Interplay between the thermotropic mesomorphic behavior and the microphase separation in dendron–liquid crystalline block copolymers

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Novel dendron–liquid crystalline (dendron–LC) block copolymers integrating Percec type (alkoxy benzyl ether) dendron molecules and liquid crystalline polymer blocks were prepared by atom transfer radical polymerization (yields ca. 80%, molecular weights were in the range of 15 000–50 000). Poly(2,5-bis(4-methoxyphenyl)oxycarbonyl)styrene) (PMPCS), of which the thermotropic mesomorphic behavior strongly relied on its molecular weight, was utilized as the liquid crystalline polymer block. Thermal property investigation of the copolymers revealed that only the glass transition temperature (111–119 °C) belonging to the PMPCS block was observed, indicating that the dendron molecule and the liquid crystalline polymer block were immiscible and the phase transition of the dendron molecule was restrained. The subtle interplay between the thermotropic mesomorphic behaviors of PMPCS and the microphase structure in these dendron–LC copolymers was discussed. With increasing molecular weight of the PMPCS block, a morphological evolution from bilayer to interdigitated lamellar structure was proposed based on the small-angle X-ray scattering (SAXS) examination. More importantly, a less-ordered columnar nematic phase instead of a hexatic columnar nematic phase which should be stabilized in the PMPCS block was identified by in situ wide-angle X-ray scattering (WAXS) experiments. The degradation of the hierarchical packing of PMPCS chains was attributed to the confinement effect originating from the interdigitated microphase structure.

Introduction

Block copolymers (BCPs) are a fascinating class of polymeric materials consisting of distinct polymeric blocks. In most cases, the distinct blocks are thermodynamically incompatible and thus the resultant copolymers give rise to a rich variety of microstructures both in bulk and in solution.1 Most research in this filed has been focused on coil–coil BCPs, where the morphologies are mainly governed by the Flory–Huggins parameter $\chi$, the degree of polymerization $N$, and the volume fraction of the blocks $f$. Notably, if the self-organization capacity such as liquid crystalline behavior is inherently possessed by one of the blocks, unanticipated structures can be generated in the liquid crystalline block copolymers (LCBCPs).1–5 Self-assembly behaviors of these copolymers are dictated by the self-organizing driving forces such as liquid crystallinity and conformational entropy.6,7 Especially, along with the formation of the microdomain structure arising from microphase separation, an order corresponding to a certain liquid crystalline phase structure would appear. Therefore, for LCBCPs, well defined organization can be found in broad length scales ranging from a few nanometres in the mesophase to hundreds of nanometres in the microphase-separated structure.

Compared with traditional coil–coil BCPs, the interplay between the mesomorphic behavior of blocks and the microphase separation effect in LCBCP systems cannot be neglected.

Thus, in recent years many groups have focused their interests on investigating the relationship between the packing restriction effect originating from microphase-separated morphologies and the ordered packing of liquid crystalline blocks.8–11 For example, Schneider and coworkers have reported the synthesis and characterization of liquid crystalline-isotropic block copolymers comprising a chiral liquid crystalline block with an azobenzene moiety and poly(hexyl methacrylate).10 Variation from lamellae to gyroid morphology was observed in the block copolymers when the liquid crystalline block underwent a phase transformation from a smectic A to isotropic phase. And the delicate competition between the morphology and the liquid crystalline phase structure was discussed. The morphology tended to be consistent with the symmetry of the smectic layers in the lamellar phase; in contrast, the gyroid morphology led to a strong deformation of the mesogens orientation.

