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Competition and Promotion between Two Different Liquid-Crystalline Building Blocks: Mesogen-Jacketed Liquid-Crystalline Polymers and Triphenylene Discotic Liquid Crystals

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ABSTRACT: Mesogen-jacketed liquid-crystalline polymers (MJLCPs) containing two triphenylene (Tp) units in the side chains, denoted as PP*nV* (n = 3 or 6, which is the number of the methylene units between the terephthalate core and Tp moieties in the side chains), were synthesized through conventional free radical polymerization, and the phase behaviors of these new combined main-chain/side-chain liquid-crystalline (LC) polymers were investigated. The chemical structures of the monomers were confirmed by elemental analysis, high-resolution mass spectrometry, and ¹H/¹³C NMR. The molecular characterizations of the polymers were performed with ¹H NMR, gel permeation chromatography, and thermogravimetric analysis. LC behaviors of the



polymers were investigated by differential scanning calorimetry (DSC), polarized light microscopy, and wide-angle X-ray diffraction (WAXD). Both polymers exhibit excellent thermal stabilities. DSC and WAXD results indicate that covalently incorporating Tp discotic liquid crystals has a tremendous effect on the LC behaviors of MJLCPs. As expected, the glass-transition temperature decreases as the spacer length increases. Both polymers form rectangular columnar (Φ_R) phases at relatively high temperatures. At low temperatures, however, Tp moieties in the side chains form a discotic nematic (N_D) phase in conjunction with the Φ_R phase developed by the rod-like supramolecular mesogen – the MJLCP chain as a whole, owing to the self-organization of the Tp moieties. For PP6V in particular, a higher symmetry hexagonal columnar (Φ_H) phase forms when temperature exceeds 225 °C. Individual ordered structures developed by these two LC building blocks are not only competitive but also promotive to each other.

INTRODUCTION

Liquid crystalline (LC) ordering offers possibilities for organic semiconducting materials to circumvent their main drawbacks owing to low charge carrier mobility.^{1–4} It has been intensively investigated that the packing of discotic liquid crystals (DLCs) into hierarchical ordered structures on both microscopic and macroscopic length scales influences the charge carrier mobility of organic semiconducting materials.^{2,5-7} The packing is dominated by the formation of columnar (Φ) LC phases based on the strong self-organizing tendency of DLCs. Because of the $\pi - \pi$ stacking of the planar aromatic cores and the van der Waals interactions of the peripheral chains, DLCs can selforganize into well-ordered, self-healable supramolecular columns, which then tend to arrange in 2D lattices. Within the columns of discotic mesogens, adjacent molecules experience a large π -orbital overlap, which results in the 1D charge-transport property with a high value of charge carrier mobility.4,5,8-11 Plenty of triphenylene (Tp)-containing side-chain LC polymers (LCPs) with flexible spacers as linkers have been investigated.¹²⁻²⁰ For example, several polysiloxanes¹²⁻¹⁴ and poly(meth)acrylates¹⁴⁻¹⁷ containing Tp moieties in the side

chains can form stable Φ phases. However, from the viewpoint of polymer conformation, utilizing polymers with more rigid backbones, like mesogen-jacketed LCPs (MJLCPs) or polypeptides that tend to adopt a more extended conformation, may be an alternative way to weaken the interactions between the polymer backbone and the discotic mesogens in the side chains. A series of Tp-containing polyacetylenes with different peripheral chain lengths show a typical hexagonal Φ ($\Phi_{\rm H}$) phase and a hexagonal lattice with mixed structures.²¹ A Tp-containing side-chain LCP with polythiophene as the polymer backbone exhibits a peculiar lamello-columnar mesophase where a 2D oblique columnar lattice and the lamellar piling coexist in the same structure.²²

Recently, calamitic mesogens have been introduced into the side chains of poly[di(alkyl)vinylterephthalate] (PDAVT, with the alkyl ranging from propyl/isopropyl to hexyl), a representative MJLCP with nonmesogenic side chains showing a 2D long-range-ordered $\Phi_{\rm H}$ phase.^{23,24} By introducing

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biphenyl groups to both ends of the PDAVT side chain, the resultant main-chain/side-chain LCPs (MCSCLCPs) with sufficient high molecular weights (MWs) exhibit hierarchical supramolecular structures with ordering on both nanometer and subnanometer length scales at low temperatures. Whereas the latter one is attributed to the packing of the biphenyl groups in the side chains, the former one is associated with a scaffold of the supramolecular structure with a 2D rectangular positional order constructed by the packing of thick MJLCP main chains. Altering the calamitic mesogen from biphenyl to azobenzene results in a similar hierarchical supramolecular structure.²⁵ Calamitic mesogens have also been introduced to other polymer backbones with a rod-like nature, such as polypeptides and ethyl cellulose (EC), to construct functional hierarchical ordered structures.^{26–28} Hence, combining rod-like LC main chains and calamitic mesogen-containing side chains can provide LCPs with hierarchical ordered structures. However, discotic mesogens have completely different selfassembling tendencies compared with the calamitic mesogens. To the best of our knowledge, attempts to construct MCSCLCPs with discotic mesogens have so far been unsuccessful.²⁹ Therefore, whether discotic mesogens act the same way as the calamitic mesogens in the supramolecular selforganization of MCSCLCPs is intriguing.

