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Introduction

Over the last thirty years, phase structures and transitions of side chain liquid crystalline polymers (SCLCPs) have been one of the important topics of study in polymer chemistry and physics, due to which SCLCPs have been designed and synthesized for their application potential in functional soft materials.¹⁻³ Therefore, researchers have focused on investigating the structure-property relationship of SCLCPs in order to understand the principles of structure formation and structure manipulation.⁴⁻⁹ Usually, SCLCPs are composed of four distinct structural components: the backbone, the flexible spacer, the mesogenic group and the terminal substituent.¹⁰ Moreover, much work in the literature has focused on the behavior of discotic liquid crystals (DLCs) since the discovery of DLCs by Chandrasekhar in 1977.¹¹⁻¹³

DLC materials are capable of self-assembling into wellordered supramolecular structures because of the π - π stacking

Design, synthesis, and phase behaviors of a novel triphenylene-based side chain liquid crystalline diblock copolymer

Jianfeng Ban, 🕩 *^a Lulu Pan, ^a Bo Shi^a and Hailiang Zhang^b

A novel double Tp-based liquid crystalline (LC) diblock copolymer (PMTS-*b*-PMT6S) composed of poly[3,6,7,10,11-pentakis (hexyloxy)-2-oxytriphenylene] (PMTS) and poly{6-[3,6,7,10,11-pentakis(hexyloxy)-2-oxytriphenylene] (PMT6S) was designed and successfully synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization. While PMTS is a rigid columnar-shaped (ϕ_{N}) polymer, PMT6S is a stable hexagonal columnar phase (ϕ_{H}) polymer. The phase behaviors of diblock copolymers were studied by DSC, POM and 1D WAXD. The results showed that the weight fraction of PMT6S (f_{PMT6S}) has a significant effect on the LC phase behaviors and phase structures of diblock copolymers. Both glass transition temperature and phase transition temperature of the diblock copolymers from LC phase to isotropic phase reduced with the weight fraction of PMT6S in the feed. When the $f_{PMT6S} \leq 58.1\%$, PMTS-*b*-PMT6S-1 to PMT5-*b*-PMT6S-3 show similar properties to PMT5, which formed a stable columnar nematic phase (ϕ_{N}), while when the $f_{PMT6S} \geq 64.2\%$, PMTS-*b*-PMT6S-4 and PMTS-*b*-PMT6S-5 show similar properties to PMT6S, which presented a hexagonal symmetry columnar phase (ϕ_{H}). Comparison between the diblock copolymer and homopolymer (PMTS and PMT6S) indicates that the content of the spacer was crucial to determine the LC structures. Through the study one can better understand the interrelation of microstructures and Tp DLC orders, which constitutes the key basis for various applications.

of the planar aromatic cores. Thus, they can be applied in organic semiconductors, superconducting materials, optical compensation films, one-dimensional conductors, photovoltaic solar cells, etc.¹⁴⁻¹⁷ Therefore, DLC materials have attracted great attention from researchers. Among DLC materials, the phase behavior and phase structure of SCLCPs containing triphenylene (Tp) derivatives with a long flexible spacer as linkers have been widely investigated, not only because of their relatively easy synthesis and thermal and chemical stability, but also because of the varieties of mesophases.¹⁸⁻²⁰ Meanwhile, our group have investigated the structure-property relationship of SCLCPs containing Tp (PBTCS) to understand the principles of structure formation and structure manipulation.²¹ The results indicated that PBTCS has a relatively high glass transition temperature and forms a higher symmetry hexagonal columnar phase ($\Phi_{\rm H}$) due to the strong "jacketing effect" between Tp and the MJLCP main chain.

