

Self-assembly and Properties of Block Copolymers Containing Mesogen-Jacketed Liquid Crystalline Polymers as Rod Blocks

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Abstract Mesogen-jacketed liquid crystalline polymer (MJLCP) has attracted great attention because of its rigid conformation, facile synthesis, and structural controllability. In this feature article, the self-assembly of MJLCP-based block copolymers (BCPs) is briefly reviewed, especially the nanostructures of rod-coil diblock copolymers (diBCPs), rod-rod diBCPs, and triblock copolymers. In addition, the properties of the self-assembled BCPs are also summarized, including their applications as liquid crystalline thermoplastic elastomers and solid polymer electrolytes. The article also discusses the major challenges and future directions in the study of MJLCP-based BCPs.

Keywords Mesogen-jacketed liquid crystalline polymer; Block copolymer; Rod block; Self-assembly; Properties

Citation: Lyu, X. L.; Pan, H. B.; Shen, Z. H.; Fan, X. H. Self-assembly and Properties of Block Copolymers Containing Mesogen-Jacketed Liquid Crystalline Polymers as Rod Blocks. *Chinese J. Polym. Sci.* 2018, 36(7), 811–821.

INTRODUCTION

In the recent decades, block copolymers (BCPs) have drawn great attention because of their potential applications in microelectronics, energy-related fields, and so on^[1–3]. The self-assembling behaviors of coil-coil diblock copolymers (diBCPs) depend mainly on three parameters, including the Flory-Huggins interaction parameter (χ), the total degree of polymerization (N), and the volume fraction of the individual block (f). Lamellae (LAM), hexagonally packed cylinders (HEX), body-centered cubic arrays of spheres (BCC), double gyroid (GYR), and other nanostructures have been observed both experimentally and theoretically^[4–6]. For rod-coil BCPs, the self-assembling behaviors become more complicated because of the geometric asymmetry between the two blocks and the orientational interaction among the rod segments. As a consequence, some non-conventional phases can appear, such as *Fddd* phase, wavy lamellar phase, zig-zag lamellar phase, and even Frank-Kasper phases^[7–9].

As a unique type of liquid crystalline polymers (LCPs), mesogen-jacketed LCP (MJLCP) has an extended backbone owing to the “jacketing” effect, *i.e.*, the steric effect, of the bulky side groups attaching to the polymer backbone *via* a single C—C bond or a short spacer^[10, 11]. Therefore, an MJLCP chain can behave like a supramolecular rod to form columnar liquid crystalline (LC) phases (Fig. 1)^[12], such as hexagonal columnar (Col_h) phase^[13, 14], columnar nematic (Col_n) phase^[15], hexatic columnar nematic (Col_{hn}) phase^[15],

and rectangular columnar (Col_r) phase^[16]. The conformation of an MJLCP chain can also be tablet-like to develop into smectic phases when side-chain interactions increase, for example, by extending the length of the conjugated structure of the side-chain core, by introducing hydrogen bonding or electrostatic interaction, and so on. For a rod-like MJLCP, the sizes of the rod can be controlled more easily compared to other rod-like polymers. The diameter of the rod can be tuned by changing the structure of the side group, while the length of the rod can be adjusted by controlling the molecular weight (MW) of the polymer when controllable polymerization methods such as nitroxide-mediated polymerization (NMP) and atom transfer radical polymerization (ATRP) are utilized. Thus, MJLCPs are excellent rod-like building blocks to prepare BCPs, and the interplay between the LC phase of the MJLCP and the microphase separation of the BCP will lead to interesting ordered nanostructures and phase behaviors^[12, 17–20].

This feature article reviews the nanostructures and properties of BCPs containing MJLCPs, including rod-coil diBCPs, rod-rod diBCPs, ABA or ABC linear triblock copolymers (triBCPs), and other types of BCPs. The challenges and future directions are also summarized. We believe that this article will help researchers to understand the self-assembling behaviors of MJLCP-containing BCPs.

SELF-ASSEMBLY

Rod-Coil diBCPs

A rod-coil diBCP containing a MJLCP block can be obtained by covalently connecting a rod-like MJLCP to a coil block. Poly-{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PMPCS)

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Received January 5, 2018; Accepted January 26, 2018; Published online March 6, 2018

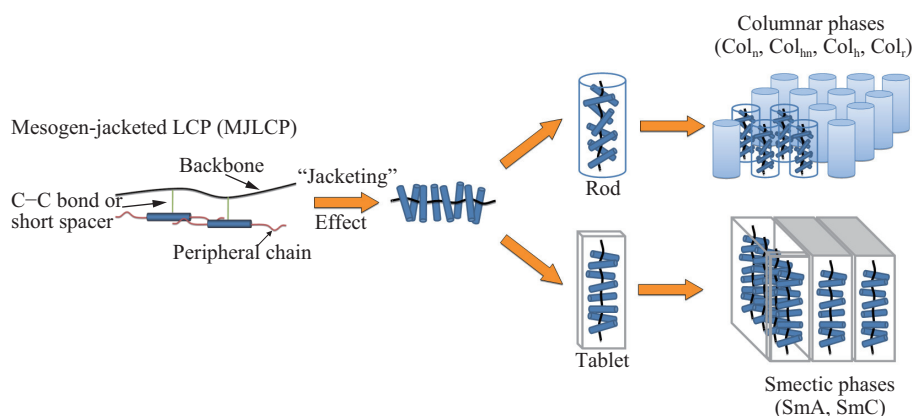


Fig. 1 Schematic representation of columnar or smectic phases formed by MJLCP supramolecular rods or tablets (Adapted with permission from Ref. [12]; Copyright (2010) the Royal Society of Chemistry)

is a frequently used MJLCP to construct BCPs. The development of living radical polymerization greatly promoted the synthesis of such BCPs. Wan and Zhou *et al.* successively synthesized polystyrene-*b*-PMPCS (PS-*b*-PMPCS) using NMP and ATRP^[21, 22]. Differential scanning calorimetry (DSC) and polarized light microscopy (PLM) were used to investigate the microphase separation of the resultant BCPs and the LC properties of the PMPCS block. Other PMPCS-based BCPs were later synthesized and characterized, such as poly(dimethylsiloxane)-*b*-PMPCS (PDMS-*b*-PMPCS)^[23], poly(methyl methacrylate)-*b*-PMPCS (PMMA-*b*-PMPCS)^[24], and poly(ϵ -caprolactone)-*b*-PMPCS (PCL-*b*-PMPCS)^[25]. Subjected to the instrumental limitation at that time, the self-assembling behaviors of these PMPCS-based BCPs were not investigated in detail. However, these studies provided viable synthetic methods and basic understanding of the properties of the BCPs, which laid solid foundation for subsequent investigation.