Dendron molecules have been widely used as precise nanoscopic building blocks in recent years due to their monodisperse and controllable structure with regular three-dimensional geometry.12,13 Many works have been devoted to the synthesis of dendron–linear BCPs with extreme architectural asymmetry to generate unique phase behaviors.14–28 Among the studies on dendron-containing BCPs, the design and synthesis of dendron–rod BCPs is more and more attractive and the field has been expanded in many different directions, including material science and biological applications.29–32 In most cases, polypeptide oligomers or LC-conjugated oligomers have been used as the rod block. Attributed to the strong leaning of maintaining ordered structures in the rod segments, microphase separation in such copolymers occurs even at much lower molecular weights in comparison with flexible block copolymers, which generally
require a higher molecular weight to display microphase separation. Thus, the synthesis of novel block copolymers possessing “dendron–rod” architecture is essential not only to enrich the variety of block copolymers but also to thoroughly reveal the correlation between the molecular structure and the self-assembled morphology. Actually, due to the difficulty in the molecular structure (e.g. length, radius) manipulation, “dendron–rod” block copolymers containing rigid mesogenic segments have seldom been reported.

In this study, a series of novel dendron–liquid crystalline (dendron–LC) block copolymers containing Percec type (alkoxy benzyl ether) dendron molecules and liquid crystalline polymer blocks based on vinyl monomers are synthesized via atom transfer radical polymerization (ATRP) process. Poly[2,5-bis-[4-methoxyphenyl]oxycarbonyl]styrene (PMPCS) in which bulky side groups are connected directly to the backbones via covalent bonds was introduced as the rod block. It is worth noting that PMPCS is a typical mesogen-jacketed liquid crystalline polymer (MJLCP). Different from conventional side-chain liquid crystalline polymers, high density bulky side groups are packed around the backbone of MJLCP and force it somehow stretched. Further investigations on the mesomorphic behaviors of MJLCP have revealed that the cooperative accommodation of the laterally attached bulky side groups surrounding the extended backbones constructs the cylindrical morphology. Actually, due to the difficulty in the molecular structure and the self-assembled morphology (e.g. length, radius) manipulation, “dendron–rod” block copolymers containing rigid mesogenic segments have seldom been reported.

In this study, a series of novel dendron–liquid crystalline (dendron–LC) block copolymers containing Percec type (alkoxy benzyl ether) dendron molecules and liquid crystalline polymer blocks based on vinyl monomers are synthesized via atom transfer radical polymerization (ATRP) process. Poly[2,5-bis-[4-methoxyphenyl]oxycarbonyl]styrene (PMPCS) in which bulky side groups are connected directly to the backbones via covalent bonds was introduced as the rod block. It is worth noting that PMPCS is a typical mesogen-jacketed liquid crystalline polymer (MJLCP). Different from conventional side-chain liquid crystalline polymers, high density bulky side groups are packed around the backbone of MJLCP and force it somewhat stretched. Further investigations on the mesomorphic behaviors of MJLCP have revealed that the cooperative accommodation of the laterally attached bulky side groups surrounding the extended backbones constructs the cylindrical building blocks, by which the polymers self-assembled into the columnar phases. Thus, though MJLCPs possess similar chemical structures to the side-chain liquid crystalline polymers, the backbone and the side groups cooperate together as a whole to form the rodlike mesogens and the polymers exhibit some main-chain liquid crystalline polymer properties.

It is noteworthy that for MJLCPs the molecular weights play a crucial role in the control of the mesomorphic behavior. As the polymerization degree (DP) of PMPCS increases, amorphous, columnar nematic (\(\Phi_{H\alpha}\)), as well as hexatic columnar nematic (\(\Phi_{HN}\)) phases have been observed. Therefore, living radical polymerization of MJLCPs and the synthesis of corresponding block copolymers provide one of the simplest synthetic techniques to manipulate the phase behavior of LC polymers and to further explore the relationship between the molecular structure and the supramolecular architecture in block copolymers.

By varying the nature and molar ratio of comonomers in the block copolymers, it is possible to exert effective control over the mesophase behavior and, to some extent, the microphase structure.

Herein, the synthesis of dendron–LC block copolymers integrating Percec type (alkoxy benzyl ether) dendron molecule and PMPCS block are described. The hierarchical ordering was investigated in detail in order to gain an insight into the subtle interplay between the thermotropic mesomorphic behavior of PMPCS and the microphase structure in these dendron–LC copolymers when the dendron architecture is introduced.

