Side-Chain Jacketed Liquid Crystalline Polymer Forming Double-Chain Supramolecular Column and Hexagonal Superlattice

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Supporting Information

ABSTRACT: We synthesized a series of poly(dialkyl 1-viny-3,5isophthalate) ($P_{3,5}$ -*n*, *n* is the number of carbons on alkyl group, *n* = 4-18), wherein the polyethylene backbone is jacketed by the isophthalate side chains. The phase behaviors of $P_{3,5}$ -n were investigated by using various techniques including thermal analysis, polarized light microscopy, and X-ray diffraction. It is identified that with $n \ge 8$ the P_{3,5}-*n* samples form the hexagonal columnar phase $(\Phi_{\rm H})$. Furthermore, P_{3,5}-16 and P_{3,5}-18 can exhibit a four-column hexagonal superlattice $(\Phi_{\rm H}^{\rm S})$, wherein one column is frustrated. After the alkyl tails are fully melted or crystallized, the Φ_{H}^{S} degrades



into the conventional $\Phi_{\rm H}$ phase. For the $\Phi_{\rm H}$ of P_{3,5}-*n* observed, the cross section area of the column (S) increases linearly with $n, S = 1.97 + 0.52n \text{ (nm}^2)$. The number of repeating units (Z_{rep}) required to be packed in the 0.44 nm thick column stratum is 4. Compared with poly(dialkyl 1-vinyl-2,5-terephthalate) ($P_{2,5}$ -*n*), which is the isomer of $P_{3,5}$ -*n* and can form the Φ_H phase based on the parallel packing of a "single-chain column", P_{3,5}-*n* possesses the intercept and slope of the linear function of *S* vs *n* and the Z_{rep} value nearly twice that found for $P_{2,5}$ -n. We propose that $P_{3,5}$ -n can self-organize into the column containing two chains laterally associated together. Namely, P_{3,5}-n takes the "double-chain column" rather than the "single-chain column" as the building block for the $\Phi_{\rm H}$ phase.

INTRODUCTION

With the aim of achieving the particular properties demanded by the ultimate applications, precisely manipulating supramolecular ordering of a polymer across various length scales via tailoring its chemical structure remains a core task in polymer science.¹ In this context, tremendous attention has been paid to side-chain polymers (SCPs). Different chemical groups can be incorporated into polymers as the side chain, making SCP a vital platform for exploring functional polymeric materials.²⁻⁵ Disregarding that in synthetic polymers the chain length, the tacticity, etc., usually present a distribution, the structure of the side chain in SCP is well-defined. Precision side-chain engineering can effectively control the properties of SCPs. One elegant example is the "flexible spacer" in side-chain liquid crystalline (LC) polymers.⁶ While direct attachment of the rod-like mesogen to the polymer backbone will result in the polymers with unpredictable phase structures in condensed states, using a reasonably long flexible spacer to link the backbone and mesogen can ensure the LC behaviors of side-chain LC polymers.⁷⁻⁹ It is unveiled that the flexible spacer can decouple the motions of the main and side chain,

promoting LC phase formation that largely depends on the properties of mesogen applied.⁷⁻⁹ Changing the flexible spacer length will further alter the phase transition temperatures. These outcomes demonstrate that modifying the side chain, even slightly, can markedly influence the dynamics and structures of SCPs.

SCPs often own the pendent groups larger than the repeating unit on the backbone. Therefore, the "side-chain jacketing" effect requires attention. Considering a SCP with polyethylene backbone, the side chain on every repeating unit can cause severe steric hindrance to the rotation around the main-chain carbon-carbon bond, resulting in the chain with reduced flexibility but enlarged persistence length.^{10,11} One extreme case is that the SCP adopts extended conformation, which can be observed in mesogen-jacketed LC polymers (MJLCPs).^{12,13} MJLCP abandons the flexible spacer; however, it possesses the rod-like mesogen attached to the backbone

Received: May 3, 2018 **Revised:** August 1, 2018 from the waist of the rod. Based on the strong coupling of the main and side chain, MJLCP tends to be cylinder-like, which can form columnar (Φ) LC phases.² It is further realized that the lateral attachment of a relatively small and flexible side chain can also offer enough strong jacketing effect, evidenced by poly(dialkyl 1-vinyl-2,5-terephthalate) (P_{2,5}-*n*, see Chart 1a).¹⁴ P_{2,5}-*ns* with *n* = 3–6 render perfect hexagonal columnar



 $(\Phi_{\rm H})$ phase and the interesting behavior of "isotropic phase reentry".^{14,15} It is identified recently that the $\Phi_{\rm H}$ phase of P_{2,5}-*n* relies on the fast motion of side chains, which causes the side chains to wrap the polyethylene backbone more commendably.¹⁵ Consequently, the side-chain jacketing effect is enhanced, resulting in the overall cylindrical conformation for the P_{2,5}-*n* chain.