Herein, we designed a series of combined LCPs utilizing an MJLCP as the main-chain LC building block and a Tp DLC as the side-chain LC building block. At the molecular structure level, two Tp moieties are connected to the repeating unit of the poly(vinyl terephthalate) main chain through several methylene units to derive the target polymer, PPnV (Chart 1), where

Chart 1. Chemical Structure of PPnV







n represents the number of methylene units. The structure of PP*n*V is designed on the basis of four considerations: (i) PDAVT and Tp DLC are selected as the main-chain and sidechain LC building blocks, respectively, because of their ready accessibility and potential capability of forming ordered Φ phases. (ii) Hexyloxy chains, unbranched alkyl chains with a medium chain length, are selected as the peripheral chains of Tp moieties to facilitate the formation of discotic Φ phases.^{30,31} (iii) Methylene units are selected as the flexible spacer owing to the easily variable length and good thermal stability. (iv) The number of methylene units, *n*, is determined on the basis of the critical alkyl chain length for PDAVT to form a highly ordered Φ phase. Mainly based on the wide-angle X-ray diffraction (WAXD) experiments, we investigated the phase structure evolution of PP3V and PP6V. The interplay between the individual phase formation of the two fundamentally distinct LC building blocks, namely MJLCPs and Tp DLCs, is also discussed. The spacer length affects the interplay between the two LC building blocks tremendously. To the best of our knowledge, this is the first report of combined LC polymers containing discotic mesogens exhibiting fascinating ordered structures, and it can guide the design of ordered functional LCPs bearing discotic mesogens.

EXPERIMENTAL SECTION

Materials. 2,2'-Azobis(isobutyronitrile) (AIBN, Beijing Chemical, 95%) was purified by recrystallization from ethanol. Chlorobenzene was washed with sulfuric acid and then distilled under reduced pressure. Tetrahydrofuran (THF, Beijing Chemical) was refluxed over sodium and distilled before use. Dichloromethane (CH_2Cl_2 , Beijing Chemical) was dried over magnesium sulfate anhydrous. All other reagents and solvents were used as received from commercial sources.

Measurements. Elemental analysis, gel permeation chromatographic (GPC) measurements, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized light microscopy (PLM), and 1D and 2D WAXD experiments were performed according to the procedures previously described.³² ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained with a Bruker ARX400 spectrometer using tetramethylsilane as the internal standard at ambient temperature and deuterated chloroform as the solvent. The chemical shifts were reported on the ppm scale. Mass spectra were recorded on a Bruker Apex IV Fourier transform ion cyclotron resonance mass spectrometer by electrospray ionization (ESI).

Synthesis of Monomers. The chemical structures and synthetic procedures of the monomers and polymers are illustrated in Scheme 1. The experimental details are described as follows. 2-Hydroxyl-3,6,7,10,11-pentakis(hexyloxy)triphenylene (PHT) and 2-vinylterephthalic acid (VTA), were facilely synthesized according to the reported procedures.^{21,33}

Synthesis of 2-(3-Hydroxypropyl)-3,6,7,10,11-pentakis(hexyloxy)triphenylene, PHT3. PHT (7.4 g, 10.0 mmol), potassium carbonate (1.4 g, 10.0 mmol), and acetonitrile (300 mL) were charged in a 500 mL three-necked flask. Then a solution of 3-bromopropan-1-ol (2.1 g, 15.0 mmol) in acetonitrile (10 mL) was added dropwise, and the mixture was refluxed for 10 h. After cooled to ambient temperature, the precipitate was dissolved in CH₂Cl₂ (50 mL). After it was filtered, the filtrate was concentrated by a rotary evaporator to give the crude product. The purified product was obtained by passing through a silica gel column with ethyl acetate and petroleum ether (v:v, 1:5) as eluent and subsequent recrystallization from petroleum ether as a white powder. Yield: 98%. ⁱH NMR (δ): 7.80-7.84 (m, 6H), 4.44 (t, 2H), 4.23 (m, 10H), 3.98 (t, 2H), 2.50 (s, 1H), 2.19 (quint, 2H), 1.91-1.98 (m, 10H), 1.34-1.62 (m, 30H), 0.93 (t, 15H). HRMS(ESI): calcd. $(M + H^+)/z$, 803.5826; found $(M + H)^+/z$, 803.5844. Anal. Calcd. for C51H78O7: C, 76.27; H, 9.79. Found: C, 76.12; H, 9.84.

Synthesis of 2-(6-Hydroxyhexyl)-3,6,7,10,11-pentakis(hexyloxy)triphenylene, PHT6. PHT6 was prepared in the same manner as described for PHT3, except that 6-bromohexan-1-ol was used instead of 3-bromopropan-1-ol. Yield: 96%. ¹H NMR (δ): 7.84 (s, 6H), 4.22– 4.25 (t, 12H), 3.68–3.71 (t, 2H), 1.91–1.98 (m, 12H), 1.39–1.60 (m, 36H), 0.94 (t, 15H). HRMS(ESI): calcd. (M + H⁺)/z, 803.5826; found (M + H)⁺/z, 845.5844. Anal. Calcd. for C₅₄H₈₄O₇: C, 76.73; H, 10.02. Found: C, 76.69; H, 10.14.