Ober *et al.* synthesized a series of MJLCP-based BCPs and studied the microphase-separated nanostructures using small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM)^[26]. The impact of topology on melt rheology was discussed. Following this important work, Li, Wan, and Zhou *et al.* investigated the self-assembled hierarchical nanostructures of PS-*b*-PMPCS with the PMPCS block forming a Col_h phase (Fig. 2)^[27, 28]. Two evident glass transition processes are observed after fast heating (40 °C/min) of slowly cooled (2.5 °C/min) samples, indicating that the BCP is microphase-separated. And both of the glass transition temperatures (T_g s) are higher than those of the respective homopolymers. For PS₁₇₁-*b*-PMPCS₃₄, the BCP microphase-separates into a LAM structure with a periodic size of 27 nm, and the PMPCS block develops into a Col_h phase at a smaller length scale. Each LC domain contains two layers of confined LC columns, similar to a bilayer smectic A (SmA) phase (Fig. 2c)^[27]. Interestingly, when the degree of polymerization (DP) of PMPCS is only slightly reduced to 32, the BCP PS₁₇₁-*b*-PMPCS₃₂ forms a new tetragonal perforated layer (TPL) structure (Fig. 2d)^[28]. The particular packing of the perforated layer (PL) and the extent of perforation are dependent on MW. With increasing

MW, the PS chains are stretched perpendicular to the interface, and they start to perforate the PMPCS domains when a critical volume fraction of PS is reached. At last, the structure changes from LAM to TPL. Due to the different flexibilities of PS and PMPCS chains, the phase boundary also shifts from $f_{\text{PMPCS}} \sim 0.37$ for the low-MW sample to $f_{\text{PMPCS}} \sim 0.5$ for a relatively high-MW one. The simultaneous formation of the LC phase and the microphase-separated nanostructure reveals the synergetic effect between them to some degree. Li and Zhou *et al.* further studied the competition between the LC formation of poly{3,5-bis[(4'-((4-tetradecanoylbenzoyl)oxy)benzoyl)oxy]styrene} (PTBOS) and the microphase separation of the BCP in PS-*b*-PTBOS^[29]. Interesting Col_h-in-LAM, Col_h-in-PL, and Col_h-in-sphere hierarchical structures are obtained in BCPs with different compositions. The structure formation in this system is dominantly controlled by the microphase separation between the two blocks, with the LC ordering of PTBOS decreased.

Chen and Zhang *et al.* used a side-chain LCP to replace the amorphous PS block and synthesized poly[ω -(4'-methoxybiphenyl-4-yloxy)hexyl methacrylate]-*b*-PMPCS (PMBHMA-*b*-PMPCS)^[30]. The LC transition of PMBHMA is greatly influenced by the microphase-separated LAM structure of the BCP and the size mismatch between the two blocks, *i.e.*, the difference in the diameters of the PMPCS rod and the layer spacing of the smectic phase of PMBHMA. As a result, the SmA phase in the PMBHMA homopolymer disappears at high temperatures whereas a more ordered smectic E (SmE) phase of the PMBHMA block forms instead in the BCP along with the Col_h LC phase of the PMPCS block at low temperatures. It is rarely reported in the literature that the nanostructure originated from the BCP composed of two LCP blocks leads to a more ordered LC phase of one block compared with that of the homopolymer. It has great implications for studying phase behaviors of LCPs confined in nanospace. Wan and Shen *et al.* studied the morphological transformation of a BCP induced by the formation of the LC phase of the MJLCP block^[31]. The LC phase of poly[2,5-di(isopropoxyloxycarbonyl)styrene] (PiPCS) causes the microphase-separated nanostructure of the BCP

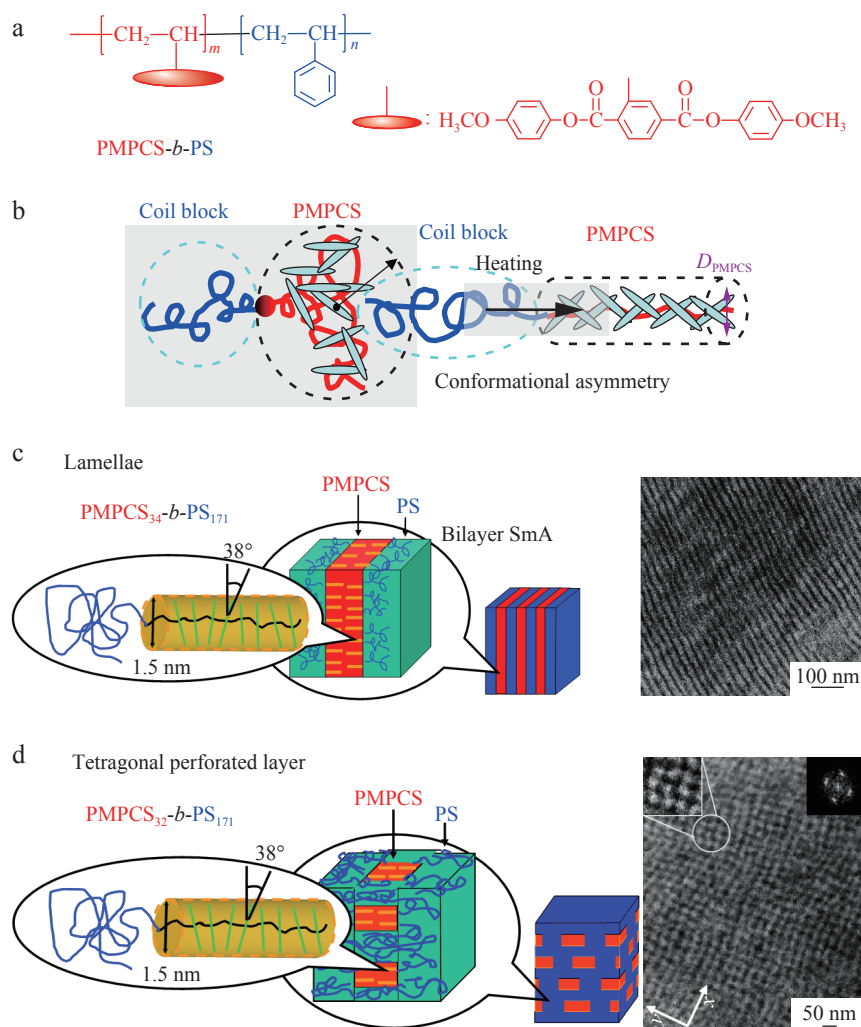


Fig. 2 Chemical structure of PS-*b*-PMPCS (a); Conformational asymmetry between the PMPCS rods and PS coils (b); LAM structure with the double-layer packed PMPCS rods that are parallel to the layer normal (c) (Adapted with permission from Ref. [27]; Copyright (2004) American Chemical Society); TPL structure with the rods parallel to the layer normal (d) (Adapted with permission from Ref. [28]. Copyright (2005) American Chemical Society)