The Φ phase of MJLCP is constructed by parallel packing of the cylindrical chains or chain segments; namely, the "singlechain column" is the building block of the Φ phase.^{14,16} For dendronized polymers having the Percec-type dendron as the side chain, it is also reported that their Φ phases are based on the "single-chain column".^{4,17,18} On the other hand, the "multichain column" consisting of a bundle of chains can also exist in Φ phases of SCPs.¹⁹ Bundling of chains is an important assembly scheme in nature, especially for cylindrical/tubular biomaterials such as microtubules, collagen, and intermediate filaments.²⁰⁻²² For self-assembly of small LC molecules, it is found in some bolaamphipiles with swallow tail lateral chains that several supramolecular chains based on hydrogen-bonding interaction of the rod-like mesogens can form a bundle, resulting in the axial-bundle Φ phases.^{23–25} In synthetic polymers, the supramolecular column of coiled coil is proposed for the LC phase of poly(n-alkyl glutamate) with long side chains.^{26,27} Very recently, it is reported that a series of peptide–dendron hybrids can form α -helical bundles that further pack into $\Phi_{\rm H}$ phase.²⁸ Recently, we are paying attention to the self-assembly of polymers bearing the wedge-shaped hemiphasmid side chain that consists of a rod-like mesogen and a half-disc moiety in series.²⁹⁻³¹ The hemiphasmid sidechain LC polymers can exhibit Φ phases with large lattice parameters (i.e., even close to 10 nm). Interestingly, it is found that the number of repeating units packed in the small column unit (Z_{rep}) is remarkably large; i.e., for a 0.44 nm thick column stratum, $Z_{\rm rep}$ can be larger than 10. In this case, we consider that the building block of these Φ phases shall be the "multi-chain column".^{32–34} Namely, the column composes of a bundle of chains laterally associated together. Moreover, the number of chains in the column can be well turned by adjusting the rigid portion on the hemiphasimid side chain.

In the present work, we intend to further explore the mechanism of multichain column through the approach of side-chain engineering. A series of poly(dialkyl 1-vinyl-3,5-isophthalate) ($P_{3,5}$ -n, see Chart 1b) were synthesized. Compared to $P_{2,5}$ -n, $P_{3,5}$ -n just has one ester group shifted from the 2- to 3-position on the benzene ring. We demonstrate that such a small modification of chemical structure changes

completely the phase behavior. $P_{3,5}$ -n can form the Φ_H phase only when the alkyl chain is sufficiently long. In the 0.44 nm thick column unit, the value of Z_{rep} is 4 rather than 2 that is found for $P_{2,5}$ -n. Partial crystallization of the alkyl chains will result in a hexagonal superlattice (Φ_H^S), which is rare in SCPs. The unit cell of the Φ_H^S phase contains four columns with one frustrated in packing. To rationalize the results obtained in various experiments, we consider that the supramolecular column of $P_{3,5}$ -n shall contain two chains rather than a single chain. Just because of this, the two isomers of $P_{2,5}$ -n and $P_{3,5}$ -nbecome totally different in phase behavior.

RESULTS AND DISCUSSION

Overall Phase Behavior of P_{3,5}-*n*. The P_{3,5}-*n*'s (n = 4, 6, 8, 12, 16, and 18) with number-average molecular weight ranging from 7×10^4 to 2×10^5 g/mol were synthesized using conventional free radical polymerization (see the Supporting Information). Their phase behaviors were investigated by using various techniques.

Under a polarized light microscope (PLM), while $P_{3,5}$ -4 and $P_{3,5}$ -6 were dark, the other four samples showed strong birefringence (Figure S4) at room temperature, indicating the LC phase. Upon heating, the birefringence would disappear, giving the LC-to-isotropic transition temperature (T_{iso}) at around 90 °C. Shown in Figure 1 are the differential scanning



Figure 1. DSC traces of $P_{3,5}$ -*n* recorded during the second heating at a rate of 10 °C/min.

calorimetry (DSC) traces of $P_{3,5}$ -*n* recorded during the second heating. Consistent with the PLM observation, $P_{3,5}$ -4 and $P_{3,5}$ -6, which shall be amorphous, exhibit only the glass transition. On the other hand, the samples with $n \ge 8$ present a small endotherm at ~90 °C, corresponding to the isotropic transition. Besides this transition, other endothermic peaks can be observed for $P_{3,5}$ -*n* with $n \ge 12$, which depend on the length of alkyl groups. $P_{3,5}$ -12 has one transition with the latent heat much larger than that of isotropization appearing at below 5 °C. Increasing *n* shifts this transition to higher temperature. For $P_{3,5}$ -16 and $P_{3,5}$ -18, there are multiple endotherms (indexed as 1, 2, and 3) showing at the temperature below 45 and 60 °C, respectively. As their transition temperatures increase with the alkyl length, we presume that these transitions are associated with the melting of crystallites of alkyl groups. The DSC cooling curves are shown in Figure S5, which indicate that transitions of $P_{3,5}$ -*n* are reversible.

