Ordered Nanostructures at Two Different Length Scales Mediated by Temperature: A Triphenylene-Containing Mesogen-Jacketed Liquid Crystalline Polymer with a Long Spacer

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ABSTRACT: A mesogen-jacketed liquid crystalline polymer (MJLCP) containing triphenylene (Tp) moieties in the side chains with 12 methylene units as spacers (denoted as PP12V) was synthesized. Its liquid crystalline (LC) phase behavior was studied with a combination of solution ¹H NMR, solid-state NMR, gel permeation chromatography, thermogravimetric analysis, polarized light microscopy, differential scanning calorimetry, and one- and two-dimensional wide-angle X-ray diffraction. By simply varying the temperature, two ordered nanostructures at sub-10-nm length scales originating from two LC building blocks were obtained in one polymer. The low-temperature phase of the polymer is a hexagonal columnar phase (Φ_{H} , a = 2.06 nm) self-organized by Tp discotic mesogens. The high-temperature phase is a nematic columnar phase with a larger dimension (a' = 4.07 nm) developed by the rod-like supramolecular mesogen-the MJLCP chain as a whole. A re-entrant isotropic phase is found in the medium

temperature range. Partially homeotropic alignment of the polymer can be achieved when treated with an electric field, with the polymer in the Φ_H phase developed by the Tp moieties. The incorporation of Tp moieties through relatively long spacers (12 methylene units) disrupts the ordered packing of the MJLCP at low temperatures, which is the first case for main-chain/side-chain combined LC polymers with MJLCPs as the main-chain LC building block to the best of our knowledge. The relationship of the molecular structure and the novel phase behavior of PP12V has implications in the design of LC polymers containing nanobuilding blocks toward constructing ordered nanostructures at different length scales. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 295–304

KEYWORDS: liquid-crystalline polymer (LCP); nanocomposite; structure-property relation; WAXD

INTRODUCTION Frustules with ordered structures across length scales are of utmost importance in the life process of diatoms for the mechanical protection, molecular and colloidal sorting, and light harvesting.^{1,2} In addition to the significance in nature, materials with ordered structures across length scales play important roles in applications of catalysis, waveguides, selective separations, sensor arrays, photonic crystals, and nanotechnology. Several strategies have been utilized to construct ordered structures across length scales both in laboratory and for industrial applications. The straightforward "top-down" approach is step-by-step photolithography or scanning beam lithography, with which a layer-by-layer coating and exposure process is required.³ This

approach is undoubtedly time-consuming, high capital and operational cost, and not suitable for large-area patterning. In addition, the construction of such nuanced materials at a sub-10-nm length scale, which is vital for miniaturizing electronic and magnetic devices, is still challenging by the "top-down" approach.⁴ An alternative "bottom-up" approach has emerged and offers opportunities to circumvent the above problems.⁵ Self-assembly of small building blocks, such as block copolymers, vesicles, micelles, and particles, allows for fast prototyping of nanostructures.⁶ A delicate molecular design on the basis of nanobuilding blocks can be expected to construct ordered nanostructures at sub-10-nm length scales.