Synthesis of 2,5-Bis[(3,6,7,10,11-pentakis(hexyloxy)triphenylen)-2-oxypropyloxycarbonyl]styrene, P3V. VTA (1.9 g, 10.0 mmol), PHT3 (16.0 g, 20.0 mmol), N,N'-dicyclohexylcarbodiimide (DCC, 6.2 g, 30.0 mmol), 4-(dimethylamino)pyridine (DMAP, 0.2 g, 2.0 mmol), and dried CH₂Cl₂ (100 mL) were mixed in a 250 mL round-bottomed flask and stirred at ambient temperature for 24 h. The floating solid was filtrated, and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography with CH₂Cl₂ as eluent and subsequent recrystallization from petroleum ether as a white powder. Yield: 50%. ¹H NMR (δ): 7.82–8.23 (m, 15H), 7.36–7.43 (q, 1H), 5.67–5.71 (d, 1H), Scheme 1. Synthetic Route of the Polymers (PPnV)



 PP6V
 56
 7.1
 1.65
 380
 21
 114 (0.3)
 225 (0.2)

 "Determined by GPC in THF using polystyrene standards. ^b5% weight loss temperature evaluated by TGA under a nitrogen atmosphere at a heating

"Determined by GPC in THF using polystyrene standards. 5% weight loss temperature evaluated by TGA under a nitrogen atmosphere at a heating rate of 10 °C/min. 'Evaluated by DSC during the second heating cycle at a rate of 40 °C/min.

5.31–5.34 (d, 1H), 4.64–4.69 (q, 4H), 4.39 (m, 4H), 4.19–4.25 (m, 20H), 2.38–2.43 (m, 4H), 1.90–1.97 (m, 20H), 1.38–1.59 (m, 60H), 0.89–0.95 (t, 30H). ¹³C NMR (δ): 166.7, 165.6, 149.1, 149.0, 148.4, 139.5, 134.7, 133.2, 130.3, 128.3, 124.1, 123.8, 123.6, 123.5, 123.4, 107.5, 107.4, 107.3, 107.1, 69.7, 69.5, 66.5, 62.5, 31.7, 31.6, 29.4, 29.3, 29.1, 25.8, 22.7, 22.6, 14.0. HRMS(ESI): calcd. (M + H⁺)/z, 1763.1863; found (M + H)⁺/z, 1763.1847. Anal. Calcd. for $C_{112}H_{160}O_{16}$: C, 76.33; H, 9.15. Found: C, 76.30; H, 9.16.

Synthesis of 2,5-Bis[(3,6,7,10,11-pentakis(hexyloxy)triphenylen)-2-oxyhexyloxycarbonyl]styrene, P6V. P6V was prepared in the same manner as described for P3V, except that PHT6 was used instead of PHT3. Yield: 58%. ¹H NMR (δ): 8.23 (s, 1H), 7.83–7.95 (m, 14H), 7.39–7.46 (q, 1H), 5.72–5.77 (d, 1H), 5.39–5.42 (d, 1H), 4.35–4.39 (m, 4H), 4.22–4.25 (m, 24H), 1.84–1.98 (m, 28H), 1.57–1.60 (m, 28H), 1.40–1.45 (m, 40H), 0.91–0.96 (t, 30H). ¹³C NMR (δ): 166.7, 165.7, 148.9, 148.8, 139.4, 134.9, 133.2, 132.5, 130.2, 128.2, 127.9, 123.6, 123.5, 117.4, 107.3, 107.1, 69.6, 69.5, 69.4, 65.3, 31.6, 29.4, 28.6, 25.8, 22.6, 14.0. HRMS(ESI): calcd. (M + H⁺)/z, 1847.2757; found (M + H)⁺/z, 1847.2763. Anal. Calcd. for C₁₁₈H₁₇₂O₁₆: C, 76.75; H, 9.39. Found: C, 76.81; H, 9.36.

Polymerization. As shown in Scheme 1, the two polymers were obtained by conventional free-radical polymerization in solution. The detailed procedure was carried out as follows. P3V (1.000 g), chlorobenzene (3.250 g), and AIBN (0.91 mg) were mixed in a glass 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 (5 mL) and then added dropwise to vigorously stirred acetone (300 mL). To eliminate the unreacted monomer completely, we repeated the precipitation process three times. By filtration and drying in vacuum

at 35 °C for 24 h, the target polymer poly{2,5-bis[(3,6,7,10,11-pentakis-(hexyloxy)triphenylen)-2-oxypropyloxycarbonyl]styrene}, PP3V, was obtained as a white solid. Yield: 78%. Poly{2,5-bis[(3,6,7,10,11-pentakis-(hexyloxy)triphenylen)-2-oxyhexyloxycarbonyl]styrene}, PP6V, was obtained similarly compared with PP3V.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Polymers. As shown in Scheme 1, monomers can be prepared in two efficient steps. PHT*n* was first synthesized by Williamson etherification with PHT and bromhydrin in a nearly 100% yield. Then PHT*n* reacted with VTA via Steglich esterification to obtain the monomers. The chemical structures of the monomers were confirmed by elemental analysis, high-resolution mass spectrometry, and ${}^{1}\text{H}/{}^{13}\text{C}$ NMR.

Polymers were synthesized in satisfactory yields through conventional free radical polymerization in chlorobenzene with AIBN as the initiator. The molecular characterizations of the polymers are summarized in Table 1. GPC analysis of the polymers shows that number-average MWs (M_n) of the PP3V and PP6V are 1.5×10^5 to 7.1×10^4 g/mol, with polydispersities of 1.97 and 1.65, respectively, confirming their polymeric nature. Figure 1 gives ¹H NMR spectra of P6V and PP6V in CDCl₃. The characteristic resonances of vinyl H appearing at δ 5.41–5.78 and 7.39–7.46 completely disappear after polymerization, and the resonance peaks of PP6V are rather broad and consistent with the expected polymer structure, indicating the successful polymerization as well.

