liquid crystal polymers” (MJLCPs) proposed by Zhou et al., whose mesogenic units are attached laterally to the main chain without or with only short spacers[4−6] could also show liquid crystalline behavior. Such a phenomenon reveals that a flexible spacer is not necessary. Because of the spatial requirement of the bulky and rigid mesogenic units, the main chain of the polymer has to take the extended conformation and the “jacket” is formed by the mesogenic units around the backbone.[7] Thus, The specific characteristic of MJLCPs is that the director of the LC phase is determined by the main chain instead of the side groups.[8] The MJLCPs have been researched in a few research groups[9] including Finklemann,[10] Keller and Hardouin,[11] Gray,[12] Percec,[13] Pugh,[14] Ober,[15] and a few others. A series of MJLCPs based on 2-vinylhydroquinone, 2-vinyl-1,4-phenylenediamine, 2-vinylterephthalic acid,[5,16−22] and vinyl terphenyl[23−26] and contained oxadiazole[27] have been successfully synthesized in our lab. The LC phase structures are found to be columnar nematic phase,[28] and hexagonal columnar LC phase[22,30] in which each cylinder is formed by a single MJLCPs chain molecule.[29] From the view of molecular structures, we notice that all the mesogenic units in these monomers have their gravity centers attached to the main-chain.[4] However, we find that such symmetry is not necessary if the steric effect is dominant. So we tried to add one phenyl unit in the middle of the mesogen to break its balance. Two new monomers, 4,4′-bis(4-butoxyphenyloxycarbonyl)-2-vinylbiphenyl (BP2VBP) and 4,4′-bis-(4-butoxyphenyloxycarbonyl)-3-vinylbiphenyl (BP3VBP), were designed and synthesized. Then the polymers were synthesized by atom transfer radical polymerization (ATRP). The mesogenic side groups are first asymmetrically bonded to main-chain. The chemical structures of the polymers are as follows:



BP2VBP : vinyl in 2 position
BP3VBP : vinyl in 3 position

Compared with other MJLCPs we previously studied, such as poly{2,5-bis[(4-methoxyphenyl) oxycarbony]styrene} (PMPCS) and poly[2,5-bis(4′-alkoxyphenyl)styrene], the new MJLCP has a more rigid asymmetry mesogenic core and a larger aspect ratio. In this paper, we describe the synthesis of the monomers and the polymers, and the specific LC phase structures and transitions of the polymers as well. Our experimental results suggest that the polymer with asymmetrical mesogenic core can develop into a well-defined smectic A (S_A) phase. This implies that the polymer molecules in the LC phase can be more ribbonlike rather than rodlike.

Experimental Section

Materials. *N*,*N*′,*N*′′,*N*′′-Pentamethyldiethylenetriamine (PMDETA) (99.5%, TCI), ethyl 2-bromo-2-methylpropionate (EBP,

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97%, Acros), methyl 4-bromo-3-methylbenzoate (98%, Alfa Aesar), 4-bromo-2-methylbenzoic acid (98%, Alfa Aesar), hydroquinone (AR. Beijing Chemical Co.), triphenylphosphine (99%, Alfa Aesar), trimethylborate (AR. Beijing Chemical Co.), 40% formaldehyde (AR. Beijing Yi Li Chemical Co.), *N,N*′-dicyclohexyl carbodiimide (DCC, 95%, Sinopharm Chemical Reagent Co. Ltd), and 4-dimethylaminopyridine (DMAP, 99%, ACRO) were used as received. Chlorobenzene was washed with H_2SO_4, $NaHCO_3$, distilled water and then distilled from calcium hydride. Tetrahydrofuran (AR; Beijing Chemical Co.) was refluxed over sodium and distilled before use. Dichloromethane (AR, Beijing Chemical Co.) was dried over magnesium sulfate anhydrous. Benzoyl peroxide (BPO) was purified by recrystallization from ethanol. CuBr was synthesized from $CuBr_2$ and purified by stirring in acetic acid and washing with methanol and then dried under vacuum before use.

Measurements. ^{1}H NMR spectra were obtained with a BRUKER ARX400 MHz spectrometer with tetramethylsilane as the internal standard at room temperature in chloroform-*d* or dimethyl sulfoxide-d_6.

Elemental analysis was carried out with an Elementar Vario EL instrument.

Gel permeation chromatography (GPC) measurements were carried out on a Waters 2410 instrument equipped with a Waters 2410 RI detector and three Waters μ-Styragel columns (103, 104, and 105 Å). The eluent was THF and the flow rate was 1.0 mL/min at 35 °C. The calibration curve was obtained with linear polystyrene as standards.

The thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C/min in nitrogen atmosphere.

Differential scanning calorimetry (DSC) examination was carried out on a TA DSC Q100 calorimeter with a programed heating procedure in nitrogen. The sample size was about 5 mg and encapsulated in hermetically sealed aluminum pans, whose weights were kept constant. The temperature and heat flow scale at different cooling and heating rates were calibrated using standard materials such as indium and benzoic acid.

Polarized optical microscopy (POM) observation was performed on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage.

One-dimensional (1D) wide-angle X-ray diffraction (WAXD) experiments were performed on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu Kα) and an X'celerator detector. The reflection peak positions were calibrated with silicon powder ($2\theta > 15°$) and silver behenate ($2\theta < 10°$). The sample stage is set horizontally, and a temperature control unit (Paar Physica TCU 100) in conjunction with the diffractometer was utilized to study the structure evolutions as a function of temperature. The heating and cooling rates in the WAXD experiments were 5 °C/min.