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Mesogen-jacketed liquid crystalline polymer (MILCP)-a supramolecular cylinder or tablet with excellent dimensional tunability—is a superb nanobuilding block for self-assembly. Taking a representative MJLCP with nonmesogenic side chains as an example, poly[di(alkyl)vinylterephthalate] (PDAVT) with alkyl groups ranging from propyl/isopropyl to hexyl forms highly ordered two-dimensional (2D) hexagonal columnar ($\Phi_{\rm H}$) phases at high temperatures.⁷ The diameter of the overall molecular cylinder is 1-2 nm determined by the length of alkyl tails. Symmetric incorporation of mesogens at the ends of the side chains of PDAVT does not influence the tendency of MJLCPs self-assembling into supramolecular cylinders. For example, a combined mainchain/side-chain liquid crystalline (LC) polymer with PDAVT as the main chain and biphenyl meosgens in the side chains exhibits hierarchically ordered structures at ambient temperature. The biphenyl groups in the side chains pack into an SmE phase with the ordering on subnanometer length scale, and the MILCP main-chain scaffold has a 2D rectangular positional order at a nanometer length scale.⁸ Similar hierarchically ordered nanostructures are obtained by altering the calamitic mesogen from biphenyl to azobenzene.⁹ A similar molecular design incorporates triphenylene (Tp), a model discotic mesogen, into the side chains of PDAVT in our previous study.¹⁰ Tp moieties and the terephthalate core are linked via 3 or 6 methylene units as flexible spacers (polymers denoted as PPnV, n = 3 or 6). At high temperatures when Tp discotic liquid crystals (DLCs) are melting, the polymers behave like typical MJLCPs, and 2D long-range-ordered rectangular columnar (Φ_R) or Φ_H phases are obtained. When Tp DLCs enter the LC phase at low temperatures, a discotic nematic (N_D) phase coexists in conjunction with the Φ_R phase, owing to the self-assembly of the Tp DLCs and the rod-like MJLCP chains, respectively. Individual ordered structures developed by the two LC building blocks are not only competitive but also promotive to each other in these two PPnV samples. Flexible spacers play an important role in tuning the phase behaviors of these polymers. With the flexible spacer length increasing, the two LC building blocks act more independently. Therefore, the phase behavior of PPnVmay be more intriguing if the flexible spacers are sufficiently long and the coupling between the two LC building blocks diminishes.

In this work, we investigated the phase behavior of an MJLCP containing Tp moieties with a spacer of 12 methylene units, denoted as PP12V (Chart 1). Interestingly, PP12V has a completely different phase behavior compared with PP3V and PP6V. With the variation of temperature, a nematic columnar (Φ_N) phase and a Φ_H phase with different length scales were observed. On the basis of the relationship between the molecular structure and the novel phase behavior of PP12V, a molecular design rule can be derived so that ordered nanostructures across length scales can be obtained by incorporating nanoscaled LC building blocks into the side chains of MJLCPs with a sufficiently long flexible spacer. Depending on the temperature range of the LC phase of the individual LC building block, namely MJLCP and DLC, the



CHART 1 Chemical structure of PP12V.

target polymer displays ordered nanostructures with lengths of 4.07 and 2.06 nm mediated by temperature. To the best of our knowledge, this is the first LC polymer displaying two LC phases with different ordered dimensions originating from tailor-made LC building blocks.

Materials and Measurements

Indium tin oxide (ITO) substrate was sequentially cleaned by detergents, deionized water, acetone, and isopropanol, and it was then dried in nitrogen at ambient temperature. All other materials were pretreated as previously reported.¹⁰

Solution NMR experiments, mass spectroscopy, elemental analysis, gel permeation chromatographic (GPC) measurements, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized light microscopy (PLM), small-angle X-ray scattering (SAXS), and one-dimensional (1D) and two-dimensional wide-angle X-ray diffraction (WAXD) experiments were performed according to the procedures previously described.^{10,11}

Solid-state NMR (ssNMR) experiments were performed on a Varian Infinityplus-400 wide-bore (89-mm) NMR spectrometer operating at a proton frequency of 399.7 MHz. A conventional 4 mm double-resonance HX CP/MAS probe was used, and the sample was placed in a 4 mm zirconia PENCIL rotor with a 52- μ L sample volume. The magic angle spinning (MAS) was automatically controlled at 5 kHz within ± 2 Hz with a MAS speed controller. ¹³C cross polarization MAS (CP/MAS) NMR experiments with total suppression of sidebands were carried out at a temperature of 26 °C. Variable-temperature ¹³C direct polarization MAS (DP/MAS) NMR experiments were carried out at a temperature of 140 °C within ± 0.1 °C with a Varian Model-L950 temperature controller. The ¹³C chemical shifts were referenced to external HMB (hexamethylbenzene) and the recycle delay was set to 3 s.

PLM experiments on electrically aligned samples were performed between ITO-coated glass slides spaced by \sim 30 μ m. The cell was equipped with electrode leads and connected to



SCHEME 1 Synthetic route of PP12V.

a direct current source. A typical heating or cooling rate of 1 $^{\circ}$ C/min was applied.