Figure 2 describes the one-dimensional (1D) X-ray diffraction (XRD) profiles of $P_{3,5}$ -*n* at 25 °C. Only the



Figure 2. 1D XRD profiles of P_{3,5}-ns collected at room temperature.

amorphous scattering is observed for $P_{3,5}$ -4 and $P_{3,5}$ -6. The samples with $n \ge 8$ present a set of diffractions in the low angle region. Given the *q*-ratio ($q = 4\pi \sin \theta/\lambda$, with λ the X-ray wavelength and 2θ the scattering angle) of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, the diffractions indicate the hexagonal packing of $\Phi_{\rm H}$ phase. While those bearing shorter alkyl chains show amorphous halo in the high angle region, $P_{3,5}$ -16 and $P_{3,5}$ -18 display two diffractions peaked at *q* of 14.95 and 15.70 nm⁻¹ (*d*-spacings of 0.42 and 0.40 nm), respectively, reminiscent of the (110) and (200) diffraction of the orthorhombic ($\beta_{\rm o}$) phase of *n*-alkane.^{32,33} This outcome suggests that the long alkyl chains can form ordered structure.

We further performed two-dimensional (2D) XRD experiments to identify the ordered structure of $P_{3,5}$ -16 and $P_{3,5}$ -18. Figure 3a depicts the 2D XRD pattern of oriented $P_{3,5}$ -18



Figure 3. (a) 2D XRD image of an oriented film of $P_{3,5}$ -18 recorded at room temperature with X-ray beam perpendicular to the shear direction (the meridian direction). (b) Schematic of the geometrical relationship between the $\Phi_{\rm H}$ lattice and the $\beta_{\rm o}$ lattice.

recorded at room temperature. The sample orientation was obtained by mechanical shearing at 80 °C followed by quenching to room temperature. With the shear direction on the meridian, the low angle diffractions of $\Phi_{\rm H}$ are on the equator, indicating that the columns are parallel to the shear direction. In the high angle region, the diffraction on the

meridian and that in the quadrant can be assigned as the (200) and (110) diffraction of the orthorhombic β_o lattice with a =0.80 nm and b = 0.49 nm (for details see the Supporting Information). Therefore, the *a*- and *b*-axis of β_o lattice (denoted as *a'* and *b'* in Figure 3b) are parallel and perpendicular to the shear direction, respectively. In this case, the alkyl chains, which are oriented along the *c*-axis of β_o (i.e., *c'*), and the column axis (*c*-axis in Figure 3b) are orthogonal. The same result can be found for P_{3,5}-16 (Figure S6). The geometrical relationship of the column and alkyl chains in P_{3,5}-16 and P_{3,5}-18 is schematically drawn in Figure 3b.

The aforementioned experiments elucidate clearly that the phase behavior of $P_{3,5}$ -*n* is alkyl length dependent. Namely, lengthening the alkyl chain changes $P_{3,5}$ -*n* from amorphous to LC. Further increasing *n* can result in the hierarchically ordered structure, including the hexagonal packing of supramolecular columns on the nanometer scale and the alkyl ordering on the subnanometer scale.

Hexagonal Superlattice of $P_{3,5}$ -16 and $P_{3,5}$ -18. Interestingly, close scrutiny on $P_{3,5}$ -16 and $P_{3,5}$ -18 further unveils that there exists a superstructure that is related to the ordered packing of alkyl groups. In Figure 2, a small diffraction at q of 1.07 nm⁻¹ is visible for $P_{3,5}$ -16 at 25 °C (see the red arrow in Figure 2). Compared to the major diffraction of hexagonal structure at q^* of 2.14 nm⁻¹, this peak in fact locates at $0.5q^*$. For $P_{3,5}$ -18, albeit absent at 25 °C, the $0.5q^*$ diffraction can be detected when varying the temperature. Figure 4 presents the 1D XRD profiles of $P_{3,5}$ -18 acquired at



Figure 4. 1D XRD profiles of $P_{3,5}$ -18 recorded at various temperatures upon heating.

various temperatures during heating. The sample maintains the $\Phi_{\rm H}$ diffractions until the isotropic transition at 86 °C. An additional diffraction, which locates at 0.5*q** in relative to the major diffraction at *q** of 2.00 nm⁻¹, emerges at 32 °C and continuously increases in intensity until 42 °C. Afterward, this diffraction reduces and finally vanishes at above 50 °C. A reversible process could be observed during cooling (Figure S7). P_{3,5}-16 behaves similar to P_{3,5}-18, although the window of



Figure 5. 2D XRD patterns of $P_{3,5}$ -18 collected at (a) 30, (b) 42, and (c) 60 °C upon heating with X-ray beam perpendicular to the shear direction (the meridian direction).