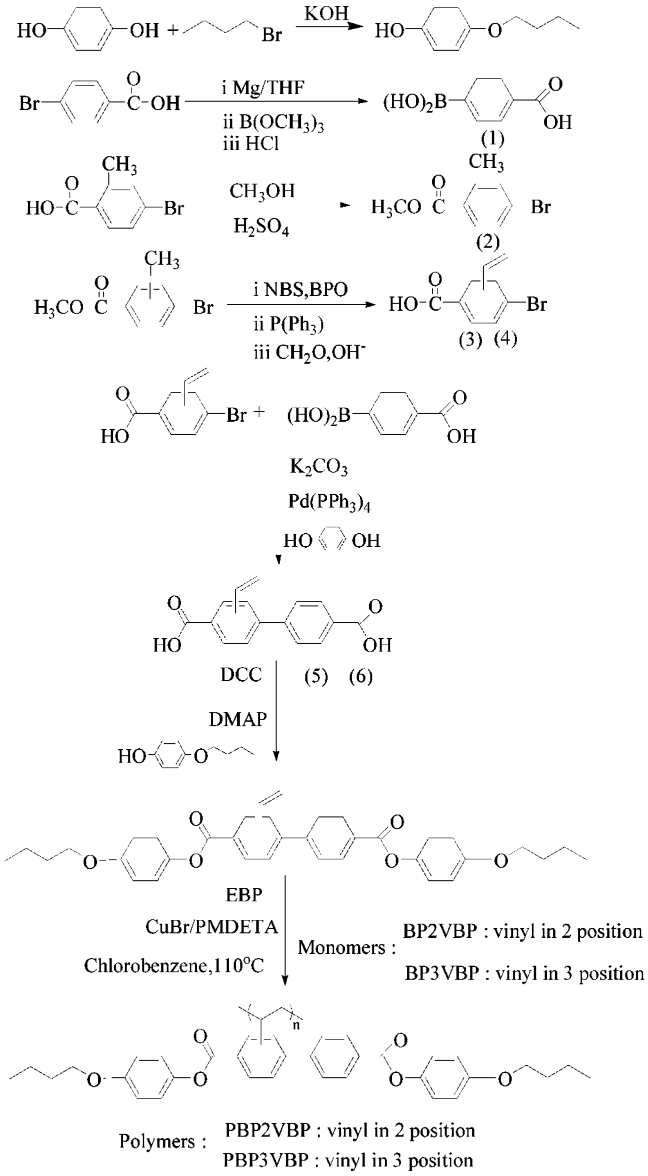
2D WAXD pattern was obtained using Bruker D8Discover diffractometer with GADDS as a 2D detector. Silicon powder and silver behenate were used as standards again. The 2D diffraction patterns were recorded in a transmission mode at room temperature. The oriented samples were prepared by mechanically shearing the films at 250 °C. The sample was mounted on the sample stage and the point-focused X-ray beam was aligned perpendicular to the mechanical shearing direction.

Synthesis of Monomer and Polymers. The chemical structure and synthesis of 4,4′-bis(4-butoxyphenyloxycarbonyl)-2-vinylbiphenyl (BP2VBP), poly[4,4′-bis(4-butoxyphenyloxycarbonyl)-2-vinylbiphenyl] (PBP2VBP), 4,4′-bis(4-butoxyphenyloxycarbonyl)-3-vinylbiphenyl (BP3VBP), and poly[4,4′-bis(4-butoxyphenyloxycarbonyl)-3-vinylbiphenyl] (PBP3VBP) are illustrated in Scheme 1. The experimental details are described as follows.

Synthesis of 4-Butoxyphenol (BOP). 4-Butoxyphenol (BOP) was prepared according to literature.[31]

Synthesis of (Triphenylphosphine)palladium. Triphenylphosphine palladium was prepared according to the method reported before.[32]

Scheme 1. Synthetic Route of Monomers and Polymers



Synthesis of 4-Boronobenzoic Acid (1). A three-necked flask charged with 4.1 g (0.17 mol) of Mg was pumped-aerated with argon three times, and then 200 mL of THF was added through a injector. Then, 28.1 g (0.14 mol) of 4-bromobenzoic acid was added dropwise to start the reaction. After 1 h, the mixture was cooled to room temperature and a black solution was obtained.

Another three-necked flask was also pumped-aerated with argon three times, and then 90 mL of THF and 32.2 mL (0.28 mol) of trimethylborate were added. The flask was set in the bath of liquid nitrogen−acetone to keep the system at −78 °C. Then the black solution obtained above was added and a white solid appeared.

Then, 100 mL of HCl (1 mol/L) was added into the mixture to dissolve the solid. The mixture was extracted with diethyl ether three times. The organic layer was combined and dried over magnesium sulfate anhydrous. The solvent was evaporated under reduced pressure to obtain a yellow solid, and then recrystallized from THF/petroleum ether (1/2). A white solid was obtained. Yield: 85%. ^{1}H NMR (δ, ppm, DMSO-d_6): 7.89−7.94 (d, 2H); 7.99−8.01 (d, 2H); 8.28 (s, 2H); 12.95 (s, 1H).

Synthesis of Methyl 4-Bromo-2-methylbenzoate (2). A 25.0 g sample of 4-bromo-2-methylbenzoic acid in 250 mL of methanol with 2 mL of sulfuric acid (98%) was refluxed for 24 h. After methanol was evaporated under reduced pressure, the crude product was dissolved in CH_2Cl_2 and extracted with saturated solution of $NaHCO_3$. The combined organic layer was dried by magnesium sulfate anhydrous. The product was obtained after the solvent removed. Yield: 92%. ^{1}H NMR (δ, ppm, DMSO-d_6): 2.37 (s, 3H); 2.57 (s, 3H); 7.29−7.40 (m, 2H); 7.76−7.80 (m, 1H).

Synthesis of 4-Bromo-3-vinylbenzoic Acid (3). A 13.2 g (0.06 mol) sample of methyl 4-bromo-3-methylbenzoate, 10.4 g (0.07 mol)of NBS, and 0.3 g (0.01 mol) of BPO were dissolved in 130 mL of CCl_4 and refluxed for 1 h. The floating succinimide was filtrated off and the solvent was evaporated. Then the residue was boiled with 26.2 g (0.10 mol) of triphenylphosphine in 200 mL of acetone for 3 h. The obtained phosphonium salt was purified by silica gel column chromatography with dichloromethane and methanol, respectively. Then, 70.0 g of 40% NaOH aqueous solution was added slowly to 190 mL of 40% formaldehyde containing 22.3 g (27.39 mmol) of the phosphonium salt. The mixture was stirred for 48 h at room temperature. After the floating substance was filtrated off, the resultant crude product was washed by 40% NaOH aqueous solution for several times. 100 mL of HCl (12 mol/L) was added to the filtrate and then white product appeared. Yield: 60%. ^{1}H NMR (δ, ppm, DMSO-d_6): 2.55 (s, 1H); 5.07−5.12 (d, 1H); 5.44−5.53 (d, 1H); 6.64−6.78 (d, 1H); 7.25−7.26 (m, 2H); 7.70 (s, 1H).