RESULTS AND DISCUSSION

Synthesis and Thermal Property of PP12V

The synthetic route for PP12V is analogous to that previously reported for PP*n*V (n = 3 or 6)¹⁰ and is depicted in Scheme 1. Details of the experimental procedures can be found in the Supporting Information. The chemical structure of the monomer P12V was confirmed by elemental analysis, high-resolution mass spectrometry, and ¹H/¹³C NMR. The molecular characterizations of PP12V are summarized in Table 1. ¹H NMR spectrum of PP12V (Fig. 1) indicates that the residue monomer has been separated completely from the polymer. GPC result shows that PP12V has a number-average molecular weight (M_n) of 1.3 \times 10⁵ g/mol, with a polydispersity index of 1.81.

The thermal properties of PP12V were investigated by TGA and DSC. As shown in Table 1, the thermal stability of PP12V is excellent with the temperature at 5% weight loss of 387 °C in nitrogen. DSC experiments were carried out to study the phase transitions of PP12V. The sample was first heated

from ambient temperature to 250 °C at a rate of 20 °C/min to erase the thermal history. The DSC thermogram for the second heating process with a heating rate of 40 °C/min was recorded after a slow cooling process.¹⁰ As shown in Figure 2, the glass transition temperature (T_{σ}) of PP12V is 6 °C, which is lower than those of PP3V and PP6V owing to the weaker steric hindrance and the stronger internal plasticization effect of the longer alkyl spacers, as expected. Upon heating, an endothermic process appears at 133 °C with an enthalpic change of 2.3 J/g. According to our previous report, this process may be related to the isotropization of Tp DLCs. The temperature of the isotropization of Tp DLCs for PP6V is 114 °C,¹⁰ which is higher than that of 2,3,6,7,10,11-hexahexyloxytriphenylene (ca. 100 °C) and Tpcontaining poly(meth)acrylates (ca. 40-80 °C). The isotropization enthalpy of Tp DLCs for PP6V is 0.3 J/g.¹⁰ For PP12V, the higher temperature and larger enthalpic change of transition than those of PP6V indicate that more ordered packing of Tp moieties may have formed in PP12V.

Liquid Crystalline Phase Behavior of PP12V

Textures of PP12V were investigated by PLM with a powder sample. Typical textures at different temperatures were

TABLE 1 Molecular Characterizations and Thermal Properties of PP12V

Yield (%)	$M_{ m n}~(imes~10^5~{ m g/mol})^{ m a}$	$M_{\rm w}/M_{\rm n}^{\rm a}$	<i>T</i> _d (°C) ^b	<i>T</i> g (°C) ^c	<i>T</i> _{transition} (°C) (Corresponding Enthalpy Change, J/g) ^c
66	1.30	1.81	387	6	133 (2.3)

min.

^a Determined by GPC in tetrahydrofuran using polystyrene standards.

^b 5% weight loss temperature evaluated by TGA under a nitrogen atmosphere at a heating rate of 10 °C/min.

Materials

° Evaluated by DSC during the second heating cycle at a rate of 40 °C/



FIGURE 1 ¹H NMR spectra of P12V (a) and PP12V (b) in CDCl₃.

recorded during cooling, as shown in Figure 3. At high temperatures before degradation, PP12V shows birefringence within the whole sample area. This birefringence becomes weaker when the sample is cooled down to below 200 °C. At 150 °C, the sample goes into the isotropic state. When the temperature decreases further, strong birefringence emerges again [Fig. 3(c)]. However, no characteristic texture is observed. Upon heating, the sample shows similar textures as those at different temperatures in the cooling process. Notably, an isotropic state appears between two LC phases from the PLM observation. This unusual LC-to-isotropic transition during cooling, which is well known as re-entrant isotropic, was also observed for other polymers, such as poly{2,5-bis[(4-butoxyphenyl)oxycarbonyl]styrene}s^{12,13} and poly[n-decyl-(RS)-2-methylbutylsilane]s.¹⁴

Phase Structure Identification

Because the phase structures of PP12V cannot be directly identified from PLM textures, variable-temperature 1D and



FIGURE 2 DSC thermogram of PP12V at a heating rate of 40 $^{\circ}$ C/min under a nitrogen atmosphere following a cooling process at 2 $^{\circ}$ C/min.