composed of PiPCS and poly(isobutyl methacrylate) (PiBMA) to change from an undetermined phase to LAM with increasing temperature (Fig. 3). When the annealing temperature exceeds the temperature for the formation of the LC phase (T_{LC}), PiPCS experiences a coil-rod conformational change and turns into a Col_h phase. That is to say, the BCP changes from a coil-coil type to a rod-coil type, and the transformation of the nanostructure of PiPCS-*b*-PiBMA occurs upon the conformational change. The increase in the order of the microphase-separated structure of the BCP is mainly induced by the increase in Flory-Huggins interaction parameter between the two blocks because of the formation of the LC phase.

Recently, we systematically studied the phase behaviors of BCPs containing PDMS as the coil block and MJLCPs as rod blocks^[32–34]. As the MW of PDMS is fixed, the nanostructures of PDMS-*b*-PMPCS varies when the MW of PMPCS increases mainly due to compositional change (Fig. 4)^[34]. When PMPCS possesses a low MW, the BCP can self-assemble into LAM, GYR, BCC, and HEX phases.

In particular, it also self-assembles into the *Fddd* structure which is single-network morphology and not frequently seen in rod-coil BCPs. It should be noted that the use of the low-MW PMPCS rod favors the formation of network structures such as GYR and *Fddd*. In addition, order-order transitions (OOTs) including GYR-*Fddd* and HEX-BCC occur with increasing temperature. When the MW of PMPCS is in excess of the critical value for the formation of the LC phase, the isotropic-LC transformation of PMPCS induces the nanostructure to undergo a HEX-LAM OOT after thermal annealing at a temperature above the isotropic-LC transition temperature T_{LC} . It should be noted, however, that the aforementioned HEX-LAM OOT is irreversible because the isotropic-LC phase transformation of PMPCS is not thermally reversible. In consideration of various nanostructures, especially their small sizes, obtained from low-MW samples of this BCP system, the self-assembled structures of PDMS-*b*-PMPCS may be used as templates for porous materials and sub-10 nm patterning. Because PDMS is a CO₂-philic block, we also realized the control over the

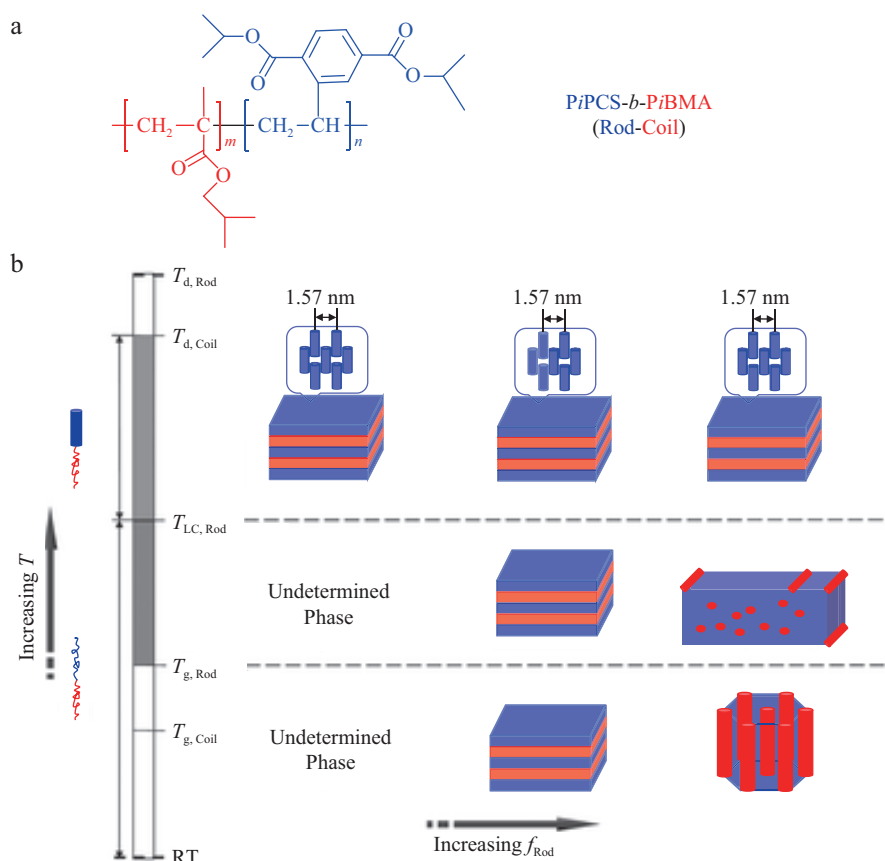


Fig. 3 Chemical structure (a) and apparent phase diagram (b) of $\text{PiPCS-}b\text{-PiBMA}$ (Adapted with permission from Ref. [31]; Copyright (2010) the Royal Society of Chemistry)

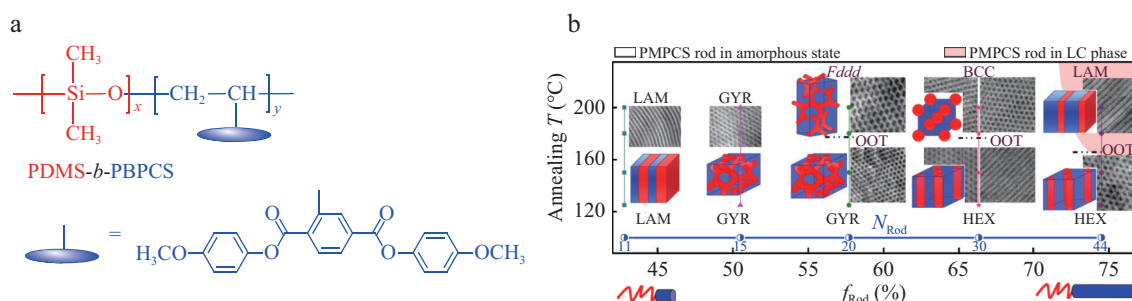


Fig. 4 Chemical structure (a) and the various nanostructures and OOTs (b) of $\text{PDMS-}b\text{-PMPCS}$ (Adapted with permission from Ref. [34]; Copyright (2013) American Chemical Society)