**Experimental section**

**Materials**

The monomer 2,5-bis-[4-methoxyphenyl]oxycarbonyl]styrene (MPCS) was synthesized according to the procedure reported previously. Copper(II) chloride (CuCl) (Aladdin Reagent Co.) was dissolved in concentrated hydrochloric acid, precipitated by DI water, washed by ethanol and ethyl ether and dried under vacuum. N,N,N’,N’’-pentamethyldiethylenetriamine (PMDETA, TCI, 99.5%) was used as purchased. Chlorobenzene (Sinopharm Chemical Reagent Co.) was distilled over calcium hydride (Sinopharm Chemical Reagent Co.) prior to being used as the polymerization solvent. Unless otherwise specified, all other solvents and reagents were purchased from Sinopharm Chemical Reagent Co. and used as received.

**Instruments and measurements**

\(\text{\textsuperscript{1}}\)H NMR spectra were recorded on a Varian Mercury plus 400M spectrometer with CDCl\(_3\) as the solvent and TMS as the internal reference. The number-average molecular weights (\(M_n\)), weight-average molecular weight (\(M_w\)) and polydispersity index (PDI, \(M_w/M_n\)) were determined by gel permeation chromatography (GPC) instrument with a G1362A refractive index detector. Tetrahydrofuran (THF) was employed as the eluant at a flow rate of 1.0 mL min\(^{-1}\) at 35 °C and the calibration curve was obtained with monodisperse polystyrenes as standards.

The thermal behaviors of the samples were investigated with differential scanning calorimetry (DSC) on a Mettler DSC-1 apparatus. Calibration for the temperature scale was performed using indium (\(T_m = 156.60 \pm 0.20\) °C and \(\Delta H_m = 28.45 \pm 0.05\) J g\(^{-1}\)) as a standard. The accuracy of temperature measured here is ±0.05 °C. All the experiments were carried out in a nitrogen atmosphere. Each sample weighed about 2–5 mg and was sealed in an aluminium pan. The cooling and subsequent heating rate was 10 °C min\(^{-1}\). All data were based on the second heating process.

Temperature-variable SAXS and WAXS experiments were performed on an Anton Paar SAXSsens instrument equipped with an Anton Paar 55 TCS300 temperature control unit. The processing of original experimental data such as data acquisition, background subtraction, and data reduction, and so on was handled by Anton Paar SAXSquant 1.0150 software and the PCG software package. The elimination of the line smearing effect due to the line-focus X-ray source from the experimental curve (desmearing) was performed by using a desmearing program according to Lake’s method. SAXS experiments were carried on a Bruker NanoStar U SAXS systems using a Cu–K\(_\alpha\) radiation source (\(\lambda = 0.1542\) nm at 40 kV and 35 mA). Data acquisition and correction were handled by Bruker small angle scattering system V4.136 software. Samples were annealed at 140 °C for 16 h before the SAXS experiments.

Mesophase textures of the samples were observed using an Olympus BX-51 polarized optical microscope (POM) with a Linkam-THMS600 hot stage. The sensor accuracy of the hot stage is 0.1 °C. The sample films were prepared by the solution-cast method from THF solution on glass microscope slides, and the thicknesses were limited to several microns. The samples were first heated to 100 °C at 10 °C min\(^{-1}\) and then slowly heated to 180 °C at 2 °C min\(^{-1}\). Nitrogen gas was purged through the hot stage during the measurements.

TEM observations were performed on a Hitachi H-600 electron microscope. Samples were annealed at 140 °C for 16 h, and embedded into the epoxy resin. Sections with thickness less than...
100 nm were microtomed with a diamond knife and stained with 4% RuO4 vapor for 30 min. RuO4 reacted with both blocks of the copolymer, and the dendron molecules were stained strongly.