FIGURE 3 PLM micrographs of PP12V at (a) 250, (b) 150, and (c) 80 °C during cooling.

2D WAXD experiments were performed. Solution-cast samples from tetrahydrofuran were prepared for 1D WAXD experiments. A typical sample contains \sim 40 mg of PP12V. The samples were dried overnight at 35 °C in a vacuum oven after most of the solvent evaporated at ambient temperature. To avoid thermal decomposition, the sample chamber was charged with nitrogen during characterization. WAXD profiles of PP12V during the first heating and subsequent cooling processes are shown in Figure 4.

As shown in Figure 4(a), a sharp diffraction peak is observed at $2\theta = 4.96^{\circ}$ (d = 1.78 nm) in the low-angle region of the powder pattern from the as-cast film at ambient temperature. In the high-angle region, two amorphous halos are found at 2 θ values of $\sim 20^{\circ}$ ($d \approx 0.44$ nm) and $\sim 25^{\circ}$ ($d \approx$ 0.36 nm). This diffraction pattern is highly reminiscent of those from Tp derivatives forming a columnar phase. Generally, Tp DLCs tend to stack on one another to self-organize into a well-ordered supramolecular column because of the π - π stacking of the planar aromatic cores and the van der Waals interactions of the peripheral alkyl chains. Many Tp derivatives including Tp-based molecules,15,16 side-chain LC polymers,¹⁷⁻²⁶ and main-chain LC polymers²⁷⁻³² have been reported to form 2D $\Phi_{\rm H}$ phases at ambient temperature. The d-spacing of \sim 0.44 and \sim 0.36 nm for the two halos in the high-angle region represent the characteristic dimensions of the amorphous packing of the alkyl chains and the π - π stacking in a discotic LC column. The d-spacing of 1.78 nm in the low-angle region is the d_{100} of the hexagonal structure formed by the discotic LC columns. Therefore, the diameter of the column is 2.06 nm, which agrees well with the simulated dimension of Tp containing six hexyl arms (\sim 2.3 nm) with the interdigitation of the alkyl chains. However, no higher-order diffractions were observed even with a synchrotron radiation X-ray source. Hence, we tentatively hypothesize that a $\Phi_{\rm H}$ phase with 2D ordering is formed at ambient temperature. The building block of the $\Phi_{\rm H}$ phase is the supramolecular discotic column formed by the stacking Tp moieties. The polystyrene main chains along with the alkyl parts of the polymer fill the spaces among the columns and stabilize the columnar phase at ambient temperature.

As the temperature increases to 150 °C, the sharp diffraction at a 2θ value of ${\sim}5^\circ$ evolves into an amorphous halo, indicating that the aforementioned $\Phi_{\rm H}$ structure and the discotic columns self-organized by Tp moieties melt. Upon heating

further to 300 °C, a small diffraction peak at a 2 θ value of 2.17° (d = 4.07 nm) develops in addition to the amorphous halo at a 2 θ value of ~5°, indicating the formation of an ordered structure with a dimension of 4.07 nm at elevated temperatures. As the diffraction peak in the low-angle region is quite close to the detection limit of the 1D WAXD equipment, SAXS experiments were conducted to ensure that no other diffraction peaks exist in even lower angles. As expected, SAXS results (Supporting Information Fig. S1) are consistent with the 1D WAXD ones. Owing to the weak intensity and the absence of higher-order diffractions, this ordered structure can be identified as a Φ_N phase developed by the rod-like supramolecular mesogen—the MJLCP chain as a whole. Herein, the molten Tp moieties are regarded as parts of the MJLCP side chains.