Synthesis of 4-Bromo-2-vinylbenzoic Acid (4). A 13.2 g (0.06 mol) sample of **2**, 10.4 g (0.06 mol) of NBS, and 0.3 g (0.01 mol) of BPO were dissolved in 130 mL of CCl_4; other processes are the same as synthesis of **3**. Yield: 56%. ^{1}H NMR (δ, ppm, DMSO-d_6): 5.51−5.54 (d, 1H); 5.90−5.96 (d, 1H); 6.95−7.04 (m, 1H); 7.73−7.80 (m, 2H); 8.15 (s, 1H); 13.32 (s, 1H).

Synthesis of 2-Vinylbiphenyl-4,4′-dicarboxylic Acid (5). 5 was synthesized via Suzuki cross-coupling reaction of **1** and **4**. A 0.9 g (4.00 mmol) sample of **1**, 1.0 g (6.00 mmol) of **4**, 0.2 g (0.80 mmol) of (triphenylphosphine) palladium, 1.6 g (14.40 mmol) of potassium carbonate, and 0.2 g (2.00 mmol) of hydroquinone were mixed in a 250 mL three-necked flask under argon atmosphere. Then 80 mL of acetonitrile/water (3/1) mixture was added and refluxed at 80 °C for 40 h. The mixture was cooled to room temperature and filtrated to remove the floating substance. A 50 mL aliquot of HCl (12 mol/L) was added to the filtrate and then white solid appeared. The mixture was filtrated, and the obtained white solid was washed with water and methanol. Yield: 71%. ^{1}H NMR (δ, ppm, DMSO-d_6): 5.34−5.38 (d, 1H); 5.84−5.90 (d, 1H); 6.58−6.67 (m, 1H); 7.46−7.51 (m, 3H); 7.89−7.97 (m, 1H); 8.04−8.24 (m, 3H).

Synthesis of 3-Vinylbiphenyl-4,4′-dicarboxylic Acid (6). 6 was obtained via Suzuki cross-coupling reaction of **1** and **3**. The processes are the same as those of (5). Yield: 71%. ^{1}H NMR (δ, ppm, DMSO-d_6): 5.50−5.54 (d, 1H); 5.90−5.95 (d, 1H); 6.94−7.00 (m, 1H); 7.61 (d, 1H); 7.70−7.74 (m, 3H); 8.23−8.27 (m, 3H).

Synthesis of 4,4′-Bis(4-butoxyphenyloxycarbonyl)-2-vinylbiphenyl (BP2VBP). A 2.7 g (10.00 mmol) sample of **5**, 5.0 g (30.00 mmol) of BOP, 10.4 g (50.00 mmol) of DCC, 0.4 g (3.10 mmol) of DMAP, and 100 mL of dried dichloromethane were mixed in a 250 mL round-bottom flask and stirred for 24 h at room temperature. The floating solid was filtrated off and the solvent was evaporated. The crude product was purified by silica gel column chromatography with dichloromethane. Yield: 58%. ^{1}H NMR (δ, ppm, DMSO-d_6): 0.97−1.01, (m, 6H); 1.48−1.55 (m, 4H); 1.75−1.82 (m, 4H), 3.97−4.00 (m, 4H); 5.33−5.36 (d, 1H); 5.85−5.90 (d, 1H); 6.66−6.69 (m,1H); 6.94−6.96 (d, 4H); 7.13−7.16 (d, 4H); 7.44−7.46 (d, 1H); 8.15 (d, 1H); 8.27−8.29 (d, 2H); 8.47−8.48 (s, 1H). Mass spectrum (m/e): 564. Anal. Found (Calcd): C, 76.63 (76.57); H, 6.45 (6.43). Melting point: 120.4 °C (by DSC).

Synthesis of 4,4′-Bis(4-butoxyphenyloxycarbonyl)-3-vinylbiphenyl (BP3VBP). A 2.7 g (10.00 mmol) sample of **6**, 5.0 g (30.00 mmol) of BOP, 10.4 g (50.00 mmol) of DCC, 0.4 g (3.10 mmol) of DMAP, and 100 mL of dried dichloromethane were mixed in a 250 mL round-bottom flask and stirred for 24 h at room temperature. The processes are the same as synthesis of BP2VBP. Yield: 56%. ^{1}H NMR (δ, ppm, DMSO-d_6): 0.94−0.98 (t, 6H); 1.44−1.51 (m, 4H); 1.69−1.76 (m, 4H); 3.99−4.02 (t, 4H); 5.49−5.52 (d, 1H); 6.02−6.06 (d, 1H); 7.01−7.03 (m, 4H); 7.22−7.25 (m, 4H); 7.45−7.52 (m, 1H); 7.90−7.92 (m, 1H); 8.07−8.19 (m, 3H); 8.21 (m, 1H); 8.24−8.26 (m, 2H). Mass spectrum (m/e): 564. Anal. Found (Calcd): C, 76.44 (76.57); H, 6.39 (6.43). Melting point: 109.1 °C (by DSC).

Synthesis of Polymers. Typically, 0.3 mg (1.70×10^{-3} mmol) of CuBr and 0.2 g (0.34 mmol) of BP2VBP (BP3VBP) were placed in a 10 mL reaction tube with a magnetic stir bar. Then, 1.3 g of chlorobenzene solution containing 3.0 mg (1.70×10^{-3} mmol) of PMDETA and 3.0 mg (1.70×10^{-3} mmol) of EBP were added with a syringe. After that, the reaction mixture was purged with nitrogen and subjected to four freeze−thaw cycles and sealed under vacuum. The tube was placed into an oil bath at 110 °C. After certain hours, the polymerization was quenched by dipping the tube in ice/water and the tube was broken. The mixture was diluted with THF, passed through a basic alumina column, and precipitated into methanol.

Results and Discussion

Synthesis and Characterization of the Monomers and Polymers. As shown in Scheme 1, the monomers were synthesized in seven steps. The structures of the monomers have been confirmed by ^{1}H NMR, elemental analysis and mass spectrometry.