Figure 6. Reconstructed relative electron density maps of $P_{3,5}$ -18 at 0 °C (a) and 42 °C (b). (c) Schematic drawing of the four-column Φ_{H}^{S} structures composed of two types of supermolecular columns indicated as A and B.

the $0.5q^*$ diffraction shifts to lower temperature side, as shown in Figure S8.

The $0.5q^*$ diffraction can also be verified by thermal 2D XRD, of which the results are shown in Figure 5. To visualize the lower angle region near the beam stop, the 2D detector was slightly rotated. With the columns aligned along the meridian, the sheared P_{3,5}-18 sample presents the low angle $\Phi_{\rm H}$ and the high angle $\beta_{\rm o}$ diffractions at 30 °C (Figure 5a). Figure 5b shows that at 42 °C the $0.5q^*$ diffraction can be found on the equator, collinear with the $\Phi_{\rm H}$ diffractions. At 60 °C, both the $0.5q^*$ diffraction and the $\beta_{\rm o}$ diffractions disappear, leaving only the (10) diffraction of $\Phi_{\rm H}$ phase (Figure 5c). A reversible process could also be observed upon cooling (Figure S9).

These experimental results reveal that the $0.5q^*$ diffraction is associated with the conditions of the alkyl crystallization. Namely, when the alkyl groups are all melted or adequately crystallized, such as at 60 or 30 °C for P_{35} -18, the 0.5q* diffraction is not detected. On the other hand, as indicated by Figure 5b, the $0.5q^*$ diffraction is arisen from the planes parallel to the columns that form the $\Phi_{\rm H}$ phase. It may be possible that the molecular motion due to alkyl melting/ crystallization can change locally the phase symmetry, resulting in a smectic structure that produces the two low angle diffractions with the q-ratio of 1:2. However, given the $0.5q^*$ diffraction of P_{3,5}-18 at 1.00 nm⁻¹, such a smectic structure, which shall have the main- and side-chain sublayers alternatively stacked together, would have the layer spacing of 6.28 nm that is much far beyond the molecular size. In this case, we consider that the appearance of the $0.5q^*$ diffraction is not associated the formation of smectic structure. Note that at low and high temperatures, where the alkyl tails sufficiently crystallized and fully melted, the sample possesses the same $\Phi_{\rm H}$

phases, albeit slightly different lattice parameters. This suggests that the essential molecular packing behavior remains during the temperature variation. In this case, we presume that the $0.5q^*$ diffraction, of which the intensity is weak, can be indicative of some additional electron density modulation within the existed hexagonal lattice that can result in a hexagonal superlattice (Φ_{H}^{S}).

We employed 2D grazing-incidence small-angle X-ray scattering (GI-SAXS) to identify the $\Phi_{\rm H}{}^{\rm S}$ structure. The measurements were performed on the sheared thin film on the silicon substrate with the thickness of a few micrometers, using $P_{3.5}$ -16 as the sample since its $0.5q^*$ diffraction reaches the maximum intensity at around room temperature (see Figure S8). The preparation procedure of the film samples is detailed in the Supporting Information. As shown in Figure S10a, with the incident X-ray beam along the shear direction, the 6-fold symmetry of the q^* diffraction corresponding to the $\Phi_{\rm H}$ lattice can be clearly identified, indicating that the supramolecular columns are lying down on the substrate and preferentially parallel to the shear direction. Moreover, the rotational disorder around the column axis is largely suppressed. The weak $0.5q^*$ diffraction can be detected when the exposure time was prolonged (Figure S10b). Noted that the $0.5q^*$ and q^* diffractions have the same azimuthal angle, which can be indexed as (10) and (20) diffraction, respectively. This result demonstrates the $\Phi_{\rm H}^{\ \ S}$ of P_{3,5}-16.

To further determine the structure of the $\Phi_{\rm H}^{~\rm S}$ superlattice, we reconstructed the relative electron density maps (EDMs) of P_{3,5}-18 based on the low angle diffractions (see Supporting Information for details). Figure 6a shows the EDM of the simple $\Phi_{\rm H}$ at 0 °C, wherein the colors of red and blue represent the high and low electron density, respectively. Given the chemical structure of $P_{3,5}$ -18, it is reasonable to assign the red area to the main chain that forms the column core and the blue area to the tails of alkyl group. To obtain the EDM of $\Phi_{\rm H}^{~~S}$, we assume that the four notable low angle diffractions are (10), (20), (22), and (42) of a hexagonal lattice. Figure 6b describes one possible EDM of P35-18 at 42 °C. Compared with Figure 6a containing only one type of column, Figure 6b shows two types of columns, which are indexed as A and B. For the A column, the yellow color of the circular portion at the center suggests the lower electron density in comparison to the red one in the B column. The blue-green area in the A column gives the regular hexagonal shape. However, the hexagon in the B column is deformed, wherein two parallel sides are longer than the other four. In this case, the hexagon looks elongated, showing the long diagonal indicated by the white solid line in Figure 6b. To satisfy the translational symmetry, the Φ_{H}^{S} demands a unit cell much larger than the $\Phi_{\rm H}$ with p6mm symmetry. Indicated by the white dashed lines, the cell contains four columns with one A and three B.