As shown in Figure 4(b), PP12V follows the opposite transition pathway upon cooling compared with that in the heating process, indicating the enantiotropic phase behavior of PP12V. The only difference between the powder patterns of PP12V in the first heating process and those in the subsequent cooling process is that the peak at a 2θ value of $\sim 5^{\circ}$ is more intense and the amorphous halo at a 2θ value of $\sim 25^{\circ}$ becomes narrower after thermal annealing. This result indicates that thermal annealing can increase the degree of order of the discotic columns, which is beneficial for electronic applications.³³⁻³⁶



FIGURE 4 One-dimensional WAXD patterns of PP12V during the first heating (a) and subsequent cooling (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 5 Two-dimensional WAXD pattern of PP12V at 30 $^\circ\text{C}$ with the X-ray beam perpendicular to the fiber direction.

Macroscopically oriented samples were used for 2D WAXD experiments. Fiber samples of PP12V were drawn with a pair of tweezers at ~190 °C. Figure 5 shows the 2D WAXD fiber pattern of PP12V at 30 °C, recorded with the X-ray incident beam perpendicular to the fiber direction. 2D WAXD experiments at higher temperatures were not conducted because the fibrous sample began to flow at elevated temperatures. As shown in Figure 5, two pairs of diffraction arcs with *d*-spacing values of 1.78 and 0.36 nm are located on the equator and the meridian, respectively. This result further confirms the conjecture on the basis of 1D WAXD experiments that the diffraction with the *d*-spacing of 1.78 nm in the low-angle region is the d_{100} of the $\Phi_{\rm H}$ phase and the *d*-spacing of 0.36 nm represents the average distance of



FIGURE 6 Schematic drawing of the molecular packing of PP12V at high temperatures (a) and at ambient temperature (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 7 ¹³C DP/MAS (up) and CP/MAS (middle) ssNMR spectra and liquid-state NMR spectrum in CDCl₃ (bottom) of PP12V. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bons in Tp Moieties

Chemical Shift (ppm)	C2	C4	C5
Solution (in CDCl ₃ , at ambient temperature)	148.5	123.2	106.6
Solid-state (140 °C)	149.6	124.3	108.7
Solid-state (26 °C)	147.8	123.1	103.8
Δ^{a}	1.8	1.2	4.9

^a Difference in chemical shifts between 140 and 26 °C.

the π - π stacking in the discotic LC columns. In addition, the relative positions of these two pairs of diffraction arcs prove that the plane of Tp molecules is perpendicular to the fiber direction. Considering that the polymer main chain is inclined to be parallel to the fiber direction, the discotic supramolecular columns self-organized from Tp moieties are oriented parallel to the main chains. Namely, the Tp columns can be oriented by orienting the polymer main chains. Thus, orienting the polymer main chains via mechanical force offers a facile technique among others to orient DLCs, which has not been reported before to the best of our knowledge.³⁷ Combining the WAXD and PLM results, we propose that PP12V shows a Φ_N phase at high temperatures, and it behaves like a regular LC polymer with Tp-pendant groups self-organized into a 2D $\Phi_{\rm H}$ phase at low temperatures. Figure 6 depicts the molecular packing of PP12V at high temperatures and at ambient temperature.

Variable-Temperature Solid-State NMR Study

To understand the phase behavior of PP12V at the molecular level, variable-temperature ssNMR experiments were carried out. Owing to the hardware limit of the instrument, the hightemperature DP/MAS experiment was conducted at 140 °C, with PP12V in the isotropic state. For comparison, ¹³C CP/ MAS spectra were also recorded at 26 °C before heating. Figure 7 shows the ¹³C ssNMR spectra of PP12V at both temperatures and ¹³C solution NMR spectrum of PP12V in CDCl₃. As is clearly shown, the lines are broadened in ssNMR spectra due to the anisotropic bulk magnetic susceptibility effects³⁸ compared with the ¹³C solution spectrum. In addition, the other reason for the line broadening is that all the chains are in an anisotropic motion or with orientation anisotropy when the polymer is in the LC state. The ring current effect also plays an important role in line broadening of aromatic systems because the radial component of the field produced by the ring current is not averaged by MAS.³⁸ Several peaks are found from the spectrum at 26 °C. Because no crystallographic splittings are observed, the lines may be easily assigned as shown in Figure 7. When the temperature is increased to 140 °C, some peaks related to Tp moieties are remaining, while Peaks 1 and 3 at 26 $^\circ\text{C}$ are too weak to be observed. The spectrum at 140 °C consists of nine wellresolved, narrower lines, presumably because of the higher mobility of the side chains. The chemical shifts are similar when the polymer is in the isotropic state or in a homogeneous solution (CDCl₃), while the chemical shifts of the resonances corresponding to the aromatic carbons of Tp moieties in the range of 100-160 ppm (C2, C4, C5) move to high field at 26 °C (Table 2). Notably, this systematic change of carbon resonances is similar to that of octa-n-undecoxyphthalocyanine that forms a columnar mesophase.³⁹ The chemical shift differences stem from the anisotropic shielding by intermolecular ring current effects between neighboring Tp moieties in the columnar LC phase. The ssNMR results further confirm the formation of the discotic supramolecular columns self-organized from Tp moieties at ambient temperature, in accordance with WAXD results.