Parts a and b of Figure 1 give the ^{1}H NMR spectra($CDCl_3$-d) of the monomer BP2VBP and the polymer PBP2VBP, respectively. The BP2VBP shows the characteristic resonances of the vinyl group at 5.33−5.90 and 6.66−6.69 ppm. After polymerization, these signals disappeared completely. The chemical shifts of PBP2VBP are quite broad and consistent with the expected polymer structure. The PBP2VBP and PBP3VBP were completely soluble in the common organic solvents such as chloroform, THF, chlorobenzene, 1,2-dichlorobenzene, etc. The molecular characterizations of the polymers are summarized in Table 1.

Polymerization Kinetics. Figure 2a and Figure 3a plots $\ln([M]_0/[M]_t)$ vs time (h) for statistical polymerizations of BP2VBP and BP3VBP, respectively. The linear behavior of $\ln([M]_0/[M]_t)$ vs time indicates that the polymerization is first order. The plots of molecular weight and molecular weight distribution vs conversion of BP2VBP and BP3VBP are illustrated in Figure 2b and Figure 3b, respectively. The M_n determined by GPC is found to increase in proportion to the BP2VBP conversion in Figure 2c, so is to BP3VBP in Figure 3c. An induction time was observed, which is probably caused by the residual oxygen and impurities.[33] These results have shown that the presence of this very large and asymmetrical mesogenic groups do not hinder the polymerization.[31] Two series of PBP2VBPm and PBP3VBPn with different M_n values and narrow polydispersity are listed in Table 1.

Phase Transitions and Phase Structures. Both monomers (BP2VBP and BP3VBP) are crystal at room temperature and form a nematic phase after the crystal melting, as evidenced by the 1D WAXD experiments. The thermal stabilities of the polymers were investigated with TGA in nitrogen atmosphere. All the polymers have very good thermal stability. The temperature at 5% weight loss is approximately 380 °C (see Table 1).

The DSC experiments of the PBP2VBP and PBP3VBP showed no transition information during the first cooling and subsequent heating scans at different rates of 4, 10, 20, and 40 °C/min. The samples were heated to 250 °C, cooled to room temperature, annealed at 90 °C for 6 h, and then heated at a rate of 40 °C/min. Only glass transitions (T_g) could be observed of all the polymers (listed in Table 1), but no more transition peaks were seen. The phenomenon is similar to some other

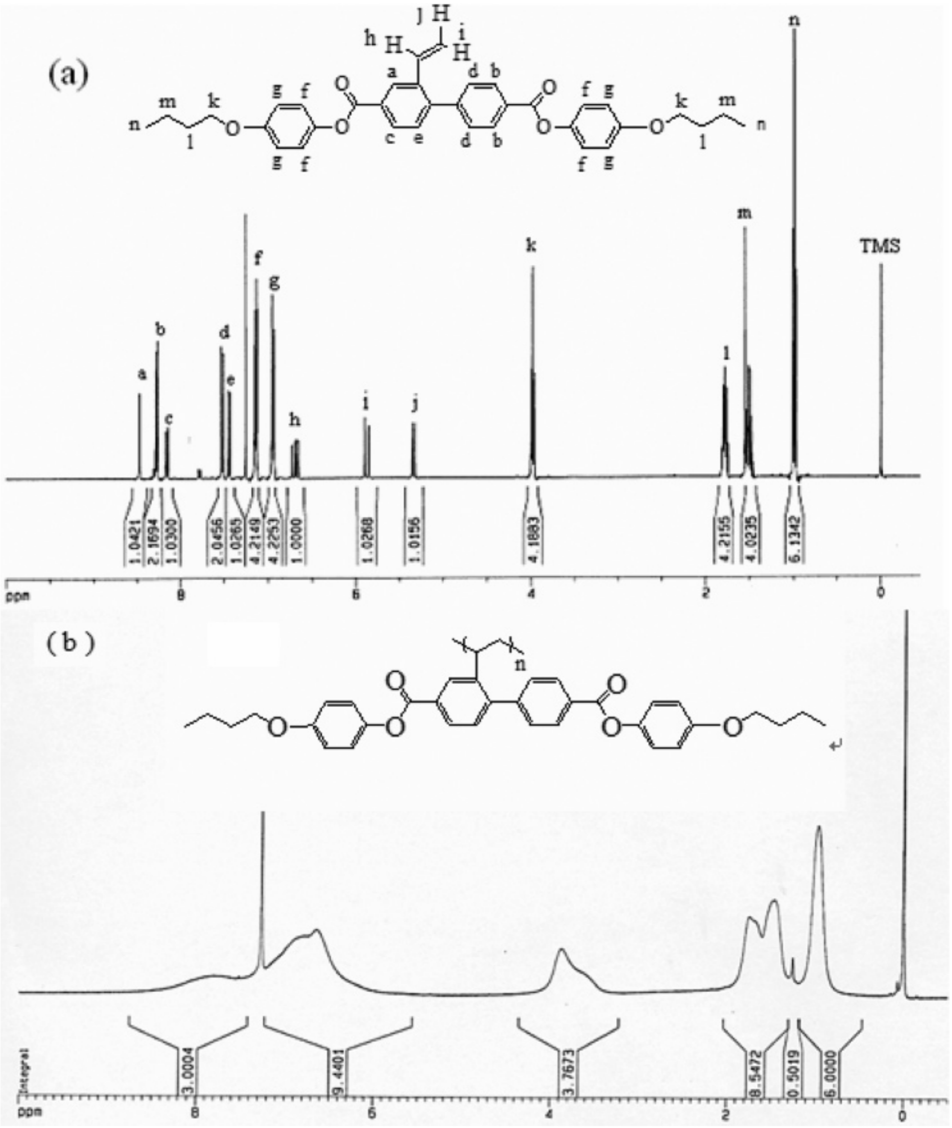


Figure 1. ^{1}H NMR spectra of (a) the monomer BP2VBP and (b) the polymer PBP2VBP in CDCl$_3$-*d*.