Synthesis

A convergent (outside-in) approach, which has been reported by Percec et al.,51 was utilized to synthesise the dendron macroinitiator.52 The dendron–LC copolymers were prepared by solution polymerization in chlorobenzene via atom transfer radical polymerization of MPCS with the dendron molecule as the macrorinitiator. In a typical polymerization procedure, MPCS (0.2 g, 0.5 mmol), dendron macrorinitiator (21 mg, 0.01 mmol), CuCl (0.1 mg, 0.01 mmol), PMDETA (1.7 mg, 0.01 mmol) and chlorobenzene (0.8 g) were successively placed in a 25 mL reaction tube. The reaction tube was degassed by three freeze-pump-thaw cycles, and then placed in an oil bath at 90 °C. After stirring for 2 h, the polymerization was stopped and the solution was diluted by 5 mL THF, passed through a neutral alumina (Al2O3) column to remove the catalyst and precipitated in 300 mL methanol. For purification, the crude product was completely dissolved in THF followed by the gradual addition of methanol. The precipitate was then dried in vacuum for 24 h (0.17 g, yield 85%). Good reproducibility of this synthetic process was shown in the repeated experiments. 1H-NMR (δ, ppm, 400 MHz, CDCl3): 0.88 (t, CH3– protons of dendron), 1.2–2.0 (b, –CH2– protons of dendron and –OCH3 protons of MPCS), 3.1–4.2 (b, –CH2–Ar protons of dendron and –OCH3 protons of MPCS), 6.2–7.0 (b, phenyl ring protons ortho to CH2 of dendron and outer phenyl ring protons of MPCS), 7.2–8.0 (b, phenyl ring protons ortho to CH2Cl of dendron and inter phenyl ring protons of MPCS).

Result and discussion

Synthesis

The block copolymers were synthesized by solution polymerization of MPCS with the dendron molecule with chlorine atom (1) as the macrorinitiator (Scheme 1). A series of copolymers, C-n (n = 1–3), were obtained and the copolymerization results are summarized in Table 1 with the mass fractions of dendron molecules ranging from 0.13 to 0.05. All the copolymers obtained had relatively high molecular weights and narrow molecular weight distributions.

Table 1 Properties of dendron–liquid crystalline block copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>M_n</th>
<th>W_D</th>
<th>PDI</th>
<th>D_PMC</th>
<th>T_c ( ^\circ C )</th>
<th>T_LC ( ^\circ C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>1.6</td>
<td>0.13</td>
<td>1.22</td>
<td>80</td>
<td>111</td>
<td>158</td>
</tr>
<tr>
<td>C-2</td>
<td>2.5</td>
<td>0.09</td>
<td>1.33</td>
<td>97</td>
<td>115</td>
<td>153</td>
</tr>
<tr>
<td>C-3</td>
<td>4.9</td>
<td>0.05</td>
<td>1.34</td>
<td>145</td>
<td>119</td>
<td>150</td>
</tr>
</tbody>
</table>

Where, \( M_n \) and PDI were measured by GPC. \( W_D \) is the mass fractions of dendron molecules. The molecular mass of the dendron is constant for all copolymers and equal to 2110 g mol\(^{-1}\). \( D_PMC \) was calculated via the NMR method. \( T_c \) was obtained by DSC. The temperature at which the sample begin to show birefringence under POM at a heating rate of 2 °C min\(^{-1}\).

Composition

The copolymers were characterized by 1H NMR and gel permeation chromatography (GPC) and the results are listed in Table 1. The chemical compositions of the resultant copolymers were estimated from 1H NMR spectra with CDCl3 as the solvent. Fig. 1 presents the 1H NMR spectrum of a representative copolymer, C-1. The average number of MPCS units in PMPCS block \((D_{PMPCS})\) was calculated by 1H NMR integration according to:

\[
D_{PMPCS} = \left[\left(\frac{I_a}{I_b}\right) \times 27 - 18\right]/6
\]

Where, \( I_a \) and \( I_b \) are the integrals of the NMR peaks at 3.1–4.2 ppm (–CH2O–Ar protons of dendron and -OCH3 protons of MPCS) and 0.88 ppm (–CH3 protons of dendron), respectively.