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Figure 1. ¹H NMR spectra of P6V (top) and PP6V (bottom) in CDCl₃.

Thermal and Liquid-Crystalline Properties of the Polymers. The thermal and liquid-crystalline properties of the polymers were investigated by TGA, DSC, and PLM. As shown in Table 1, both polymers exhibit excellent thermal stabilities with the temperatures at 5% weight loss above 370 °C in nitrogen.

The phase-transition behaviors of the polymers were investigated by DSC. With the consideration of the effect of thermal history, the samples were heated from ambient temperature to 250 °C at a rate of 20 °C/min first. DSC experiments were carried out at a heating rate of 40 °C/min under a nitrogen atmosphere following a cooling process at a rate of 2 °C/min. The glass-transition temperatures $(T_{\sigma}s)$ and the data corresponding to phase transitions of PPnV are summarized in Table 1. As expected, T_g decreases as the spacer length increases owing to the lower steric hindrance and the stronger internal plasticization effect of the longer alkyl spacers. The DSC thermograms of both polymers during the second heating process are shown in Figure 2. The DSC profile of PP3V from -50 to 250 °C shows only a glass-transition step but no endothermic peak correlating to a phase transition. For PP6V, two endothermic peaks are observed at 114 and 225 °C besides the glass-transition step. Considering the small value of the enthalpic changes of transitions, these two endothermic peaks might be attributed to two transitions involving LC phases. According to the literature,⁵ the endothermic peak at



Figure 2. DSC traces of PP*n*V at a heating rate of 40 $^{\circ}$ C/min under a nitrogen atmosphere following cooling at 2 $^{\circ}$ C/min.

114 °C may be correlated to the isotropization of Tp DLCs. Interestingly, this phase-transition temperature is higher than that of 2,3,6,7,10,11-hexahexyloxytriphenylene (ca. 100 °C)³⁴ and Tp containing poly(meth)acrylates (ca. 40–80 °C),^{14,16,17} which suggests that ordered structures formed by Tp DLCs are stabilized by incorporating Tp moieties into the side chains of rod-like MJLCPs. In other words, the rod-like MJLCPs stabilize the ordered structures of Tp DLCs, whereas the

flexible poly(meth)acrylates disrupt the regular packing of Tp DLCs.

Birefringence of the polymers was observed by PLM with powder samples. A typical PLM texture of PP6V is shown in Figure 3. Both polymers exhibit strong birefringence that always remains, and the isotropic state was not observed in the



Figure 3. Representative texture of PP6V at 80 °C from PLM observation. The powder sample was cooled from 250 °C.

whole temperature range before degradation, indicating that LC phases of the polymers are rather stable. However, no characteristic textures were observed.

Phase Structure Identification of the Polymers. Because the PLM textures were ambiguous for the phase structure identification of PP*n*V, variable-temperature 1D and 2D WAXD experiments were performed. Film samples for 1D WAXD experiments were cast from the homogeneous solutions in hexane onto a copper substrate. Solvent was then allowed to evaporate at ambient temperature, and the samples were dried overnight at 35 °C in a vacuum oven before characterization. The samples were under a nitrogen atmosphere during 1D WAXD experiments to avoid thermal degradation. In 2D WAXD experiments, oriented film samples of PP3V and PP6V were sheared from the bulk polymer with a relatively large mechanical force at 170 and 150 °C, respectively, during cooling from higher temperatures. All samples were thermally annealed overnight at an appropriate temperature above $T_{\rm g}$ of the corresponding polymers before 2D WAXD experiments. 2D WAXD patterns were recorded with the X-ray incident beam perpendicular to the shear direction.

1D WAXD profiles of PP3V during the first heating and subsequent cooling processes are shown in Figure 4a,b, respectively. The patterns of the low-angle region during cooling are shown in Figure 4c for clarity. During the first heating process, the as-cast sample renders two peaks in the low-angle region, indicating the existence of some ordered structure. The broad halo in the wide-angle region is characteristic of the amorphous packing of the alkyl chain. After heating to higher temperatures, more peaks develop in the low-angle region, and the broad halo in the wide-angle region slightly shifts to lower angles due to thermal expansion. At 270 °C, seven sharp peaks are observed in the low-angle region (Figure 4c), and they remain during the cooling process. The corresponding *d*-spacing values of the seven peaks are 3.74, 3.20, 2.30, 1.88, 1.60, 1.50, and 1.23 nm, which can be assigned as (100), (010), (110), (200), (020), (120), and (300) diffractions of a rectangular structure with a = 3.74 nm, b =3.20 nm, and $\gamma = 90^\circ$, as identified in Figure 4c. The absence of (*hkl*) diffractions with $l \neq 0$ indicates that this rectangular structure possesses only a 2D positional order, exhibiting features of a columnar phase, similar to many other MJLCPs.^{23,25,35} The simulated length of the Tp moiety with all-trans conformation of C6 alkyl arms is ca. 2.3 nm. Because of the possible rotation of the flexible spacer and ester linkage, the whole side-chain length cannot be precisely estimated. However, depending on the relative position of Tp moieties in the side chain, the dimension of the whole side chain should be in the range of 2.3-4.6 nm. This range includes the sizes of the aforementioned 2D rectangular structure (a = 3.74 nm and b =3.20 nm). Therefore, we speculate that PP3V forms a 2D rectangular columnar (Φ_R) phase developed by the rod-like supramolecular mesogen - the MJLCP chain as a whole at 270 °C.