nanostructure of $\text{PDMS-}b\text{-PMPCS}$ by treating the BCP sample in supercritical CO_2 (scCO_2) [32]. The sample was put in a high-pressure container filled with CO_2 and annealed under supercritical conditions (120 °C and 110 bar) for 2 h. For a particular sample $\text{PDMS}_{58}\text{-}b\text{-PMPCS}_{66}$ which should be located close to the HEX-LAM phase boundary, its nanostructure is HEX under ambient conditions. The structure becomes LAM after being treated using scCO_2 . Such an OOT is attributed to the increases in both the effective interaction parameter (χ_{eff}) and the volume fraction of PDMS which is swelled more by scCO_2 . The resulting LAM morphology is fixed during the degassing process which lowers the temperature to be below the T_{g} of PMPCS. And the LAM structure turns back to the HEX structure after the sample is annealed above the aforementioned T_{g} because

the HEX morphology is the thermodynamically stable state. Because of the fast kinetics under supercritical conditions and the fast release of scCO_2 , such an approach provides an excellent means for structural control.

Poly{2,5-bis[(4-butoxyphenyl)-oxycarbonyl]styrene} (PBPCS) is an MJLCP with a re-entrant phase behavior [35]. Similar to PMPCS, PBPCS with a low MW is always in the amorphous state. The case is different for a high-MW PBPCS sample. It exhibits a reversible but re-entrant phase transition: it is amorphous at low temperatures and becomes liquid crystalline at high temperatures; and the LC phase becomes isotropic during cooling. By taking advantage of the reversible LC phase transformation of PBPCS, we succeeded in obtaining a thermoreversible BCC-HEX OOT from $\text{PDMS-}b\text{-PBPCS}$ (Fig. 5) [33]. $\text{PDMS-}b\text{-PBPCS}$

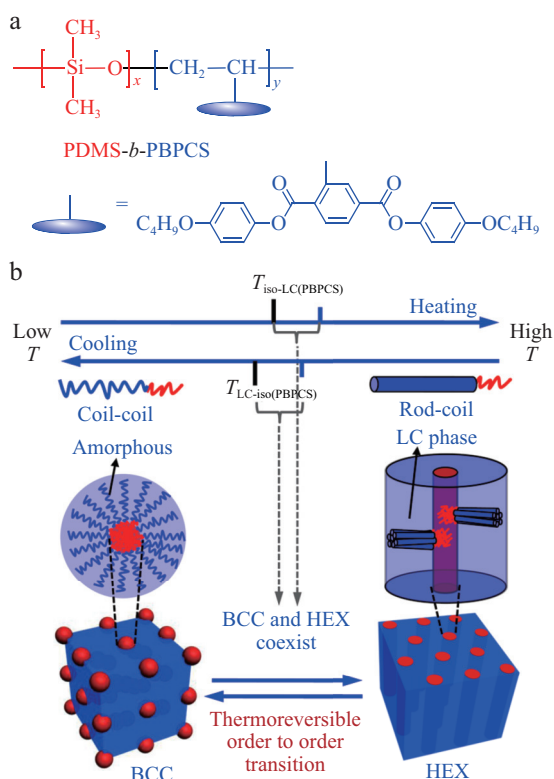


Fig. 5 Chemical structure (a) and the thermoreversible OOT (b) of PDMS-*b*-PBPCS with a high MW accompanied by the reversible isotropic-LC phase transition of the PBPCS block (Reprinted with permission from Ref. [33]; Copyright (2012) American Chemical Society)

containing a high-MW PBPCS block self-assembles into a BCC structure when PBPCS is in the amorphous state. The nanostructure changes to a HEX morphology when the temperature is increased and PBPCS enters into the LC phase. When the temperature is decreased to be below the isotropization temperature (T_i) again, a reversed HEX-BCC transition occurs. Because the sequence of the LC transformation is reversed, the sequence of OOT should also be reversed compared to other BCPs with LCPs exhibiting regular LC phase behaviors.

Chen and Zhou *et al.* investigated the crystallization and melting of MJLCP-based BCPs with a crystalline poly(ethylene oxide) (PEO) block[36, 37]. The BCP studied is composed of PEO and PMPCS. The PEO block in PEO-*b*-PMPCS forms the monoclinic crystal. The melting temperature (T_m) of PEO increases monotonically with increasing crystallization temperature (T_c). The equilibrium T_m of PEO in the BCP is predicted to be 65.4 °C on the basis of the Thomson-Gibbs equation. Square-shaped crystals appear after isothermal crystallization in a supercooling range of 14 °C to 30 °C. They further studied the morphological change of PEO-*b*-PMPCS thin films on the mica and glow-discharged carbon surfaces at different temperatures by using atomic force microscopy (AFM). The flat-on LAM structures in thin films form after isothermal crystallization in the melt, and the monoclinic crystalline structure of PEO is further confirmed by selective area electron diffraction (SAED) experiments. At $T_c < 44$ °C,

dendritic crystals appear in the monolayer. At $T_c > 48$ °C, square crystals having (100) and (020) edges form. An intermediate monolayer morphology develops at 44 °C $< T_c < 48$ °C. The thickness of the monolayer LAM structure, which is larger than that of the crystal in bulk, increases monotonically with increasing T_c . Chen, Fan, and Zhou *et al.* also investigated a LAM-LAM transition in PCL-*b*-PMPCS and the crystallization of the PCL block[38]. When the amorphous PMPCS block transforms into the LC phase at a high temperature, the original microphase-separated LAM structure develops into a new LAM structure with an increased layer spacing. Because the T_m of PCL is much lower than the T_g of PMPCS, the crystallization of PCL is confined in a layered space. The SAXS results show that the crystallization of PCL does not affect the layer spacing of the LAM structure because of the hard confinement, which suggests that the thickness of the crystalline PCL layer in the BCP with LC PMPCS is larger than that with amorphous PMPCS. In addition, the T_m of PCL crystal also monotonically increases when T_c is increased. Chen *et al.* further studied the orientation and melting of the PCL block in PCL-*b*-PMPCS[39]. The BCP self-assembles into a LAM structure with the thickness of the PCL sublayer at 15.2 nm when the PMPCS block enters into an LC phase. As previously mentioned, the crystallization of PCL is confined in a layered space. When $T_c \geq 10$ °C, the *c*-axis of the PCL crystal is parallel to the LAM layer normal. And the *c*-axis begins to tilt when T_c is decreased, and the degree of tilting increases with decreasing T_c . Meanwhile, the *b*-axis of the PCL crystal remains to be perpendicular to the LAM layer normal. When T_c is decreased to -78 °C, the crystals are randomly oriented. In addition, the sample exhibits a double melting behavior at $T_c \leq 10$ °C. The BCP systems mentioned above are excellent examples in elucidating the relationship among microphase separation, crystallization, and LC formation.