Thermal behavior

The thermal behavior of the copolymers was studied by DSC experiments. A heating rate of 10 °C min\(^{-1}\) was employed to scan the annealed copolymers, which were prepared by being cooled at a rate of 10 °C min\(^{-1}\). A crystalline melting transition at 63.3 °C with temperature rising was identified in the DSC trace of the dendron molecule (Fig. 2a). And for PMPCS, DSC curves were featureless except for the glass transitions. In comparison, the blend of dendron molecule and PMPCS \((W_D = 0.05)\) displayed two phase transitions. The crystalline melting transition of the dendron molecule in the blend was consistent with that in the neat sample, which was evidence of molecular-level heterogeneity in the copolymers. A similar phenomenon has been

![Scheme 1 Synthesis of dendron–LC copolymers composed of Percec type dendron molecules and poly[2,5-bis{(4-methoxyphenyl)oxy-carbonyl]styrene.](Image)

Fig. 1 1H NMR spectrum of dendron–LC block copolymer C-1. (CDCl3, 400 MHz).
reported by Frechet et al. for blends of poly(benzyl ether) dendrons and polystyrene.  

DSC thermograms of the copolymers are shown in Fig. 2b and the curves were featureless except for the glass transitions. With increasing molecular weight of PMPCS block, the corresponding \( T_g \) increased. However, no distinct first-order transition peaks of dendron molecules have been identified in these traces. It also indicated that the dendron molecules were covalently connected to the PMPCS since the phase transition of the former disappears in the DSC experiment.

Microphase-separated structure

Since the dendron molecules and PMPCS chains are thermodynamically incompatible, unique microstructures of the resultant copolymers were expected in the bulk state. The microphase-separated structures of these copolymers were first examined with SAXS experiments. The samples were annealed at 140 °C for 16 h in order to allow the substantial mesophase development of PMPCS and the SAXS profiles are shown in Fig. 3a. For the C-1 sample, two scattering peaks at \( q = 0.29 \) nm\(^{-1}\) and 0.58 nm\(^{-1}\) were observed and the ratio of the scattering vectors of peaks was 1 : 2, which was indicative of a lamellar structure. The repeat distance (d-spacing) of the lamellar structure was calculated to be 21.6 nm which is consistent with the TEM image shown in Fig. 3b (~21 nm). According to the molecular weight of PMPCS and the \( d \)-spacing, assuming a zigzag conformation of the PMPCS backbones, it can be inferred that two layers of the macromolecular columns were formed within each PMPCS domain, indicating a bilayer structure with “rods” (molecular columns) perpendicular to the lamellar layer in sample C-1. For the other two samples, similar features were shown in the SAXS curves and lamellar structures can also be concluded. The corresponding \( d \)-spacings are listed in Table 2. Nevertheless, the bilayer structure with “rods” perpendicular to the lamellar layer cannot be supported in C-2 and C-3 by comparison of the \( d \)-spacings of the samples, both of which have much longer PMPCS block lengths in extended conformations. Thus, a tilted or interdigitated structure was supposed for the samples of C-2 and C-3. Within each PMPCS domain, two layers of the molecules were inclined or arranged in an interdigitated structure, which was expected to strongly affect the liquid crystallinity of the PMPCS blocks.

The microphase-separated structure of dendron–PS copolymers has been studied by Mackay and evolution from lamellar to cylinder phase with increasing PS fraction has been reported.  

Notably, the cylinder structure was recognized in the dendron–PS copolymer with the same \( W_D \) as sample C-1. However, sample C-n (n = 1–3) here showed a planar inter-material dividing surface (IMDS). This might due to the existence of long rod-like PMPCS segments which were incompatible with the curved IMDS.