On the other hand, the phase behavior of SCLCPs can be tailored not only by changing the chemical structure, but also by changing the external conditions. For example, copolymerization²² represents the simplest synthetic technique, which can be used to tailor the phase behavior of SCLCPs and broaden their application range as high-performance materials. For example, Tang *et al.* have reported that 2,5-di(*n*-butoxycarbonyl)styrene was employed

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^a College of Chemical Engineering, Guangdong University of Petrochemical Technology, Maoming, 525000, China. E-mail: banban997@sina.com

^b Key Laboratory of Polymeric Materials and Application Technology of Hunan Province, Key Laboratory of Advanced Functional Polymer Materials of Colleges and Universities of Hunan Province, College of Chemistry, Xiangtan University, Xiangtan, Hunan Province, 411105, China

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to tailor the mesomorphic property of PMPCS by random radical polymerization.²² Percec and Lee have systematically studied the influence of the length of the flexible spacer on the phase behavior of poly(x-[4-cyano-40-biphenylyl)oxy]alkylvinyl ethers and copolymers, in which the mesogenic units were identical but the spacer lengths were varied.^{23,24} By using the reversible addition-fragmentation chain transfer (RAFT) polymerization method, Y. Zhao et al. have synthesized a diblock polymer bearing two different mesogenic groups of azobenzene and biphenyl.²⁵ Although several double LC diblock copolymers have been reported, the precise control of the chemical structure and composition still remains a challenge. Therefore, the understanding of the phase behavior of such double LC diblock copolymers at different length scales is rather limited, and double Tp based diblock copolymers are unknown according to our knowledge. Thus, through studying double Tp based diblock copolymers, it is expected that the combination of microphase separation and LC can lead to new materials with superior properties, which meet the requirements for practical application.

In our previous work, we systematically studied the phase behavior of side-chain liquid crystalline polymers containing Tp discotic mesogen units, including the influence of the spacer and molecular weight on the phase behavior (PMTS and PMT6S),²⁶ the effect of different length flexible spacers on the self-organization of PMTnS,²⁷ and the effect of spacer on the phase behavior of poly(MTSx-co-MT6Sy) copolymers.²⁸ From our experimental results, the LC phase structures of PMTS were found to be strongly dependent on M_n , but PMT6S was independent of $M_{\rm n}$. The length of spacer has significant effects on the LC phase behavior of PMTnS. The content of PMT6S has significant effects on the LC phase behavior and phase structures of poly(MTSx-co-MT6Sy). According to our experimental results, we have proved that PMTS formed a stable columnar nematic phase (Φ_N) due to the bulky rigid side chains of Tp wrapped around the main chain and the whole rigid columnar shaped molecule of PMTS acts as a building block for the LC phase. PMT6S exhibited a stable hexagonal columnar phase ($\Phi_{\rm H}$) due to the decoupling and self-organization of Tp moieties. Also, the comparison between PMTS and PMT6S indicates that the length of the spacer was crucial to determine the LC structures.

In this work, a novel series of Tp-based side chain liquid crystalline diblock copolymers (PMTS-*b*-PMT6S) were for the first time synthesized *via* reversible addition–fragmentation chain transfer polymerization (RAFT). According to our previous work, we found that PMTS-*b*-PMT6S was composed of the rigid columnar-shaped molecules of PMTS and PMT6S with a stable hexagonal columnar phase ($\Phi_{\rm H}$), owing to the decoupling and self-organization of the Tp moieties (see Scheme 1). This research would help us to deeply understand the interrelation between Tp mesogenic orders and overall morphological structures. Also, it can contribute to our knowledge of the phase behaviors and provide information about the structure variation of the Tp-based diblock copolymers, which will be useful for fundamental research and real applications.



Scheme 1 The model for PMTS-b-PMT6S.

Experimental

Materials

Anhydrous tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon and used immediately. Triethylamine (TEA) and dichloromethane (CH_2Cl_2) were dried over anhydrous magnesium sulfate. 2,2-Azobisisobutyronitrile (AIBN) was freshly recrystallized from methanol. Chlorobenzene (Acros, 99%) was purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing first with 5% sodium carbonate solution and then with water before it was dried with anhydrous calcium chloride and distilled. All other reagents and solvents were used without further purification.

Instruments and measurements

All NMR measurements were performed on a Bruker ARX400 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard at ambient temperature. The chemical shifts were reported on the ppm scale.