Influence of Electric Field on Alignment of PP12V

Although DLCs can be regarded as quasi-1D conductors because of the large π -orbital overlap in the supramolecular columns, the control of the structural order and alignment of columns is critical to attain high charge-carrier mobility.^{37,40} The alignment and LC ordering can be induced by applying an electric field owing to the permanent dipole moment of the LC building blocks.^{41,42} The response of PP12V to an applied longitudinal electric field was investigated. In a typical sample treatment, PP12V was sandwiched between two ITO-coated glass plates separated by \sim 30 μ m. To obtain a better effect of alignment or annealing, a typical processing procedure was applied as follows. The cell was cooled down from 150 °C, with the sample remaining in the isotropic state, to ambient temperature at a cooling rate of 1 °C/min with (or without) a longitudinal electric field of about 10⁶ V/m. PLM was utilized to monitor the aligning process.



FIGURE 8 PLM micrographs of PP12V at 100 °C before (a) and after (b) electric field treatment and during annealing after the electric field was removed (c).



FIGURE 9 One-dimensional WAXD patterns of the as-cast, thermally annealed, and electrically aligned PP12V at ambient temperature (a) and the patterns in the low-angle region (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 shows the PLM micrographs of PP12V at 100 °C before and after electric field treatment. A relatively uniform texture [Fig. 8(a)] always remains the same after annealing for several times before the electric field treatment. However, when an electric field of about 10^6 V/m is applied to the sample during the cooling process, the bright areas partially turn dark as shown in Figure 8(b). This is likely due to a partially homeotropic alignment of discotic columns. Notably, a completely homeotropic alignment cannot be achieved even when the sample was carefully annealed for several times under the aforementioned condition. In addition, this alignment is reversible. When the voltage across the cell is removed, the sample slowly relaxes back to the homogeneous alignment during annealing, and the similar uniform texture as that observed before applying the electric field emerges again as shown in Figure 8(c).

The disconnected arrangements of the microstructures have been found in the electrical alignment of 2,3,6,7,10,11-hexapentaloxy Tp on ITO glasses.⁴³ Thus, this partial alignment observed from PLM should be mainly due to the alignment of the Tp moieties in side chains. Furthermore, the texture does not change when an electric field of about 10^6 V/m is applied at ambient temperature for hours. This suggests that the alignment only occurs when the temperature is much higher than the glass transition temperature of the polymer. Effective alignment takes place when the polymer is mobile enough at relatively high temperatures. The remaining orientation of the polymer main chains may render the partially homeotropic alignment of the discotic columns.

Correlation Length of the Discotic Columns in PP12V

One-dimensional WAXD experiment on the electrically aligned sample was conducted to investigate the influence of electric field on the phase structure of PP12V. Similar 1D WAXD profile with that from the as-cast sample was obtained. To study the ordering of the discotic columns in PP12V, the correlation lengths of the diffraction peak at the d-spacing of 1.78 nm and the amorphous halo at the d-spacing of \sim 0.36 nm, which represent the apparent diameter of the columns and the average distance between neighboring Tp discs along the long-axis direction of the columns, respectively, were estimated with the Scherrer equation.⁴⁴ Assuming that the diffraction peak shape obeys a Gaussian function, we used the Warren's correction to account for instrument broadening.45 Figure 9 shows the 1D WAXD patterns of the as-cast, thermally annealed, and electrically aligned PP12V at ambient temperature. To precisely identify the center *d*-spacings and the values of the full width at halfmaximum (FWHM) of the amorphous halo at the d-spacing of ${\sim}0.36$ nm, the two scattering halos in the high-angle region were deconvoluted into two components using Gaussian functions (Supporting Information Fig. S2). The correlation lengths and correlation numbers (apparent numbers of the building blocks, that is, the discotic columns for the diffraction peak at the d-spacing of 1.78 nm and Tp discs for the amorphous halo at the *d*-spacing of \sim 0.36 nm, along the normal of the diffraction planes) are listed in Table 3.