The influence of the thermotropic behavior of PMPCS block on the microphase-separated structure of dendron–LC block...
copolymers during the heating process was further investigated via temperature-variable SAXS experiments of solution-cast samples. SAXS profiles of sample C-2 during the heating process is shown in Fig. 4. At the room temperature, a weak peak at $q = 0.47 \text{ nm}^{-1}$ was observed, which indicated a microphase-separated structure with a $d$-spacing of 13.3 nm. Upon heating, the peak suddenly shifted to a lower $q = 0.31 \text{ nm}^{-1}$ at 140 °C. This indicated that the mesophase transition of PMPCS induced the variation of microphase-separated structure of the copolymers. With temperature increasing up to 180 °C, this peak reached at $q = 0.25 \text{ nm}^{-1}$ and high-order reflection at $q = 0.50 \text{ nm}^{-1}$ was observed. A similar phenomenon has been reported in diblock copolymers based on poly[2,5-di(isopropyloxycarbonyl)styrene] (PiPCS) and poly(isobutyl methacrylate). The evolution of the original microphase-separated structure into the lamellar morphology during the isotropic-to-LC transition of PiPCS was identified through temperature-variable SAXS experiments. Analogously, it can be supposed that the occurrence of higher order organization in Fig. 4 was induced by the mesophase development of PMPCS. The absence of high-order peaks below 140 °C may due to the lack of long-range order in the microphase structure of the copolymers.

Similar temperature-variable SAXS patterns were observed in sample C-1 and C-3. However, the reflections of sample C-3 are much weaker than the other two samples. Even at 180 °C, no obvious high-order reflections could be observed, which might be due to a weaker microphase-separation tendency in the copolymers.

Mesomorphic behavior

As mentioned above, due to the microphase separation of dendron and PMPCS, PMPCS segments are confined within the dendron molecules lamellae and are forced to form layer structures. Thus, the confined environment rendered by the microphase-separated structure may influence the mesomorphic behavior of the PMPCS blocks. In the block copolymers consisting of PS and poly[3,5-bis(d-((4'-tetradecanoylbenzoyloxy)benzoyloxy)styrene) (PTBOS), a lamellar structure was formed with a hexagonal columnar ($\Phi_H$) phase of the PTBOS block when the volume fractions was approximately equal. A perforated layer structure, where the PTBOS layer was perforated by a PS chain could be observed with increasing volume fraction of PS block. Meanwhile, the mesophase structure of PTBOS degenerated from the $\Phi_H$ phase to a columnar nematic ($\Phi_N$) phase, which was due to the lateral repulsion of PS chains. However, in the previous study on PMPCS-containing block copolymers, the influence of the microphase-separated environment on the mesomorphic behavior of PMPCS had not been reported.

The mesomorphic behavior of dendron–LC block copolymers was first studied by POM at a heating rate of 2 °C min$^{-1}$. No birefringence could be observed at room temperature in the as-cast film of the three samples. With heating, a birefringent texture appeared and the temperatures at which birefringence began to occur are listed in Table 1. All these samples exhibit schlieren textures which could be kept during the cooling run. This stability may due to the significant chain rigidity of PMPCS. The high rigidity and consequent slow motion of the polymer have a strong impact on the stabilization of the mesophase once it is formed. Fig. 5 shows the typical schlieren texture of sample C-2 taken at 180 °C.

To examine the ordered structures developed in these copolymers, 1D WAXS experiments were carried out with the as-cast samples. Fig. 6 illustrates the temperature-variable 1D WAXS patterns of sample C-2, which were recorded during the first heating run. At ambient temperature, the sample was in the amorphous state and the scattering halo at low 2θ angle of 5.1° was observed. At 140 °C, the scattering halo became asymmetric and a narrow reflection peak developed on its shoulder, which indicated the development of a mesophase in the PMPCS blocks. It is worth noting that a dramatic change was observed in the microphase-separated structure at the same temperature as shown in Fig. 4. As a result, it can be verified that the development of mesophase of PMPCS blocks contributed to the evolution of a microphase-separated structure. Upon heating to 180 °C, the intensity of reflection peak increased with its center at 2θ = 5.6° ($d$-spacing of 1.58 nm). In higher 2θ regions, the broad scattering halo retained the same shape and upon heating the center of halo slightly shifted from 20° ($d$-spacing of 0.44 nm) to 19.2° ($d$-spacing of 0.46 nm).