The apparent number average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) were measured on a GPC (WATERS 1515) instrument with a set of HT3, HT4 and HT5. The μ -styragel columns used THF as an eluent and the flow rate was 1.0 mL min⁻¹ at 38 °C. The GPC data were calibrated with polystyrene standards.

TGA was performed on a TA SDT 2960 instrument at a heating rate of 20 $^{\circ}$ C min⁻¹ in a nitrogen atmosphere.

DSC traces of the polymer were obtained using a TA Q10 DSC instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at cooling and heating rates of 10 $^{\circ}$ C min⁻¹. The sample with a typical mass of about 5 mg was encapsulated in sealed aluminum pans.

The LC texture of the polymer was examined under a POM (Leica DM-LM-P) equipped with a Mettler Toledo hot stage (FP82HT).

One-dimensional wide-angle X-ray diffraction (1D WAXD) experiments were performed on a BRUKER AXS D8 Advance diffractometer with 40 kV FL tubes as the X-ray source (Cu K α) and the LYNXEYE_XE detector. Background scattering was recorded and subtracted from the sample patterns. The heating and cooling rates in the 1D WAXD experiments were 10 °C min⁻¹.

Synthesis of monomers

The precursor 2-hydroxyl-3,6,7,10,11-pentakis(hexyloxy)triphenylene (PHT) and the two monomers, [3,6,7,10,11-pentakis(hexyloxy)-2-oxytriphenylene]methacrylate (MTS) and 6-[3,6,7,10,11-pentakis-(hexyloxy)-2-oxytriphenylene]hexyl methacrylate (MT6S), were



Scheme 2 The chemical structures of MTS and MT6S

easy to synthesize and purify following the procedures reported in our previous work.²¹ The chemical structures of the monomers were confirmed by 1 H/ 13 C NMR and Mass Spectrometry (MS) as in the previous work. The chemical structures of MTS and MT6S are shown in Scheme 2.

Synthesis of the chain transfer agent

The chain transfer agent 2-(2-cyanopropyl)dithiobenzoate (CPDB) was easy to synthesize following the procedure described by Winnik.²⁹ The procedures and chemical structures of CPDB are shown in Scheme 3. ¹H NMR (CDCl₃): 7.87–7.93 (d, 2H, $-C_6H_4$), 7.50–7.62 (m, 1H, $-C_6H_4$), 7.28–7.42 (m, 2H, $-C_6H_4$), 1.91–1.93 (s, 6H, -CH).

Synthesis of the diblock copolymer

The synthetic route toward PMTS-*b*-PMT6S is described in Scheme 4. To prepare the first block, macromolecular CTA



Scheme 3 Synthetic route toward CBDP.



Scheme 4 Synthetic route towards PMTS-b-PMT6S.

(PMTS-CTA): AIBN, CPDB and MTS were added to a reaction tube strictly in the ratio of 1/4:1:*m* (*m* = 30, which is the polymerization degree of PMTS), followed by the addition of 3 mL of THF. After being degassed with three freeze-thaw cycles, the tube was sealed under vacuum. The polymerization was carried out at 75 °C for 6 h. Then, the reaction solution was diluted with dichloromethane (10 mL) and dripped into methanol (400 mL). The polymer precipitate was further purified by repeated dissolution in dichloromethane and precipitation in methanol three times. The obtained PMTS-CTA was dried in a vacuum oven at 35 °C for 20 h before use. The gel permeation chromatography (GPC) measurement indicated that PMTS-CTA possessed a low polydispersity index (PDI) of 1.19 and an apparent number-average M_n of 1.69 × 10⁴ g mol⁻¹.