After cooling to ambient temperature, all diffraction peaks developed at high temperatures remain with slightly lower intensities, whereas no diffraction peak is observed at $2\theta \approx 25^{\circ}$ which represents the $\pi-\pi$ stacking, indicating that Tp moieties do not self-organize into a well-ordered supramolecular



Figure 4. 1D WAXD patterns of PP3V during the first heating (a) and subsequent cooling (b) and the pattern in the low-angle region during cooling (c).

column. Notably, a new diffraction peak appears at $2\theta = 5.16^{\circ}$ which corresponds to a *d*-spacing of 1.71 nm. This *d*-spacing cannot be fitted into the 2D rectangular structure developed at high temperatures. Actually, several Tp-containing mole-cules^{36,37} and LCPs^{18,38,39} have a diffraction peak at 2θ of ca. 5° (ca. 1.7 to 1.8 nm) in their powder WAXD patterns. Hence, this peak may be characteristic of ordered structures of Tp derivatives. Considering the intensity and shape of this peak, we reason that the new diffraction peak can be attributed to an ordered structure formed by Tp DLCs in conjunction with the 2D rectangular scaffold constructed by MJLCPs, although there can be other possibilities. The ordered structure corresponding to the 2θ value of 5.16° (1.71 nm) formed by Tp moieties can be attributed to the lateral spacing of a discotic nematic (N_D) mesophase of Tp moieties. Therefore, the high-temperature phase of PP3V is a 2D Φ_R phase developed by the rod-like MJLCP chain as a whole, whereas the low-temperature phase is the same Φ_R phase in conjunction with an N_D phase owing to the self-organization of the Tp moieties.

It is difficult to calculate the density of PP3V using the abovementioned supramolecular structure at ambient temperature. However, we can roughly estimate the density of PP3V using the 2D $\Phi_{\rm R}$ structure based on the MJLCP scaffold. Taking the values of *a* and *b* measured at ambient temperature and assuming a value of 0.25 nm for *c* (the projection length of one repeating unit on the *c* axis with C–C bond length and angle of 0.154 nm and 109.5°, respectively),⁴⁰ we estimate the density of PP3V to be ca. 1.04 g/cm³, which is slightly larger than the measured value of 0.94 g/cm³ at ambient temperature. The slightly larger estimated density is reasonable with the consideration of the poor packing of the Tp moieties in the side chain and the structural imperfection of the whole polymer in the LC state than in the crystalline state.

The 1D WAXD profiles in the second heating process follow the opposite transition pathways to those in the first cooling process, indicating the enantiotropic phase behavior of PP3V. Figure 5 shows plots of the *d*-spacing of the (100) diffraction (d_{100}) against temperature. A discontinuous increase of d_{100} is observed at ~150 °C during heating, even though the transition cannot be detected in DSC. This indicates a first-order phase transition upon heating.^{40–42} Upon cooling, the first-order transition with a less dramatic *d*-spacing change compared with that in the heating process is observed at ~130 °C, indicating the formation of a new phase. However, the degree of order of this low-temperature phase does not change much compared with the high-temperature one, which is consistent with the DSC results and our preceding speculation on the phase behavior of PP3V.

Owing to the dimensionality limit of 1D WAXD, 2D WAXD experiments were conducted with mechanically sheared samples. Figure 6a shows the 2D WAXD pattern of PP3V at 170 °C, and similar patterns were recorded at low temperatures due to the limited resolution of our equipment. Nonetheless, several pairs of sharp arcs in the low-angle region appear on the equator, indicating the existence of ordered structures on the nanometer scale with lattice planes oriented primarily parallel to the meridian direction. In general, the polymer chain will be oriented parallel to the direction of the shear force. Hence, the absence of the diffractions on other directions except those on the equator in the low-angle region ensured that all of the lowangle diffractions can be attributed to (hk0) diffractions. This observation is consistent with the assignment of the diffraction peaks in 1D WAXD patterns. In addition, the weak scattering



Figure 5. *d*-Spacing values of the first diffraction peak in the 1D WAXD patterns of PP3V during the first heating (solid squares) and subsequent cooling (solid circles) processes as a function of temperature.



Figure 6. 2D WAXD pattern of PP3V at 170 $^{\circ}$ C with the X-ray beam perpendicular to the shear direction (a) and the shearing geometry (b), where X and Z are the shear direction and shear gradient, respectively.

halo at $2\theta \approx 25^{\circ}$ (*d*-spacing of ~0.36 nm) corresponding to the vertical distance between neighboring aromatic rings is more or less concentrated on the meridian with rather broad azimuthal distributions, indicative of subnanometer structures with a short-range order existing with lattice planes mainly parallel to the equatorial direction. Therefore, all Tp moieties are aligned with the aromatic plane perpendicular to the polymer main chain to form a low ordered N_D phase. 2D WAXD patterns serve as the additional evidence to support our preceding speculation on the phase structures of PP3V.



Figure 7. 1D WAXD patterns of PP6V during the first heating (a) and subsequent cooling (b) and the pattern in the low-angle region during cooling (c).