Main-chain/side-chain combined LCP (MCSCCLCP) is a special kind of LCPs which may self-assemble at two different length scales. The influence of the MCSCCLCP block on the microphase-separated structure was studied by Xie, Zhang, Chen and co-workers[40]. Poly(2,5-bis {[6-(4-butoxy-4'-oxybiphenyl)hexyl]oxycarbonyl}styrene) (PBBHCS) is an MJLCP-based MCSCCLCP and shows hierarchical LC structures on two length scales[41]. After thermal annealing at 180 °C for 2 h, PS-*b*-PBBHCS microphase-separates into LAM and rectangular cylindrical structures, and the PBBHCS block still displays LC properties, with the rectangular main-chain scaffold surrounded by the ordered side chains. Such a BCP system provides a hierarchically ordered structure on three different scales.

We further studied the macro- and microphase separation of AB/AC blends in thin films by mixing PDMS-*b*-PMPCS (DMPCS, AB) with a coil-coil BCP PDMS-*b*-PMMA (DMMA, AC)[42]. When the weight fraction of one BCP is equal to or higher than 75% in the blends of HEX-structured DMPCS (DMPCS_{HEX}) and HEX-structured DMMA (DMMA_{HEX}), the blends macrophase-separate into 100–200 nm HEX-like microdomains which are ordered HEX

nanostructures formed by the microphase separation of the two BCP components. In the blends of LAM-structured DMPCS (DMPCS_{LAM}) and DMMA_{HEX}, hamburger-like structures with a few layers form in the DMPCS_{LAM} macromatrix when the weight fraction of DMPCS_{LAM} is 75% in the blend whereas the DMPCS_{LAM} layers are dispersed in the DMMA_{HEX} macromatrix when the weight fraction of DMPCS_{LAM} is 25%. The complex hierarchical structures of the blends may be used to fabricate nanoporous templates having different pore sizes by selective etching of PDMS.

Rod-Rod diBCPs

Rod-rod diBCP is an important type of BCPs owing to their predictable sizes and absence of chain entanglement. However, the synthesis of such BCPs is relatively difficult. We successfully synthesized a rod-rod BCP containing PMPCS and poly(γ -benzyl-L-glutamate) (PBLG) by combining ATRP, ring-opening polymerization (ROP), and click chemistry (Fig. 6)^[43]. The resulting BCP exhibits hierarchical structures which depend on its composition. When the volume fraction of PBLG (f_{PBLG}) is ~ 0.50 , the BCP microphase-separates into a LAM nanostructure. The PBLG block with an α -helix conformation develops into a Col_h LC phase evidenced by the scattering vector ratio of $1:3^{1/2}:4^{1/2}:7^{1/2}$ in the wide-angle X-ray diffraction (WAXD) profile. Therefore, the BCP self-assembles into a hexagon-in-lamella morphology. When f_{PBLG} is increased to ~ 0.69 , the BCP forms a hexagon-in-cylinder hierarchical structure, in which the PMPCS rods are located in the center of the

cylinders whereas the PBLG rods in the Col_h phase serve as the matrix. We further studied the effect of size disparity on the self-assembly of a rod-rod BCP composed of an MJLCP poly[octyl-4'-(octyloxy)-2-vinylbiphenyl-4-carboxylate] (PVBP) and PBLG^[44]. The diameter of the PVBP rod is significantly larger than that of PBLG. Although PVBP-*b*-PBLG also shows hierarchical structures, the two rods are oriented in a tilted fashion due to their different rod diameters. Such a difference in rod diameters also leads to the frustrated packing of the two rods in which the ordered arrangement of one kind of rods makes the packing of the other kind of rods more difficult. In addition, with increasing f_{PVBP} , the packing scenario of the rods in the microphase-separated nanostructure changes, in particular, from an interdigitated packing to a bilayer one. Compared to PMPCS-*b*-PBLG, PVBP-*b*-PBLG displays a much wider LAM region in its phase diagram, possibly also owing to the difference in the diameters of the two rods.

In addition, rod-rod BCPs can also be synthesized more conveniently by employing non-covalent approaches such as the use of host-guest interactions between a rod-coil BCP precursor as the host and guest molecules. Zhang *et al.* prepared a rod-rod BCP composed of PMPCS and the inclusion complex (IC) formed by PCL and α -cyclodextrin (α -CD)^[45]. Results from WAXD and solid-state ¹³C cross polarization/magic angle spinning (CP/MAS) NMR spectroscopy confirm that the IC forms a tunnel-like structure. The phase behavior of the supramolecular rod-rod BCP is influenced by both PMPCS and the IC. Recently we