1D WAXS experiments of other copolymers were also performed and similar phenomena to sample C-2 were observed. The copolymers had the same value of $d$-spacing (1.58 nm at 180 °C), corresponding to the narrow reflection peak at low angle (2θ = 5.6°). It demonstrated that by tuning the molecular weight of the PMPCS block, the mesophase dimension of the dendron–LC copolymers was invariable. It has been reported

![Fig. 5](image-url) Schlieren texture of sample C-2 taken at 180 °C.
that the mesophase structure of PMPCS is strongly molecular weight dependent. \(^4\) When the molecular weight in equivalent of standard polystyrenes \((M_n)\) is lower than 1.0 × 10\(^4\) g mol\(^{-1}\) the PMPCS samples were amorphous. When 1.0 × 10\(^4\) g mol\(^{-1}\) < \(M_n\) < 1.6 × 10\(^4\) g mol\(^{-1}\), a columnar nematic (\(\Phi_N\)) phase with a \(d\)-spacing of 1.58 nm was stabilized. When the \(M_n\) is higher than 1.6 × 10\(^4\) g mol\(^{-1}\), a hexatic columnar nematic (\(\Phi_{HN}\)) phase with a \(d\)-spacing of 1.48 nm was observed. On the basis of the 1D WAXS results, it can be concluded that the mesophase in the dendron–LC block copolymers should be a \(\Phi_N\) phase regardless of the copolymer compositions and the diameter of cylindrical building block was in the vicinity of 1.82 nm.

In sample C-1, depending upon the molecular weight of the “rods”, a \(\Phi_N\) phase with a \(d\)-spacing of 1.58 nm was stabilized and a bilayer structure was assigned to the PMPCS blocks (Scheme 2a). Particularly, though the molecular weight of the PMPCS block was higher than the critical value, a less ordered \(\Phi_N\) phase instead of a \(\Phi_{HN}\) phase was developed in samples C-2 and C-3, which has never been observed in PMPCS-containing block copolymers (Scheme 2b).\(^{45,46}\) Considering the PMPCS blocks as the “rods” and the dendron molecule as the “soft tails”, a bilayer structure can be favorable in the present series of block copolymers. However, attributed to the strong leaning of maintaining ordered structures in the rod segments, the interplay between the packing restriction effect originating from microphase-separated morphologies and the ordered packing of liquid crystalline blocks could not be ignored. The ordered structure of liquid crystalline blocks is due to the packing requirements at the interface. The area per junction for the PMPCS in the \(\Phi_N\) phase was estimated to be ~2.6 nm\(^2\) according to the WAXS observation of C-1. Whereas in the case of C-2 and C-3, assuming a \(\Phi_{HN}\) phase with a \(d\)-spacing of 1.48 nm was formed, the molecular column has an area per junction of below 2.3 nm\(^2\). Thus, an interdigitated structure was adopted to solve the packing problem caused by the mismatch of the junction area and a less ordered \(\Phi_N\) phase instead of a \(\Phi_{HN}\) phase was developed in C-2 and C-3. The degradation of the hierarchical packing of PMPCS chain was attributed to the confinement effect originating from the interdigitated structure.

**Conclusion**

A series of dendron–LC BCPs comprising Percec type dendron molecules and liquid crystalline polymer blocks have been synthesized to investigate the phase structures and morphologies. The morphologies of these copolymers were found to evolve from bilayer to interdigitated lamellae with increasing the mass fraction of PMPCS. When the PMPCS segments were forced to form an interdigitated arrangement in domains, the LC ordering of PMPCS degraded from a hexatic nematic phase into a columnar nematic phase. Compared with the systems described by Percec and coauthors, which are based on dendrons with identical branching elements and similar structures, interplay between the mesomorphic behavior of semi-rigid linear blocks and microphase separation effect in LCBCPs system was highlighted. The self-assembly behavior of these copolymers are dictated by balancing the driving forces such as ordered packing of liquid crystalline blocks and the packing restriction effect originating from microphase-separated morphologies. Moreover, by varying the nature and composition of the block copolymers, it is possible to provide an effective approach to manipulate the mesomorphic behavior and, to some extent, the microphase structure in the polymeric liquid crystals.

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**Notes and references**