One-dimensional WAXD profiles of PP6V during the first heating and subsequent cooling processes are shown in Figure 7a,b, respectively. The low-angle patterns during cooling are shown in Figure 7c for clarity. The 1D WAXD profiles of PP6V are similar to those of PP3V to some extent. As shown in Figure 7a, several peaks are observed in the low-angle region at 30 °C, indicative of an ordered structure in the as-cast film. Seven peaks also develop at elevated temperatures. The corresponding d-spacing values of the seven peaks at 150 °C are 3.89, 3.28, 2.40, 1.96, 1.64, 1.57, and 1.28 nm, which can be assigned as (100), (010), (110), (200), (020), (120), and (300) diffractions of a 2D $\Phi_{\rm R}$ phase with a = 3.89 nm, b = 3.28 nm, and $\gamma = 90^{\circ}$, as identified in Figure 7c. The larger *a* and *b* values in the 2D rectangular unit cell of PP6V compared with PP3V are owing to the increased spacer length from three methylene units to six. Notably, when the temperature goes to 300 °C, three peaks with a scattering vector ratio of $1:3^{1/2}:7^{1/2}$ appear, demonstrating a long-range ordered hexagonal lattice with a = b =4.35 nm and $\gamma = 120^{\circ}$. The three peaks are indexed as the (100), (110), and (210) diffractions, as identified in Figure 7c. Upon cooling, the seven peaks representing the 2D $\Phi_{\rm p}$ phase develop again, indicating the enantiotropic phase behavior of PP6V. As the temperature further decreases to ambient temperature, intensities of all diffraction peaks slightly decrease, with the diffractions from the 2D Φ_R scaffold of MJLCPs developed at 150 °C remaining. Similar to 1D WAXD profiles of PP3V during cooling, a new diffraction peak appears at a 2θ value of 5.01° corresponding to a *d*-spacing of 1.76 nm. Interestingly, its intensity is higher than that for PP3V. The difference of intensity may be related to the competition between the two LC building blocks, which will be discussed in the next section. No diffraction peak is observed at $2\theta \approx 25^{\circ}$, which represents the $\pi - \pi$ stacking at ambient temperature, indicating that Tp moieties do not self-organize into a wellordered supramolecular LC column. This new diffraction peak appearing at a 2θ value of 5.16° (1.71 nm) is also assigned to the lateral distance of an N_D mesophase formed by Tp moieties due to the absence of higher-ordered diffractions and the characteristic π - π stacking in the discotic LC column (~0.35 nm).

Figure 8a,b shows the 2D WAXD patterns of PP6V at 150 and 30 °C, respectively. Variable-temperature 2D WAXD

experiments at 300 °C were not conducted because the sample began to decompose in air at such a high temperature. As shown in Figure 8a, the 2D WAXD pattern of PP6V at 150 °C is similar to that of PP3V at high temperatures, indicative of the existence of a 2D Φ_{R} structures on the nanometer scale with the supramolecular rod oriented primarily parallel to the meridian direction. The 2D WAXD film pattern of PP6V at 30 °C (Figure 8b) shows that the diffraction arcs on the equator in the low-angle region are similar to those at 150 °C. In addition, the intensity of the scattering halo at $2\theta \approx 25^{\circ}$ (0.36 nm) in the high-angle region becomes much stronger upon cooling, although the scattering halo at $2\theta \approx 25^{\circ}$ (0.36 nm) in 1D WAXD patterns of PP6V is not observed even after an overnight thermal treatment. This intensity increase indicates that a more ordered N_D phase is formed. This phenomenon suggests that the discotic mesogens in the side chains of PP6V can be further oriented and packed into a higher ordered structure. Therefore, PP6V possesses three LC phases with two enantiotropic phase transitions according to the DSC and WAXD studies. The high-temperature phase of PP6V is a 2D $\Phi_{\rm H}$ phase developed by the rod-like supramolecular mesogen – the MJLCP chain as a whole - while the medium-temperature one is a 2D $\Phi_{\rm R}$ phase developed by the rod-like MJLCP supramolecular mesogen. Furthermore, the low-temperature phase is the same 2D Φ_R phase as the medium-temperature one in conjunction with an N_D phase owing to the self-organization of the Tp moieties.

Interplay between the Two LC Building Blocks. Figure 9 depicts a schematic drawing of the molecular packing of PPnV at different temperatures. From the whole phase evolution diagram, we found that with two fundamentally distinct LC building blocks in one polymer, PPnV exhibits a complex phase behavior involving the competition of these two building blocks. Specifically, comparing the diffraction peaks at $2\theta \approx 5^{\circ}$ (1.7 to 1.8 nm) in the 1D WAXD patterns during cooling at ambient temperature (Figure 10), we found that the diffraction peak of PP6V exhibits higher intensity, indicating that the ordered structure formed by Tp moieties in PP6V is more ordered. This intensity difference suggests that longer flexible spacers between MJLCP main chain and Tp moieties in the side chains offer a stronger decoupling effect, which allows

Macromolecules



Figure 8. 2D WAXD patterns of PP6V at 150 °C (a) and 30 °C (b), respectively, with the X-ray beam perpendicular to the shear direction and the shearing geometry (c), where X and Z are the shear direction and shear gradient, respectively.

for the two LC building blocks to act more independently. Therefore, we can speculate that when the flexible spacer is shorter between the main-chain MJLCP and the side-chain



Figure 10. 1D WAXD patterns of PP3Vand PP6V at ambient temperature during cooling, with the arrows pointing out the diffraction peaks associated with the discotic mesogens.

DLC, the whole polymer behaves more like the individual MJLCPs, and Tp moieties become more-or-less part of the side chains of the MJLCP because of the strong coupling effect of the DLC moieties and the MJLCP main chain. With the length of the flexible spacer increasing, however, the interaction between the two LC building blocks, the MJLCP and the Tp DLC, is gradually weakened, and then both LC building blocks act more independently and tend to display their individual selforganizing properties. Moreover, when the flexible spacer is sufficiently long, the coupling between the two LC building blocks will diminish, and the resultant polymer may have fascinating self-assembling behaviors. To this end, further work is currently in progress.