Similar four-column hexagonal superlattices have been observed in Φ phases of discotic molecules³⁴ as well as selfand coassembly of dendrons.^{35,36} Recently, we have also reported that poly(dialkyl 1-ethynyl-3,5-isophthalate) bearing chiral alkyl side groups can present the four-column hexagonal superlattice.³⁷ The "lone" one, i.e., the A column shown in Figure 6b, is frustrated. The geometrical frustration of column/ chain packing is usually found for the three-column hexagonal lattice involving two/three different kinds of columns/ chains.^{38,39} One important feature is that the three-column hexagonal lattice exhibits a honevcomb structure, wherein the frustrated column sits inside the honeycomb cell and the others locate at the apexes of the cell (Figure S11). For the superlattice of P_{3.5}-18, a honeycomb structure can also be identified. However, when the A column is placed at the cell center, the surrounding B columns actually locate on the sides of the honeycomb (Figure 6b and Figure S12). Consequently, the four-column hexagonal lattice can be ensured.

Worthy to note is that the Φ_{H}^{S} phase of $P_{3,5}$ -16 and $P_{3,5}$ -18 can be only observed in a particular temperature window. In other words, the superlattice formation is correlated to the partial melting or crystallization of alkyl groups. As mentioned, the endotherms 1, 2, and 3 shown in Figure 1 can be attributed to the melting of the octadecyl in P_{3.5}-18. After normalization, the total heat of fusion is estimated to be 21.70 kJ/mol for the octadecyl group (Figures S13 and S14). Wang et al. have studied the phase behaviors of grafted polymers bearing octadecyl side chain.⁴⁰ Compared to the data they reported, the crystallinity of the octadecyl groups in P_{3.5}-18 is around 40%. We presume that the methylene units close to the ester group cannot crystallize because of the large steric hindrance and limited mobility. On the other hand, the tail parts of the alkyl chains, which locate in the blue area of Figure 6a, can form β_0 crystallites.

Once all the tails of alkyl groups are crystallized or melted, the columns become identical and thus no frustration. However, melting a part of tails may result in different columns. Figure 6b shows that the boundaries between the A and B column and that between the B and B column are blue and light-blue in color, respectively (also see the schematic drawing in Figure 6c). This implies that in the superlattice the alkyl groups surrounding the A column are melted and thus possess the lowest electron density. The melting at the A–B boundary also leads the B column to deviate from the

orthohexagonal shape. In the honeycomb cell, the number of both the A–B and B–B boundaries is 6 (Figure 6c). Therefore, the superlattice shown in Figure 6b for P₃₅-18 at 42 °C corresponds to the condition that the A–B boundaries, which contain a half of the alkyl tails, are melted. We performed peak deconvolution to estimate the heat of fusion (ΔH) of the endotherm 1, 2, and 3 on the DSC heating trace of P_{35} -18 (Figure S13). The outcome indicates that the value of $\Delta H_1/(\Delta H_1 + \Delta H_2 + \Delta H_3)$ is of ~0.5 (11.10 vs 21.7 kJ/ mol; see Table S2). Note that 42 °C is rather close to the ending of endotherm 1 and at that temperature P3.5-18 presents the strongest $0.5q^*$ diffraction (Figure 4). This correlation suggests that endotherm 1 can be attributed to the melting of the A–B boundaries. It is observed that the $0.5q^*$ diffraction appears at 32 °C, which may be due to that partial melting can lead to the formation of superlattice in same local areas.

The experimental evidence suggest that the well-developed superlattice of $\Phi_{\rm H}^{\rm S}$ is associated with a half of the alkyl tails in molten state. Different from the case discussed above (Figure 6b), another possibility is that around the frustrated A column the alkyl tails in the A–B boundaries remain crystalline, while that in B–B boundaries are melted. The corresponding EDM is shown Figure S15, wherein a four-column hexagonal lattice can be also identified. On the basis of the experimental results obtained currently, we cannot discriminate these two possibilities. As the superlattice formation depends on the complex thermodynamics and subtle density undulation mechanism of the soft matter, further investigation about the possibilities and detailed reason for such a delicate melting behavior is required.