Table 1. Molecular Characteristics and the Phase Transition Temperatures of Polymers

samples	$M_n \times 10^{-4\,a}$	M_w/M_n^a	T_g (°C)^b	T_d (°C)^c	LC phase
		PBP2VBP*m*			
PBP2VBP-1	2.4	1.18	108.9	395.0	S_A
PBP2VBP-2	3.6	1.14	110.0	389.3	S_A
PBP2VBP-3	6.2	1.24	109.8	387.9	S_A
PBP2VBP-4	7.2	1.12	109.7	387.7	S_A
PBP2VBP-5	8.3	1.19	109.1	391.1	S_A
PBP2VBP-6	9.2	1.16	109.9	391.7	S_A
		PBP3VBP*n*			
PBP3VBP-1	2.9	1.20	103.0	396.9	S_A
PBP3VBP-2	3.2	1.21	104.1	398.4	S_A
PBP3VBP-3	3.7	1.26	104.5	399.2	S_A
PBP3VBP-4	4.6	1.20	104.5	396.9	S_A
PBP3VBP-5	5.3	1.29	104.5	405.3	S_A
PBP3VBP-6	8.1	1.20	104.7	406.0	S_A

[a] Obtained from GPC, linear PS as standards. [b] Evaluated by DSC at a rate of 40 °C/min. [c] The temperature at which 5.00% weight loss of the sample was reached from TGA under nitrogen atmosphere.

MJLCPs systems.[34] Polymers in each series exhibited similar thermal transitions.

Birefringence of the polymers were observed with POM. The samples were cast from THF solution and slowly dried at room temperature. The liquid crystalline birefringence did not appear until the samples were heated to a temperature much higher than T_g (Figure 4). When cooled to room temperature from 250 °C, the birefringence of the sample remained the same. It implies that the ordered structure formed at high-temperature kept unchanged upon cooling. These are similar to other MJLCPs synthesized in our group.[34]

The phase transition of the polymer was further verified on the 1D WAXD instrument. About 30 mg samples were cast from THF solution. Figure 5 describes the structurally sensitive 1D WAXD patterns of the PBP2VBP-5 in PBP2VBP*m*s from 40 to 260 °C. Upon the first heating (see Figure 5a), a scattering halo at a low 2θ angle of 4−2.91° is observed from the as-cast amorphous sample. Moreover, higher orders of the diffractions were visible. The ratios of the lower diffraction peak angles (2θ) with respect to the highest angle are 1:2:3, indicating a smectic structure of the sample. When the sample is cooled, the smectic phase is unchanged as shown in Figure 5b. The maximum *d*-spacing value (3.00 nm) of the sample is almost identical to the calculated length of the rigid mesogenic units in monomers (2.97 nm), which means the side chain of the mesogenic units is perpendicular to the main chain. So we presume that the structure of the liquid-crystalline phases is layer S_A. All other polymers in PBP2VBP*m*s have similar results.

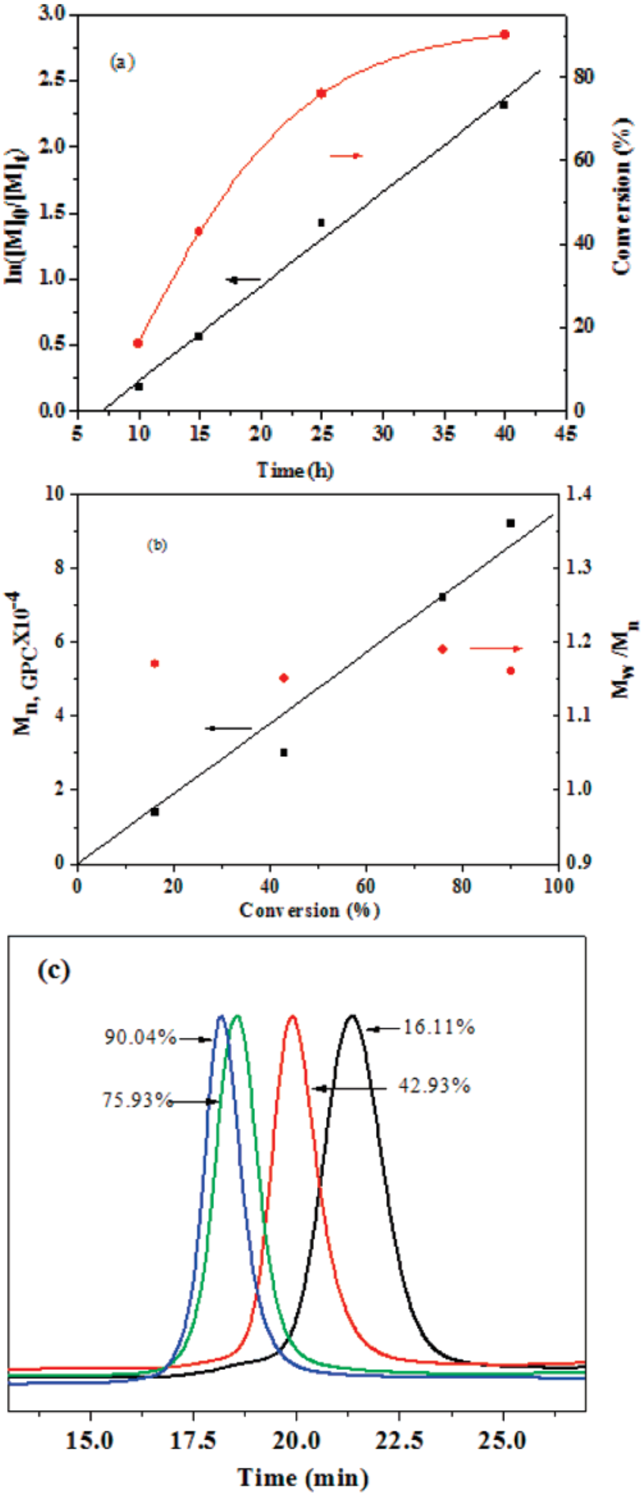


Figure 2. BP2VBP polymerization kinetic plot of time dependence of ln($[M]_0/[M]_t$) and monomer conversion. Conditions: $[BP2VBP]_0$:[EBP]:[CuBr]:[PMDETA] = 200:1:1:1, $[BP2VBP]_0$ = 0.29 mol L^{-1}, in chlorobenzene at 110 °C (a). Dependence of molecular weight and molecular weight distribution by GPC on the conversion of BP2VBP (b). GPC curves of the polymers (c).