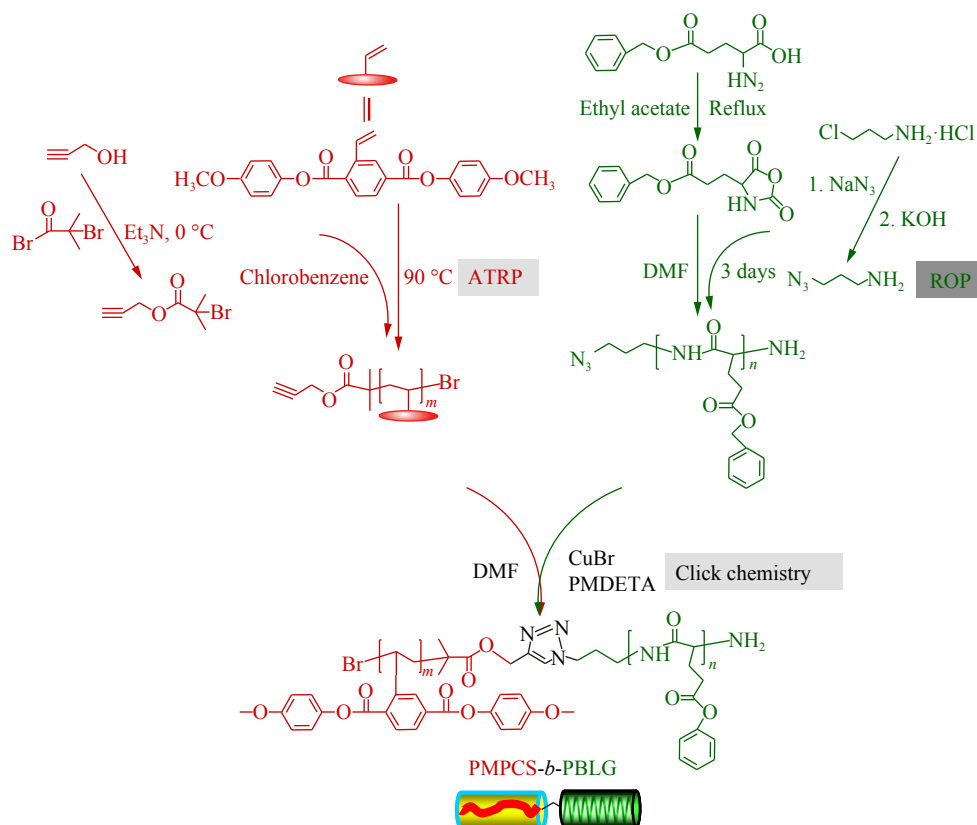


Fig. 6 Synthetic route to PMPCS-*b*-PBLG

utilized the host-guest interaction between tris-*o*-phenylenedioxycyclotriphosphazene (TPP) and the rod-coil BCP PEO-*b*-PVBP to construct a rod-rod BCP P(EO@TPP)-*b*-PVBP as shown in Fig. 7[46]. Because TPP molecules can recognize and capture ethylene oxide units in PEO-*b*-PVBP, it is easy to convert the rod-coil BCP to a rod-rod one in this way. When the annealing temperature is below the T_{LC} of PVBP, the PVBP block is in the amorphous state, and the P(EO@TPP) block is arranged into a hexagonal crystalline structure on the basis of the wide-angle X-ray scattering (WAXS) results. SAXS results reveal that the BCP forms a HEX nanostructure. Therefore, the supramolecular BCP self-assembles into a double hexagonal structure as shown in Fig. 7(b). However, the Col_h LC phase of the PVBP block formed at high temperatures destroys both the nanostructure of the BCP and the hexagonal crystalline structure of the P(EO@TPP) IC. Such a behavior may also be traced to the difference in sizes of the crystalline P(EO@TPP) and LC PVBP. Compared with click reactions to connect two rod blocks, constructing rod-rod BCPs with the host-guest interaction is a relatively easy way.

triBCPs

In addition to various diBCPs, linear rod-coil-rod ABA-type BCPs (Fig. 8) have also been investigated by our research

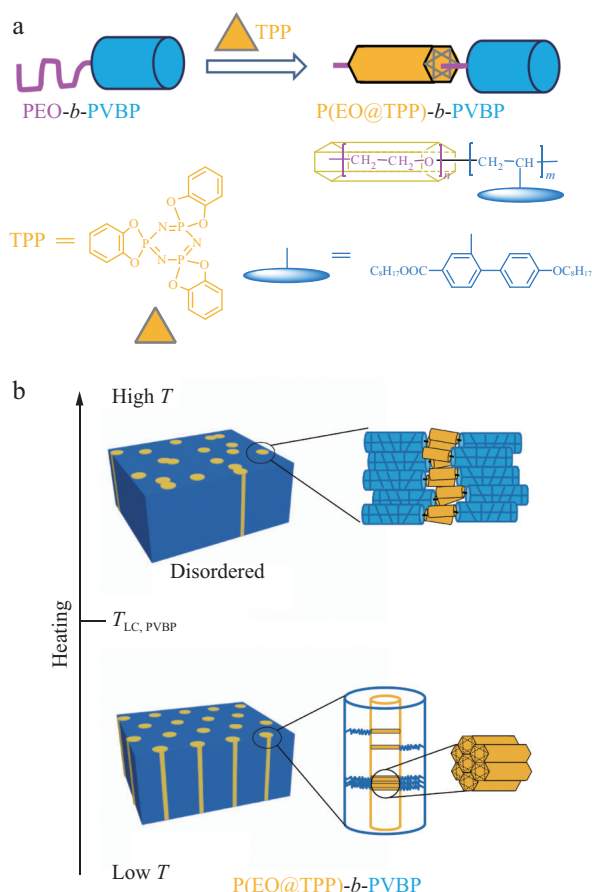


Fig. 7 Schematic representation of the preparation and chemical structure (a) and the phase diagram (b) of P(EO@TPP)-*b*-PVBP (Adapted with permission from Ref. [46]; Copyright (2016) WILEY-VCH)

group. For example, the PMPCS block in rod-coil-rod BCP PMPCS-*b*-polyisoprene-*b*-PMPCS forms a Col_h phase on the basis of one-dimensional (1D) and two-dimensional (2D) WAXD results, while the BCP microphase-separates into a LAM nanostructure in the bulk sample[47]. We also studied the phase behavior of another rod-coil-rod BCP PMPCS-*b*-PIB-*b*-PMPCS[48]. With variation in the MW of the BCP, nanostructures including LAM, HEX, and an intermediate one between the former two can be obtained. When PMPCS enters into the LC phase after being thermally annealed, the nanostructures remain unchanged. Another MJLCP poly(4'-(methoxy)-2-vinylbiphenyl-4-methyl ether) (PMVBP) with a high T_g of about 200 °C[14] has also been used to prepare BCPs. We studied the hierarchical structures of the resultant rod-coil-rod BCP PMVBP-*b*-PDMS-*b*-PMVBP in which the two blocks have a huge difference in their T_g s[49]. The BCP self-assembles predominantly into LAM structures, and the formation of the LC phase of PMVBP increases the layer spacing values. These rod-coil-rod triBCPs can be potentially useful as LC thermoplastic elastomers (TPEs).



Fig. 8 Schematic representation of a linear rod-coil-rod ABA-type BCP

Besides rod-coil-rod BCPs, linear coil-coil-rod ABC-type BCPs containing MJLCPs have also been studied by different research groups. Zhang *et al.* synthesized a coil-coil-rod BCP composed of PEO, PMMA, and rod-like PMPCS[50]. The PMPCS rods form an LC phase when its MW exceeds 1.82×10^4 g/mol, similar to the PMPCS homopolymer. We observed an interesting OOT between two complex nanostructures in PDMS-*b*-PS-*b*-PMPCS with increasing temperature (Fig. 9)[51]. When PMPCS is in the amorphous state, the BCP forms a core-shell HEX (CSH) structure (Fig. 9b), in which the PDMS domain in the center of the cylinder is surrounded by the PS shell and the core-shell cylinders are distributed in the PMPCS matrix. After the sample is annealed above the T_{LC} of PMPCS, the PMPCS block enters into the Col_h LC phase, which induces the CSH complex nanostructure to become a three-phase four-layer LAM (LAM-3P4L) morphology with interdigitated PMPCS rods (Fig. 9c). And the LAM-3P4L structure remains unchanged when the temperature is decreased to be below the T_{LC} of PMPCS because of the irreversible LC transition of PMPCS. We obtained similar results in PDMS-*b*-PS-*b*-PBPCS (DSB)[52]. The sample D120S100B50 forms a CSH structure during the whole temperature range until thermal decomposition, while the sample D120S100B120 self-assembles into a CSH morphology at low temperatures and forms a LAM-3P4L structure when the temperature exceeds the T_{LC} of PBPCS like in the case of PDMS-*b*-PS-*b*-PMPCS. However, the CSH and LAM-3P4L structures can be reversibly transformed owing to the reversible isotropic- Col_h transition of PBPCS during heating and cooling. The complex nanostructures from these BCPs are useful to obtain complex nanopatterns.