Chain Packing of the Supramolecular Column. As discussed above, when a part of alkyl groups are crystallized/ melted, two kinds of supramolecular columns can be observed. This implies that the supramolecular column of $P_{3,5}$ -*n* possesses a sort of flexibility. To better understand this intriguing behavior, we further analyze how the chains are assembled together in the LC state.

For the $P_{3,5}$ -*n* samples with Φ_H phase, the hexagonal unit cell area (S) increases with *n*. Shown in Figure 7 is the plot of S vs *n* at 70 °C, where the alkyl groups are completely melted. The data can be well fitted with a linear line, giving the intercept (S_0) and slope (k) of 1.97 and 0.52 nm², respectively. The supramolecular column of $P_{3,5}$ -*n* should have a nano-



Figure 7. Plot of *S* vs *n* for $P_{3,5}$ -*n* and $P_{2,5}$ -*n*. *S* is the hexagonal unit cell area.

Table 1. Calculation of the Number of R	epeating Units in the 0.44 nm	1 Thick Column	Unit (Z_{rep})) and Number of	Chains ((N_b)
in a Column of P _{3.5} - <i>n</i> and P _{2.5} - <i>n</i> Based	on the 1D XRD Results at 70)°C	1			

	phase structure	$M_{\rm rep}~({ m g/mol})$	$d_{100} (nm)$	$S(nm^2)$	t (nm)	ρ^a (g/cm ³)	$Z_{\rm rep}$	$N_{ m b}$
P _{3,5} -8	$\Phi_{ m H}$	416.59	2.31	6.16	0.44	1.01	4.0	2
P _{3,5} -12	$\Phi_{ m H}$	528.81	2.66	8.18	0.44	0.94	3.9	2
P _{3,5} -16	$\Phi_{ m H}$	641.02	2.98	10.23	0.44	0.96	4.1	2
P _{3,5} -18	$\Phi_{ m H}$	697.13	3.14	11.40	0.44	0.96	4.1	2
P _{2,5} -3	$\Phi_{ m H}$	276.33	1.32	2.01	0.44	1.05	2.0	1
P _{2,5} -4	$\Phi_{ m H}$	304.38	1.41	2.30	0.44	1.04	2.1	1
P _{2,5} -5	$\Phi_{ m H}$	332.43	1.49	2.60	0.44	1.03	2.1	1
P _{2,5} -6	$\Phi_{ m H}$	360.49	1.57	2.92	0.44	1.02	2.2	1
^a Density dete	cted at room temperat	ure, which is approx	rimately equal to	that at 70 °C.	considering a l	ittle thermal expan	sion evidend	ed by the

"Density detected at room temperature, which is approximately equal to that at 70 °C, considering a little thermal expansion evidenced by th temperature-dependent 1D XRD results (Figure 4, Figures S7 and S8).

segregation along the radius direction, with the alkyl group forming the shell and the rest part of the polymer chains locating at the core of the column. Note that S_0 is just the core area. Assuming a round shape, the core diameter is estimated to be 1.6 nm, fairly agreeing with the size of the high electron density core shown in Figures 6a and 6b.

We are aware that both the values of S_0 and k of $P_{3,5}$ -n are significantly larger than that of $P_{2,5}$ -n with the Φ_H phase we studied before.¹⁴ As plotted in Figure 7, the data of $P_{2,5}$ -n at 70 °C follows the linear line of S = 1.17 + 0.29n (nm²). A similar result has been also obtained in poly(dialkyl 1-ethynyl-2,5terephthalate),⁴¹ which has the backbone of polyacetylene and the side group same to $P_{2,5}$ -n. The remarkable difference of $P_{3,5}$ -n and $P_{2,5}$ -n in terms of S_0 and k indicates that a slight modification of the substituent position can dramatically alter the molecular assembly, although both of the polymers can form the Φ_H phase.

It is realized that $P_{2,5}$ -*n* takes the single chain with the overall cylindrical conformation, i.e., "single-chain column", as the building block of its $\Phi_{\rm H}$ phase.^{2,14} To verify this chain packing scheme, the number of repeating units per column unit $(Z_{\rm rep})$ is calculated: $Z_{\rm rep} = (N_{\rm A}/M_{\rm rep})(St)\rho$, where $N_{\rm A}$ is the Avogadro number, $M_{\rm rep}$ is the molar mass of repeating unit, *S* is the hexagonal unit cell area, *t* is the thickness of the column unit, and ρ is the experimental density. From the 2D XRD pattern of the oriented $\Phi_{\rm H}$ samples we studied, it is observed that the high angle scattering concentrates more or less on the meridian (i.e., the column axis), of which the intensity maximum locates at the position of ~0.44 nm. This scattering is mainly due to the interference of side groups which are largely perpendicular to the column axis. In this case, here we assume that the value of *t* is of 0.44 nm. As listed in Table 1, the $Z_{\rm rep}$ values of all the $P_{2,5}$ -*n* samples with $\Phi_{\rm H}$ phase are of ~2.