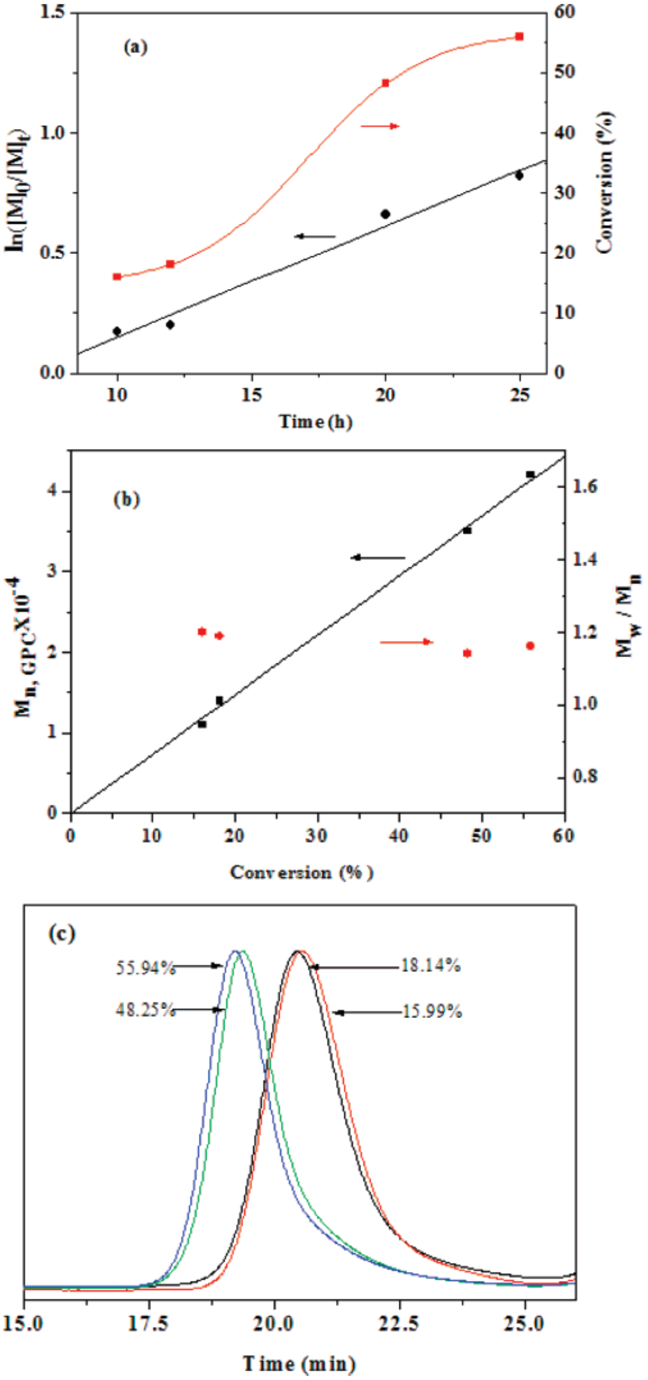


Figure 3. BP3VBP polymerization kinetic plot of time dependence of ln($[M]_0/[M]_t$) and monomer conversion. Conditions: $[BP3VBP]_0$:[EBP]:[CuBr]:[PMDETA] = 200:1:1:1, $[BP3VBP]_0$ = 0.29 mol L^{-1}, in chlorobenzene at 110 °C (a). Dependence of molecular weight and molecular weight distribution by GPC on the conversion of BP3VBP (b). GPC curves of the polymers (c).

Figure 6 describes the structurally sensitive 1D WAXD patterns of the PBP3VBP-3 in PBP3VBP*n*s from 40 to 250 °C, and the sharp diffractions appear at 180 °C. Upon the first heating (see Figure 6a), a scattering halo at low 2θ angle of 3.61−3.13° is observed from the as-cast amorphous sample. When the sample is cooled, Figure 6b shows that a higher order of the diffractions was visible. A clearer pattern of the second-order diffraction is showed in Figure 6c whose scale is from 5 to 10° (2θ). The ratios of the lower diffraction peak angle (2θ) with respect to the higher angle are 1:2, indicating a smectic structure of the sample. The maximum *d*- spacing value (2.82 nm) of the sample is almost identical to the calculated length of the rigid mesogenic units in monomers (2.97 nm), which means the side chain of the mesogenic units is perpendicular to the main chain. So we presume that the structure of the liquid-crystalline phases of PBP3VBP-3 is similar to PBP2VBP-5. All other polymers in PBP3VBP*n* have similar results.

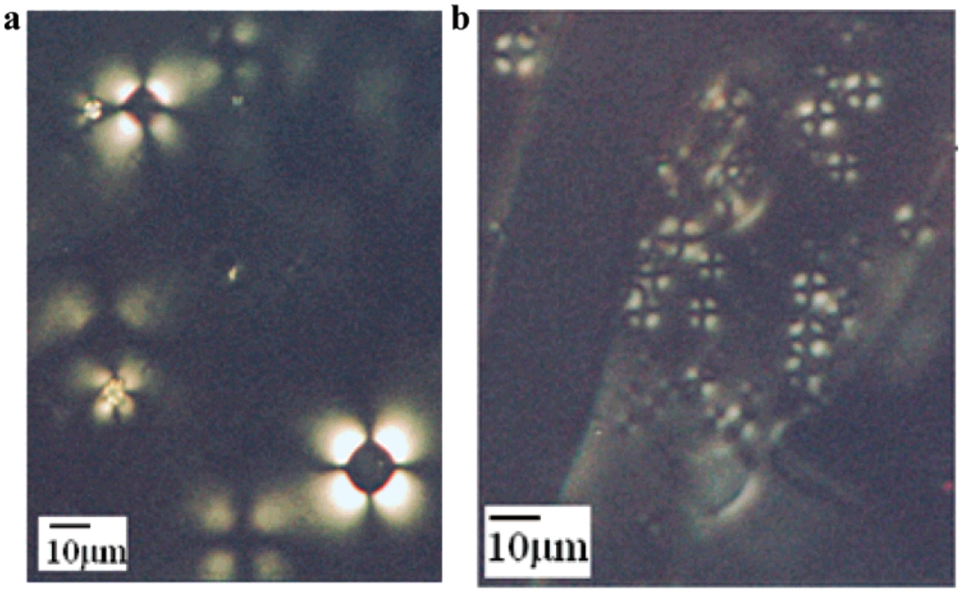


Figure 4. Representative textures of (a) PBP2VBP-5 and (b) PBP3VBP-3 at 250 °C with POM.