Ordered structures developed by the two LC building blocks separately stabilize each other. Of particular interest is the fact that PP6V can retain the Φ_R phase during cooling with merely a slight intensity decrease, whereas its homologous polymer, PDAVT with hexyl tails, is relatively disordered after cooling to ambient temperature.²⁴ Retaining of the ordered structures may be associated with the stabilizing effect of the discotic moieties, and this stabilizing effect may be originated from the increased "jacketing" effect due to the attachment of the Tp units. Moreover, DSC results suggest that ordered structures formed by Tp DLCs are also stabilized by incorporating Tp moieties into the side chain of rod-like MJLCPs. Therefore, individual ordered structures developed by these two LC building blocks are not only competitive but also promotive to each other.



Figure 9. Schematic drawing of the whole phase evolution diagram for PPnV at different temperatures.

CONCLUSIONS

Using conventional free-radical polymerization, we synthesized a series of MJLCPs bearing Tp DLCs as pendant groups, PPnV, with sufficiently high MW ($M_n > 10^4$ g/mol) to construct MCSCLCPs with DLCs as the side-chain LC building block. With the increasing length of the flexible spacer, which links the two fundamentally distinct LC building blocks, the phase behaviors of PPnV vary tremendously. PP3V exhibits two mesophases. The high-temperature one is a 2D Φ_{R} phase developed by the rod-like MJLCP supramolecular mesogen as a whole, and the low-temperature one is the same 2D Φ_{R} scaffold in conjunction with an N_D phase owing to the poor packing of the Tp moieties. However, PP6V displays three different mesophases. At high temperatures, PP6V exhibits a 2D $\Phi_{\rm H}$ phase developed by the supramolecular MJLCP mesogen, whereas the medium-temperature phase is a 2D $\Phi_{\rm R}$ phase formed by the same mesogen. The low-temperature phase is the same 2D Φ_R phase as the medium-temperature one in conjunction with an N_D phase, which is similar to the lowtemperature phase of PP3V. Both polymers act like MJLCPs with Φ phases (Φ_R or Φ_H) when Tp DLCs isotropilize at relatively high temperatures. When temperature decreases to ambient temperature, however, Tp moieties in the side chain tend to self-organize into an N_D phase. In conjunction with the Φ_{R} scaffold developed by the rod-like supramolecular mesogen of the MJLCP chain, an N_D phase coexists in the lowtemperature phases for both polymers. With the flexible spacer length increasing, the two LC building blocks act more independently, and ordered structures developed by these two LC building blocks are not only competitive but also promotive to each other.

As expected, introducing DLCs into the side chains of MJLCPs can enrich the phase behaviors of LC polymers, which is of great importance for both fundamental research and real applications. On the basis of our work, LC building blocks with various topologies and functions can be covalently linked together and investigated to exploit new functional materials with fine-tuning ordered structures.

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Notes

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REFERENCES

(1) O'Neill, M.; Kelly, S. M. Adv. Mater. 2011, 23, 566-584.

(2) Pisula, W.; Zorn, M.; Chang, J. Y.; Mullen, K.; Zentel, R. Macromol. Rapid Commun. 2009, 30, 1179–1202.

- (3) Funahashi, M. Polym. J. 2009, 41, 459-469.
- (4) Kaafarani, B. R. Chem. Mater. 2011, 23, 378–396.
- (5) Kumar, S. Chemistry of Discotic Liquid Crystals: From Monomers to Polymers; CRC Press: Boca Raton, FL, 2011.

(6) Sergeyev, S.; Pisula, W.; Geerts, Y. H. Chem. Soc. Rev. 2007, 36, 1902–1929.

- (7) Debije, M. G.; Piris, J.; de Haas, M. P.; Warman, J. M.; Tomović, Ž.; Simpson, C. D.; Watson, M. D.; Müllen, K. J. Am. Chem. Soc. 2004, 126, 4641–4645.
- (8) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119–1122.
- (9) Feng, X.; Marcon, V.; Pisula, W.; Hansen, M. R.; Kirkpatrick, J.; Grozema, F.; Andrienko, D.; Kremer, K.; Mullen, K. *Nat. Mater.* **2009**, *8*, 421–426.
- (10) Chandrasekhar, S.; Sadashiva, B.; Suresh, K. *Pramana* **19**77, *9*, 471–480.
- (11) Adam, D.; Schuhmacher, P.; Simmerer, J.; Haussling, L.; Siemensmeyer, K.; Etzbachi, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, 371, 141–143.
- (12) Hüser, B.; Spiess, H. W. Macromol. Rapid Commun. 1988, 9, 337-343.

(13) Hueser, B.; Pakula, T.; Spiess, H. W. Macromolecules 1989, 22, 1960–1963.

(14) Werth, M.; Spiess, H. W. Macromol. Rapid Commun. 1993, 14, 329-338.