It is worthy to note that for vinyl polymers with a helical conformation the projection length of one repeating unit (l_{rep}) on the helical axis is around 0.20–0.22 nm, corresponding to the two carbon–carbon bonds with one *trans* and one *gauche* conformation.⁴² As examples, for the 3₁ helix of isotactic polystyrene and the 4₁ helix of isotactic poly(*o*-methylstyrene), the values of l_{rep} are 0.22 and 0.20 nm, respectively.⁴² We have studied the lamellar microphase separation of a series of rod–coil diblock copolymer with poly(2,5-bis[4-methoxyphenyl]-oxycarbonyl)styrene) (PMPCS) as the rod and poly(*e*-caprolactone) (PCL) as the coil.^{43,44} PMPCS is a typical MJLCP, of which the central part of the side chain possesses the chemical structure same as that of P_{2,5}-*n*.^{16,45} With sufficiently lager molecular weight, the rod-like PMPCS chains can pack parallel to form the hexagonal columnar nematic

phase.¹⁶ From the lamellar morphology of PMPCS-*b*-PCL, we have found that the PMPCS layer thickness (L_{PMPCS}) is proportional to the degree of polymerization of PMPCS (N_{PMPCS}): $L_{PMPCS} = 0.2N_{PMPCS}$ (nm).⁴⁴ Namely, the rod-like PMPCS has its l_{rep} of 0.2 nm. With these data in mind, we consider that the Z_{rep} of 2 for the 0.44 nm thick column unit, which is equivalent to one repeating unit per 0.22 nm, is an indicative of the "single-chain column".

Using the same analysis protocol, we estimated the Z_{rep} for the $P_{3,5}$ -*n* samples in the Φ_H phase. Taking again t = 0.44 nm, we find that the Z_{rep} values are all around 4, twice that of $P_{2,5}$ -*n*. We may assume that the 4 repeating units come from a same chain which adopts a 4_1 helical-like conformation with the identity period of 0.44 nm. Using Materials Studio, we draw a model of such chain containing 16 repeating units with the chain length of 1.76 nm (= 4 × 0.44 nm). The top view of the chain (left part of Figure 8a, the alkyl groups are omitted)



Figure 8. Molecular models of (a) "single-chain column" and (b) "double-chain column" of $P_{3,5}$ -18 containing 16 repeating units with the chain length of 1.76 nm (= 4 × 0.44 nm). In the left part (a), the alkyl chains omitted; the right parts of (a) and (b) only show the backbone of carbon–carbon bonds.

shows that the chain backbone is squeezed heavily at the column center and thus is distorted to a great extent. This disfavored conformation can be indicated more clearly in the side view of the backbone (right part of Figure 8a). In this case, the chain energy is extremely high. Any attempt of energy minimization immediately lets the distorted chain to relax to the one with carbon–carbon bond conformation of alternative *trans* and *gauche*. One might argue that the energy cost for forming such a helical-like conformation may be compensated by the strong interactions among side-chains.¹⁷ However, all the alkyl groups of $P_{3,5}$ -*n* are melted at 70 °C, making even this possibility not likely.

Alternatively, we consider that the four repeating units can belong to two different chains. When the two chains are laterally associated together to construct the supramolecular column, they can largely avoid the disfavored conformation. Figure 8b presents the model of "double-chain column" for P₃₅-18 created in Materials Studio after energy minimization. The top view confirms that the column can be separated into the shell of alkyl groups and the core occupied by the rest of the polymer. The core area is of $\sim 2.0 \text{ nm}^2$, in agreement with the S_0 (the intercept) obtained in Figure 7, and the column diameter of 3.8 nm is close to the *a* of the hexagonal lattice. Figure 8b also depicts the side view of chain backbones in the "double-chain column". It can be seen that while the two main chains are rather close to each other, the carbon-carbon bonds still comfortably adopt the trans and/or gauche conformation. This modeling supports the existence of "double-chain column". We think that this type of supramolecular column is the building block for the $\Phi_{\rm H}$ phase of P_{3,5}-n, similar to that we found in hemiphasmid side-chain LC polymers.^{29–31}