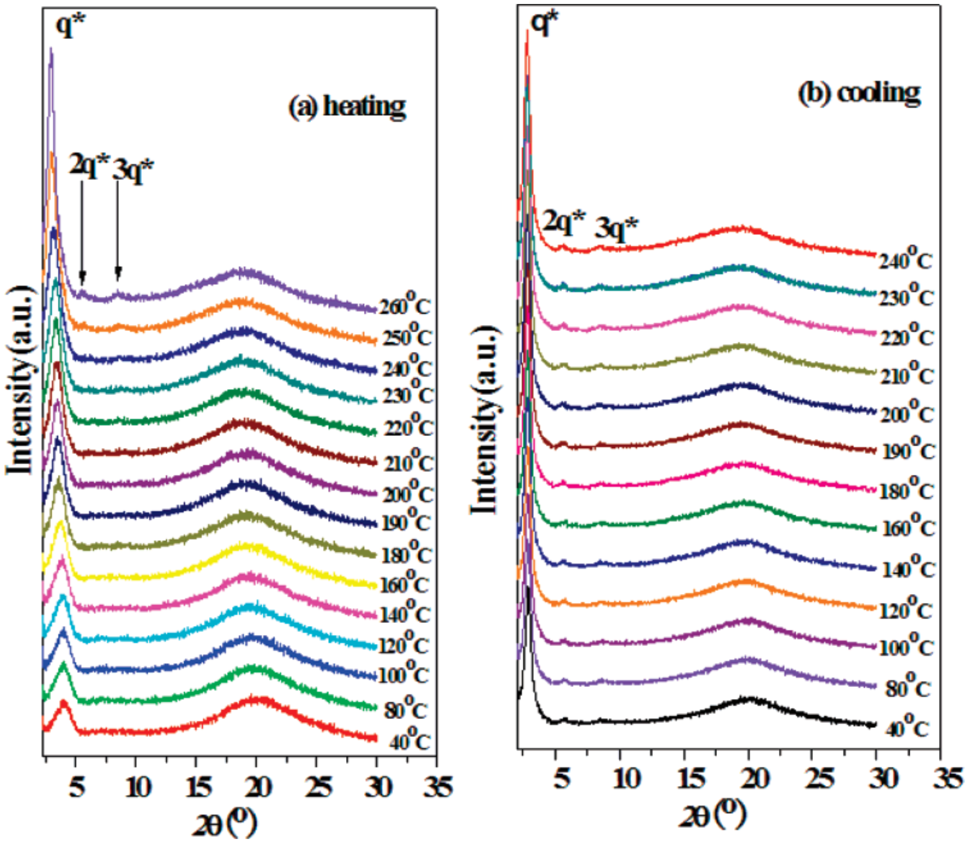


Figure 5. 1D WAXD patterns of sample PBP2VBP-5 obtained during the first heating (a) and first cooling (b) of the as-cast film.

To further confirm the smectic structure of the polymers, the 2D WAXD experiments were carried out. We mechanically sheared the films at 250 °C. Figure 7a shows the 2D WAXD patterns of the oriented PBP2VBP-5 sample recorded at room temperature with X-ray incident beam perpendicular to the shear direction. Three pairs of strong diffraction arcs can be found on the equator at $2\theta = 3.0$, 5.8, and 8.8° (d-spacing is 3.01, 1.51, and 1.01 nm), indicating that the order structure is developed parallel to the shear direction on the nanometer scale, which is perfect consistent with the 1D WAXD results. Meanwhile, two scattering halos in the high 2θ angle are more or less concentrated on the meridians with rather broad azimuthal distributions. This reveals that only the short-range orders exist along the shear direction.[29] The 2D WAXD pattern in Figure 7a proves that the PBP2VBP-5 forms a typical S_A phase. Similar patterns were obtained from different samples in PBP2VBP*m*.

Figure 7b shows the 2D WAXD patterns of PBP3VBP-3. In the pattern, X-ray incident beam perpendicular to the shear direction. Two pairs of strong diffraction arcs can be found on the equator at $2\theta = 3.37°$, 6.62° (d spacing is 2.62 nm and 1.34 nm), indicating that the order structure is developed parallel to the shear direction on the nanometer scale, which is perfect