- (15) Ringsdorf, H.; Wüstefeld, R.; Zerta, E.; Ebert, M.; Wendorff, J. H. Angew. Chem., Int. Ed. 1989, 28, 914–918.
- (16) Boden, N.; Bushby, R. J.; Lu, Z. B. Liq. Cryst. 1998, 25, 47–58.
 (17) Stewart, D.; S. Mchattie, G.; T. Imrie, C. J. Mater. Chem. 1998, 8, 47–51.
- (18) Weck, M.; Mohr, B.; Maughon, B. R.; Grubbs, R. H. Macromolecules 1997, 30, 6430-6437.
- (19) Catry, C.; Van der Auweraer, M.; De Schryver, F. C.; Bengs, H.; Häussling, L.; Karthaus, O.; Ringsdorf, H. *Macromol. Chem. Phys.* **1993**, *194*, 2985–2999.

(20) Imrie, C. T.; Inkster, R. T.; Lu, Z.; Ingram, M. D. Mol. Cryst. Liq. Cryst. 2004, 408, 33–43.

- (21) Xing, C. M.; Lam, J. W. Y.; Zhao, K. Q.; Tang, B. Z. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 2960–2974.
- (22) Tahar-Djebbar, I.; Nekelson, F.; Heinrich, B.; Donnio, B.; Guillon, D.; Kreher, D.; Mathevet, F.; Attias, A.-J. *Chem. Mater.* **2011**, 23, 4653–4656.
- (23) Xie, H.-L.; Jie, C.-K.; Yu, Z.-Q.; Liu, X.-B.; Zhang, H.-L.; Shen, Z.; Chen, E.-Q.; Zhou, Q.-F. J. Am. Chem. Soc. **2010**, 132, 8071–8080.
- (24) Yin, X. Y.; Ye, C.; Ma, X.; Chen, E. Q.; Qi, X. Y.; Duan, X. F.; Wan, X. H.; Cheng, S. Z. D.; Zhou, Q. F. J. Am. Chem. Soc. **2003**, 125, 6854–6855.
- (25) Xie, H.-L.; Wang, S.-J.; Zhong, G.-Q.; Liu, Y.-X.; Zhang, H.-L.; Chen, E.-Q. *Macromolecules* **2011**, *44*, 7600–7609.
- (26) Schaefer, K. E.; Keller, P.; Deming, T. J. Macromolecules 2005, 39, 19–22.
- (27) Hu, T. H.; Xie, H.-L.; Xiao, J. B.; Zhang, H. L.; Chen, E. Q. Cellulose **2010**, *17*, 547–558.
- (28) Hu, T.; Yi, J.; Xiao, J.; Zhang, H. Polym. J. 2010, 42, 752–758.
 (29) Karthaus, O.; Ringsdorf, H.; Ebert, M.; Wendorff, J. H.
- Macromol. Chem. Phys. **1992**, 193, 507–513.
- (30) Deibel, C.; Janssen, D.; Heremans, P.; De Cupere, V.; Geerts, Y.; Benkhedir, M. L.; Adriaenssens, G. J. Org. Electron. 2006, 7, 495–499.
- (31) Green, M. M.; Ringsdorf, H.; Wagner, J.; Wüstefeld, R. Angew. Chem., Int. Ed. 1990, 29, 1478–1481.

(32) Xu, Y. D.; Yang, Q.; Shen, Z. H.; Chen, X. F.; Fan, X. H.; Zhou, Q. F. *Macromolecules* **2009**, *42*, 2542–2550.

- (33) Tu, H. L.; Zhang, D.; Wan, X. H.; Chen, X. F.; Liu, Y. X.; Zhang, H. L.; Zhou, Q. F. *Macromol. Rapid Commun.* **1999**, *20*, 549–551.
- (34) Boden, N.; Borner, R. C.; Bushby, R. J.; Cammidge, A. N.; Jesudason, M. V. *Liq. Cryst.* **1993**, *15*, 851–858.
- (35) Chen, X.-F.; Shen, Z.; Wan, X.-H.; Fan, X.-H.; Chen, E.-Q.; Ma, Y.; Zhou, Q.-F. *Chem. Soc. Rev.* **2010**, *39*, 3072–3101.
- (36) Paraschiv, I.; Giesbers, M.; van Lagen, B.; Grozema, F. C.; Abellon, R. D.; Siebbeles, L. D. A.; Marcelis, A. T. M.; Zuilhof, H.; Sudhölter, E. J. R. *Chem. Mater.* **2006**, *18*, 968–974.
- (37) Paraschiv, I.; de Lange, K.; Giesbers, M.; van Lagen, B.; Grozema, F. C.; Abellon, R. D.; Siebbeles, L. D. A.; Sudholter, E. J. R.; Zuilhof, H.; Marcelis, A. T. M. *J. Mater. Chem.* **2008**, *18*, 5475–5481.

Macromolecules

(38) Wan, W.; Monobe, H.; Tanaka, Y.; Shimizu, Y. *Liq. Cryst.* 2003, 30, 571–578.

(39) Talroze, R. V.; Otmakhova, O. A.; Koval, M. A.; Kuptsov, S. A.; Platé, N. A.; Finkelmann, H. *Macromol. Chem. Phys.* **2000**, 201, 877– 881.

(40) Tu, H. L.; Wan, X. H.; Liu, Y. X.; Chen, X. F.; Zhang, D.; Zhou, Q. F.; Shen, Z. H.; Ge, J. J.; Jin, S.; Cheng, S. Z. D. *Macromolecules* **2000**, *33*, 6315–6320.

(41) Yu, Z. N.; Tu, H. L.; Wan, X. H.; Chen, X. F.; Zhou, Q. F. J. Polym. Sci., Part A: Polym. Chem. 2003, 41, 1454–1464.

(42) Zhang, L.; Wu, H.; Shen, Z.; Fan, X.; Zhou, Q. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 3207–3217.