The different column structures of $P_{3,5}$ -*n* and $P_{2,5}$ -*n* shall be the result of the different mechanisms of Φ phase formation. We reported the alkyl size effect on the phase behavior of $P_{2.5}$ $n.^{14,15}$ With n < 3 and n > 10, $P_{2,5}$ -n is amorphous. $P_{2,5}$ -8 and P_{2.5}-10 only can develop the Φ phase partially. For n = 3-6, $P_{2.5}$ -n forms perfect Φ_H phase with the long-range 2D positional order. The LC $P_{2,5}$ -*n* exhibits the behavior of "isotropic phase re-entry".^{2,14} The $\Phi_{\rm H}$ phase of $P_{2,5}$ -*n* appears when the amorphous samples are heated to high temperatures. However, upon cooling, the diffraction of $\Phi_{\rm H}$ phase reduces in intensity. $P_{2,5}$ -6 can fully return to the isotropic state after cooling to room temperature, while the others remain the $\Phi_{
m H}$ phase which is frozen by glass transition. Our temperaturedependent solid-state NMR experiments reveal that the $\Phi_{
m H}$ phase in $P_{2,5}$ -*n* is tightly related to the side-chain motion.¹ Once the side-chain motion is activated at high temperatures, the alkyl groups at the 2- and 5-position of benzene ring gain more entropy, enhancing the "side-chain jacketing effect" to the polyethylene backbone and thus forcing the chain to extend. Consequently, the whole chain or a segment of $P_{2.5}$ -n becomes cylinder-like, which can serve as the building block of the $\Phi_{\rm H}$ phase. In this case, the $\Phi_{\rm H}$ phase formation of P_{2.5}-*n* is entropy-driven, of which the latent heat of transition was not detected by DSC.

Different from $P_{2,5}$ -*n*, $P_{3,5}$ -*n* presents the Φ_H phase when *n* is sufficiently large $(n \ge 8)$, showing the normal enantiotropic phase transition. For $P_{2,5}$ -*n*, the large alkyl groups with n > 10act more like "bounded" solvent. Their strong motion at high temperatures increases the "solubility", leading to the "homogenous solution". On the contrary, the usage of large alkyl groups promotes the $\Phi_{\rm H}$ phase in P_{3,5}-*n*. This implies that the formation of $\Phi_{\rm H}$ phase of P_{3.5}-*n* relies more on the assembly of side chain. Comparing to P2,5-n, P3,5-n has one ester group shifted from the 2- to 3-position on the benzene ring. As this ester group is a little far away from the polyethylene backbone, the "jacketing effect" is partly released. On the other hand, it is worthy to note that the two ester groups, which point to the two directions 120° away from each other, can make the side-chain bearing long alkyl groups more fan-like. Similar to the dendrons with fan or tapered shape, the side chain of $P_{3,5}$ - $n \ (n \ge 8)$ will intend to assemble into a disklike structure, based on which the column can be constructed. From this viewpoint of supramolecular assembly, the fan-like units in the column, i.e., the side chains of $P_{3,5}$ -n, can be

contributed by two different chains which are spatially close to each other. This assembly scheme offers the supramolecular column of $P_{3,5}$ -*n* with flexibility. When alkyl tails partly undergo melting/crystallization, the two chains sitting in the same column have the freedom to adjust their conformation and position. Therefore, the column deformation is allowed, leading to the appearance of the $\Phi_{\rm H}^{\rm S}$ structure.

CONCLUSION

In summary, we have investigated the self-organization behaviors of $P_{3,5}$ -n. Compared with its isomer $P_{2,5}$ -n, $P_{3,5}$ -n just has one ester group shifting from the 2- to 3-position of the benzene ring. Nevertheless, this slight modification substantially changes the phase behavior. While the Φ_{H} phase formation of P2.5-n is entropy-driven, P3.5-n presents the $\Phi_{\rm H}$ phase relying more on the assembly of the side chain, and thus a sufficiently long alkyl group is required (i.e., $n \ge 8$). One surprising observation is that $P_{3,5}$ -*n* with *n* of 16 and 18 can present the Φ phase with a hexagonal superlattices (Φ_{H}^{S}). In $\Phi_{\rm H}^{S}$, the hexagonal lattice contains four columns with one frustrated. It only appears in a certain temperature window. Fully melting and/or crystallization of the alkyl tail erase the column frustration, resulting in the LC phase of the ordinary $\Phi_{\rm H}$. For the $\Phi_{\rm H}$ phase, we identify that the cross section area of column (S) is linearly proportional to the alkyl length n. However, the intercept and slope is nearly twice of that found for $P_{2,5}$ -*n*. Moreover, the numbers of repeating units packed in the 0.44 nm thick column stratum (Z_{rep}) for $P_{3,5}$ -n and $P_{2,5}$ -n are 4 and 2, respectively. On the basis of this comparison, we propose that the self-organization of $P_{3,5}$ -*n* chains leads to the "double-chain column" rather than the "single-chain column" that is adopted by $P_{2.5}$ -n. This chain packing scheme endows the column of $P_{3,5}$ -*n* a certain flexibility, allowing the column to be deformed apparently during the crystallization or melting of the alkyl tails. Our work demonstrates that the precision sidechain engineering is a powerful tool to tune the properties of side-chain polymer, which can provide us with great opportunities for the exploration of advanced functional polymeric materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b00943.

Experimental details of synthesis and characterization of monomers and polymers, characterization techniques, calculation of relative electron density maps, and additional experimental data (PDF)

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Notes

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