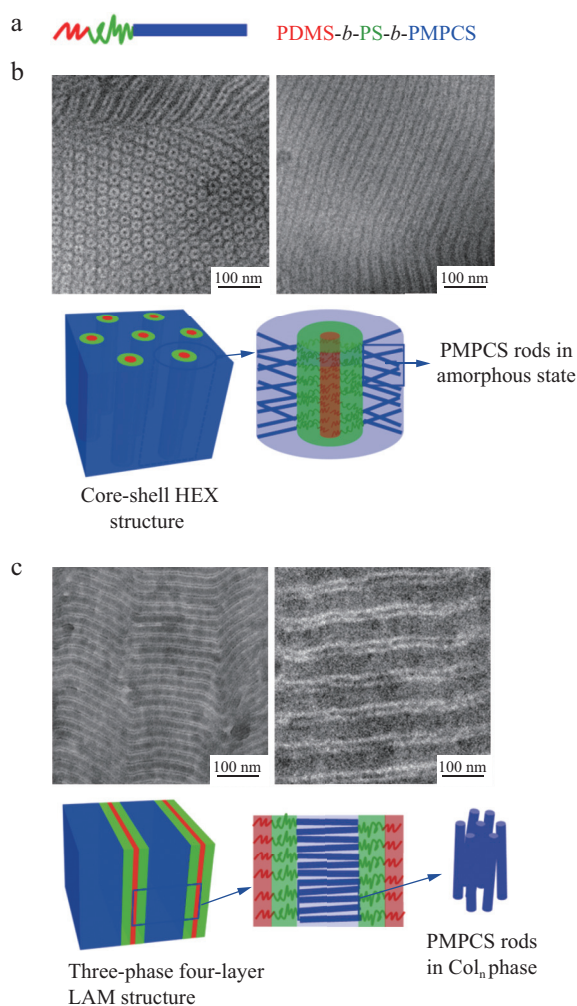


Fig. 9 Schematic representation of PDMS-*b*-PS-*b*-PMPCS (a); TEM micrographs and the packing model of the CSH structure with amorphous PMPCS rods (b); TEM micrographs and the packing model of the LAM-3P4L structure with PMPCS rods in the LC state (c) (Reprinted with permission from Ref. [51]; Copyright (2014) Springer Nature)

The self-assembled structures of linear rod-coil-rod triBCPs can also be tuned by blending them with the homopolymers of the composing blocks, as we demonstrated using PMPCS-*b*-PIB-*b*-PMPCS as an example^[53]. LAM structures can be obtained starting from either a LAM-structured or HEX-structured triBCP sample by adding the homopolymer of PMPCS or PIB, respectively. The layer spacing of the LAM structure is influenced by both the coil size and the tilting angle of the rods.

Other Types of BCPs

Zhang *et al.* synthesized a series of star-shaped BCPs containing different rod-coil BCP arms with PMPCS as the rod block and investigated their LC behaviors^[54, 55]. The star-shaped BCPs with the MW of PMPCS in each arm in excess of a critical value can also form highly stable LC phases. We designed a star-shaped polymer with three rod-rod BCP arms, (PMPCS-*b*-PBLG)₃^[56]. The PMPCS block forms a Col_n phase, and the PBLG block develops into a Col_h phase, similar to the respective homopolymers. On the basis of the

TEM and 2D WAXD results, the BCP microphase-separates into a LAM structure, in which both rod-like PMPCS and PBLG blocks are aligned parallel to each other with the three arms arranged in two opposite directions. The PMPCS rods are packed in a bilayer fashion, and the hexagonally packed PBLG blocks are arranged in a similar way. Therefore, a hexagon-in-lamella morphology is obtained in this star-shaped BCP.

Tang and Wu *et al.* prepared a dendron-LC BCP with a Percec-type dendron molecule and PMPCS^[57]. The SAXS and WAXD results reveal that the BCP evolves from a bilayer LAM structure with PMPCS in a Col_h phase to an interdigitated LAM morphology with the PMPCS block in a Col_n phase with increasing f_{PMPCS} . The self-assembly of the dendron-LC BCP is greatly influenced by the interplay between the LC property of PMPCS and the microphase separation of the BCP. Thus, when the PMPCS rods are forced to arrange in an interdigitated way, the LC arrangement of the PMPCS block becomes less ordered into a Col_n phase from the Col_h phase.

PROPERTIES AND APPLICATIONS

Based on the control over nanostructures of BCPs containing MJLCPs, the properties and applications of these BCPs have also been explored. Because of the rigid nature and the ease in synthesis of MJLCPs, BCPs with MJLCPs as hard blocks can be used as TPEs. Zhou *et al.* prepared the first LC TPE (LCTPE) from a linear ABA-type rod-coil-rod BCP with PMPCS as the rigid A block and poly(*n*-butyl acrylate) (PnBA) as the soft B blocks^[58]. The BCP sample displaying LCTPE properties has a relatively high MW, with a number-averaged MW (M_n) higher than 7.0×10^4 g/mol, and thus the LC PMPCS domains can serve as the physical crosslinking points. Again, the Col_n phase of the PMPCS block is thermally stable from the T_g of PMPCS to the decomposition temperature of the sample. The BCP self-assembles into a LAM structure which can also be used as physical crosslinking. Dynamic mechanical analysis (DMA) results show two transition processes in the curve of the dynamic shear storage modulus (G'). The existence of a rubbery plateau is characteristic of TPEs, and an additional rubbery plateau appearing at temperatures above the T_g of the PMPCS block is attributed to the remaining of the physical crosslinking network because of the stable LC phase of PMPCS in the whole experimental temperature range (up to 200 °C). Results from tensile testing on the BCP sample reveal that a low stress can generate a large strain. The mechanical properties of this MJLCP-based TPE are only equivalent to those of PMMA-*b*-PnBA-*b*-PMMA in the literature^[59].