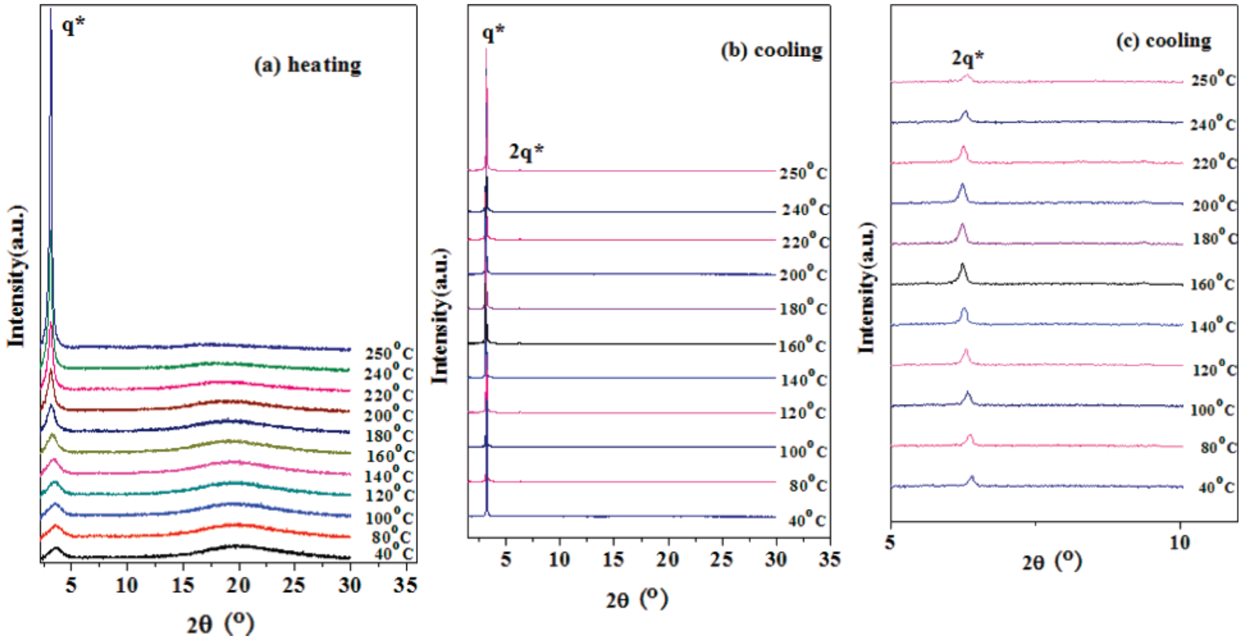


Figure 6. 1D WAXD patterns of sample PBP3VBP-3 obtained during the first heating (a), first cooling (b) and the partial cooling pattern of 2θ from 5° to 10° (c) of the as-cast film.

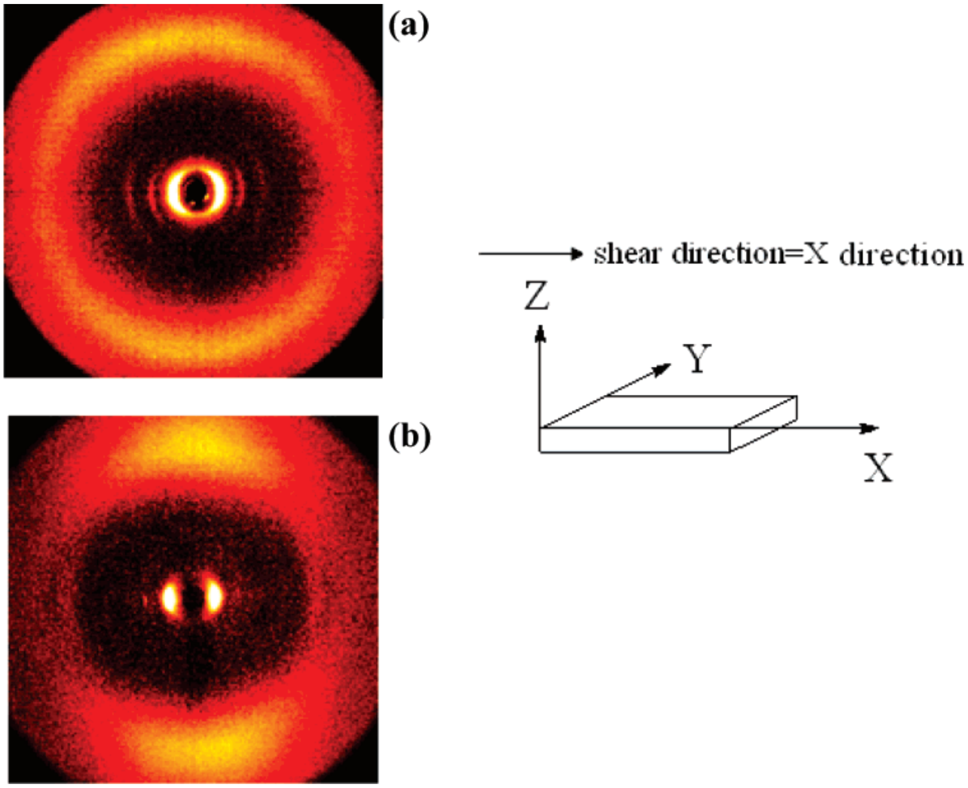


Figure 7. 2D WAXD film pattern of polymers recorded at room temperature. (a): PBP2VBP-5; (b): PBP3VBP-3.

consistent with the 1D WAXD results. Meanwhile, two scattering halos in the high 2θ angle are more or less concentrated on the meridians with rather broad azimuthal distributions. This reveals that only the short-range orders exist along the shear direction.[29] The 2D WAXD pattern in Figure 7b proves that the PBP3VBP-3 forms a typical S_A phase. Similar patterns were obtained from different samples in PBP3VBP*n*.

From all these results, we know the polymers form a smectic A (S_A)phase at a temperature higher than T_g and the side chains of the mesogenic units are perpendicular to the main chain. So

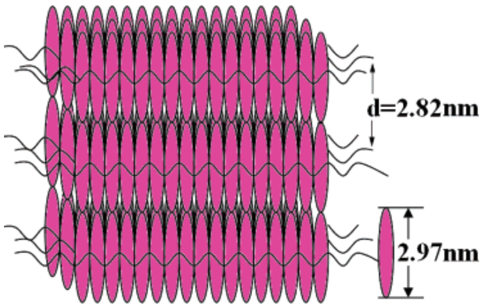


Figure 8. Schematic drawing of the layer structure of the polymers.

we presume the schematic drawing of the polymers with rigid asymmetry mesogenic core is in Figure 8.

Conclusion

Two kinds of monomers with rigid asymmetrical mesogenic core, 4,4′-bis(4-butoxyphenyloxycarbonyl)-2-vinylbiphenyl (BP2VBP) and 4,4′-bis(4-butoxyphenyloxycarbonyl)-3-vinylbiphenyl (BP3VBP), were first synthesized. Through ATRP, we obtained the mesogen-jacketed liquid crystalline polymers with asymmetrical mesogenic core, PBP2VBP*m*s and PBP3VBP*n*s, separately. The chemical structures of the monomers and polymers were confirmed by various characterization techniques. Their phase structures and transitions of the polymers were investigated with DSC, POM and WAXD. Well-defined smectic A (S_A) phase was identified for the first time, which is quite unusual comparing with other MJLCPs. As asymmetrical mesogenic core are laterally jacketed to the polyethylene backbone through a single carbon−carbon bond, the parallel packing of the mesogenic groups of the PBP2VBP*m* and PBP3VBP*n* in the S_A phase makes the molecules somewhat ribbonlike.

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