As shown in Table 3, the comparison of the 1D WAXD results of the three samples demonstrates that PP12V has ordered domains of different sizes, although they all form the same $\Phi_{\rm H}$ phase. Correlation length derived from the diffraction with the *d*-spacing of 1.78 nm represents the apparent

TABLE 3 One-Dimensional WAXD Results of PP12V Obtained from Different Conditio	ons
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Sample	<i>d</i> -Spacing (nm) ^a	FWHM (°) ^a	Correlation Length (nm) ^b	Correlation Number ^c
As-cast	1.78	0.250	38.1	18
	$\sim 0.36^{d}$	_d	_	-
Annealed	1.78	0.210	48.8	24
	0.354	1.74	4.89	14
Electrically aligned	1.78	0.143	78.3	38
	0.357	1.58	13.4	38

^a Deconvolution with two Gaussian functions was utilized to precisely identify the center *d*-spacings and FWHMs of the two scattering halos in the high-angle region.

^b Estimated from the FWHM of the X-ray diffraction using Scherrer equation.

^c Determined by the ratio of the correlation length to the intercolumn distance or the disc-to-disc distance.

 d The scattering halo at a 2θ value of ${\sim}25^\circ$ is too broad to be deconvoluted.

ordered dimension along the (100) direction of the $\Phi_{\rm H}$ phase, namely the direction perpendicular to the discotic columns. The correlation length gradually increases in the order of the as-cast, thermally annealed, and electrically aligned samples, corresponding to 18, 24, and 38 columns in the (100) direction, respectively. The correlation length obtained from the scattering halo with the *d*-spacing of \sim 0.36 nm, which represents the apparent length of the discotic column, shows that 14 and 38 Tp moieties stack together in the columns of the thermally annealed and electrically aligned samples, respectively. The correlation length estimation of the three samples shows that thermal annealing increases the ordered domain size by a third, while electrical alignment doubles the ordered domain size. Electrical alignment also increases the column length to a large extent by inducing more Tp moieties stacking together, which is much more effective than thermal annealing. The above results clearly show that electrical alignment offers a better way for aligning discotic LCs, which is crucial for electronic applications.

CONCLUSIONS

In summary, we have synthesized an MJLCP, PP12V, which contains Tp moieties with 12 methylene units as spacers, and investigated its novel LC phase behavior. With the incorporation of Tp moieties in the side chains of the MJLCP, PP12V forms two ordered nanostructures at sub-10-nm length scales at different temperatures. The low-temperature phase of the polymer is a $\Phi_{\rm H}$ phase (*a* = 2.06 nm) self-organized by Tp discotic mesogens. A re-entrant isotropic phase is found at medium temperatures. And the high-temperature phase is a $\Phi_{\rm N}$ phase with a larger dimension (a' = 4.07 nm) developed by the rod-like supramolecular mesogen-the MJLCP chain as a whole. Partially homeotropic alignment of the polymer in the $\Phi_{\rm H}$ phase formed by the Tp moieties is achieved when treated with an electric field. Compared with the previously reported MJLCPs containing Tp moieties with shorter spacers (PP3V and PP6V)¹⁰ or MJLCPs with calamitic mesogens (biphenyl or azobenzene),^{8,9} the main chain of PP12V loses its 2D positional order at low temperatures, and the LC building block in side chains dominates the ordered self-assembly. The delicate molecular design based on MJLCPs containing the Tp discotic LC building block provides an efficient and modular strategy to construct ordered nanostructures with tailored dimensions and versatile functions.

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