Recently we replaced PnBA with polybutadiene (PB) which is a much better soft block and prepared a new PMPCS-based TPE material (Fig. 10)^[60]. Similar DMA results were obtained as mentioned above. Meanwhile, the initial G' and loss modulus (G'') values of the TPE are indeed significantly increased after thermal annealing because the LC phase of PMPCS formed at high temperatures is retained at ambient temperature (Fig. 10b). Tensile testing results

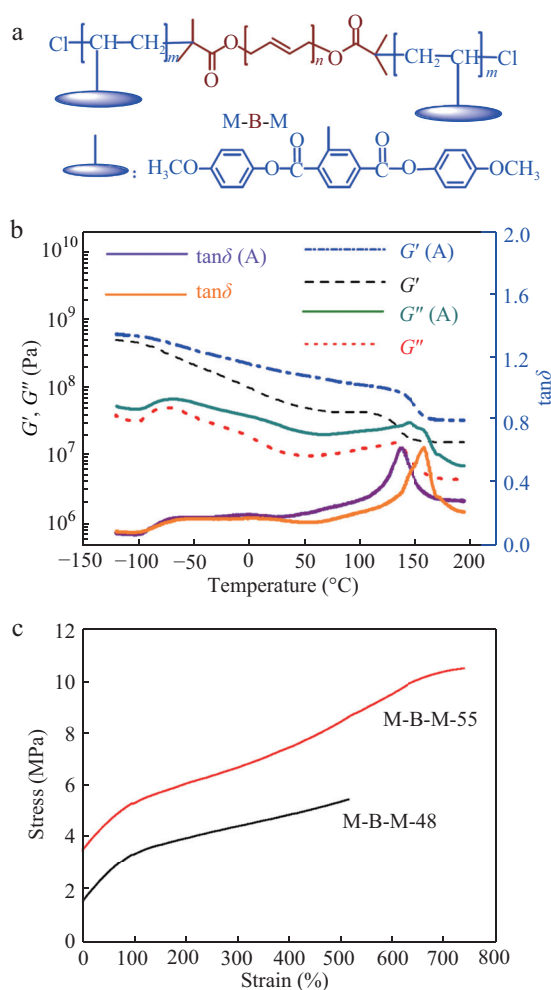


Fig. 10 Chemical structure (a), DMA results (b), and tensile testing results (c) of M-B-M (Reprinted with permission from Ref. [60]; Copyright (2016) American Chemical Society)

demonstrate that the mechanical properties of PMPCS-*b*-PB-*b*-PMPCS (M-B-M) are better than those of the commercial SBS-1401, with a maximum elongation at break at 736% and a tensile strength at 10.6 MPa (Fig. 10c). And the stretching strength at 300% of the LCTPE is 6.7 MPa. More importantly, the high-temperature performance of this LCTPE is much better than that of SBS-1401, owing to the existence of the LC phase of PMPCS. To further improve the high-temperature properties, we used another MJLCP, PMVBP, as the hard block because PMVBP has a higher T_g (~ 200 °C) compared with PMPCS[61]. The BCP sample does not become liquid-like even at 270 °C owing to the appearance of a new rubbery plateau above the T_g of PMVBP which forms a stable Col_{h} LC phase at high temperatures. Tensile testing results indicate that the maximum elongation at break of the LCTPE is 692%, with a corresponding tensile strength of 4.5 MPa. The stretching strength at 300% is 3.2 MPa. Although the mechanical properties of PMVBP-*b*-PB-*b*-PMVBP (V-B-V) are not as good as those of M-B-M, the TPE based on V-B-V has a higher G' , and its rubbery plateau extends to a higher temperature. Therefore, this LCTPE may be used at even higher temperatures.

In a recent work, we prepared a solid polymer electrolyte (SPE) based on a brush BCP (BBCP) which possesses a polynorbornene backbone and has rigid PMPCS and flexible PEO side chains (gPEO-*b*-gPMPCS), as shown in Fig. 11(a)[62]. The doping of lithium salt bistrifluoromethanesulfonimide lithium ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$, namely LiTFSI) into the disordered gPEO-*b*-gPMPCS sample leads to an ordered complex with a self-assembled LAM structure that has a layer spacing of ~ 37 nm and can serve as the nanochannels for transporting Li ions (Fig. 11b). The ionic conductivity (σ) of the gPEO-*b*-gPMPCS/LiTFSI complex increases with increasing temperature. The σ value at 200 °C reaches a high level for PEO-based SPEs at 1.58×10^{-3} S/cm. In addition, because of the stable LC phase of PMPCS, the nanostructures of the complexes are stable even at 240 °C, which is the highest experimental temperature. Thus, the resulting BBBCP/LiTFSI complexes may be used as SPEs in lithium ion batteries, especially for high-temperature applications.

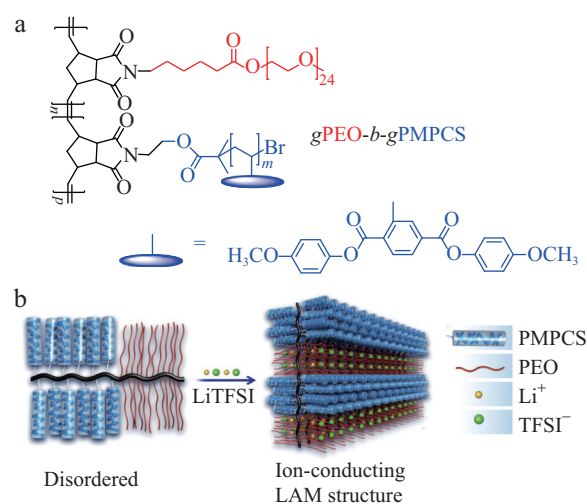


Fig. 11 Chemical structure of gPEO-*b*-gPMPC (a) and formation of the LAM structure of the gPEO-*b*-gPMPC/LiTFSI complex (b)

CONCLUSIONS AND OUTLOOK

A lot of work has been performed in the fundamental research of synthesis and self-assembly of MJLCP-based BCPs. The phase behaviors of MJLCP-based BCPs have been systematically studied, with a variety of nanostructures observed. Functional materials based on these BCPs have also been prepared, with their structure-property relationships explored. These BCPs are potentially useful as LCTPEs, SPEs, etc., owing to the unique rigid properties and the thermally stable LC phases of MJLCPs. However, there are still some questions and challenges remaining. Firstly, studies on the properties of functional materials based on MJLCP-containing BCPs are limited. Secondly, the systematic investigations on the relationships among the chemical structures, morphologies, and properties are yet to be conducted. Therefore, future work in this area should focus more on functionalities and applications of these materials.

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