The target diblock copolymer (PMTS-*b*-PMT6S) was synthesized through the RAFT chain extension reaction using PMTS-CTA. Typically, AIBN, PMTS-CTA and MT6S were added to a reaction tube strictly in the ratio of 1/4:1:n (*n* is the polymerization degree of the PMT6S segment in block copolymers), followed by the addition of 3 mL of THF. The polymerization conditions and the purification procedure were the same as that used for the synthesis of PMTS-CTA. To eliminate the unreacted monomers completely, the purification was repeated three times, until no peak was observed at the elution time of the monomers in gel permeation chromatography (GPC) measurements. After purification, the moist copolymers were dryed at 50 °C under vacuum for 20 h. And then, the target diblock copolymers of PMTS-*b*-PMT6S were obtained.

Results and discussion

Synthesis and characterization of PMTS-CTA and PMTS-*b*-PMT6S

Although it has been reported that the atom-transfer radical polymerization (ATRP) method can readily synthesize some homopolymers, our attempts at using ATRP to synthesize the diblock copolymers of PMTS-*b*-PMT6S failed. Then, we found that the RAFT method was a versatile and facile way to prepare the diblock.

This is the first time that the RAFT method has been applied to obtain Tp mesogen based diblock copolymers. The diblock copolymers of MTS and MT6S in chlorobenzene were studied at different monomer to monomer ratios in the feed. As shown in Fig. 1, the GPC trace of the resultant PMTS-CTA and PMTS-*b*-PMT6S is unimodal with a fairly narrow M_w distribution (PDI \leq 1.4). Table 1 summarizes the copolymerization results of PMTS-*b*-PMT6S. As we predicted, with the increase in the polymerization degree of PMT6S (*n*) from 10 to 100, the molecular weights of the diblock copolymers gradually increased, which indicates that a series of diblock copolymers PMTS-*b*-PMT6S with different molecular weights were successful synthesized.

Fig. 2 provides the ¹H NMR spectra of PMTS-CTA and PMTS*b*-PMT6S, wherein the assignments of resonance peaks are included. According to the result, the signals attributed to the PMT6S block superimpose on the spectrum of PMTS after the



Fig. 1 GPC traces of PMTS-CTA and the corresponding diblock copolymers PMTS-*b*-PMT6S.

 Table 1
 The properties of the macromolecular initiator and the diblock copolymers

Sample	$M_{\mathrm{n}}^{\ a} \left(imes 10^{-4} ight)$	n	PDI ^a	$f_{\rm PMT6S}{}^{b}$ (%)
PMTS-CTA	1.69	_	1.19	_
PMTS-b-PMT6S-1	1.94	10	1.28	10.8
PMTS-b-PMT6S-2	2.79	30	1.35	32.9
PMTS-b-PMT6S-3	4.32	50	1.33	58.1
PMTS-b-PMT6S-4	5.36	70	1.40	64.2
PMTS-b-PMT6S-5	8.22	100	1.38	80.6

 a Obtained from Waters 1515 instrument, linear PS as standards. b Calculated from eqn (1) according to the peaks $I_{\rm c}$ and $I_{\rm f}$ of ¹H NMR.



RAFT chain extension reaction. On the basis of the spectrum of the diblock copolymers, the weight fraction of the PMT6S block (f_{PMT6S}) can be estimated according to

$$f_{\rm MT6S} = \frac{913 \times I_{\rm c}}{913 \times I_{\rm c} + 813 \times I_{\rm f}}$$
(1)

where 813 and 913 is the molecular weight of the repeating units MTS and MT6S respectively. I_c represents the integral intensities of PMTS and PMT6S that belong to the Tp mesogen, and the signals at 8.13 ppm (peak a) and 7.79–7.91 ppm (peak b) are shown in Fig. 2. I_f represents the integral intensities of PMTS and PMT6S that belong to the methoxy group, and the signals at 4.22 ppm (peak c) and 1.57–1.91 ppm (peaks d, e) are shown in Fig. 2. The calculation results are shown in Table 1.

Phase transitions and phase structures of PMTS-CTA

Fig. 3 depicts the DSC thermograms of PMTS-CTA recorded during cooling and subsequent heating at a rate of 10 $^\circ C$ min $^{-1}$





under a nitrogen atmosphere after eliminating the thermal history. In our previous studies, we had particularly researched the phase behaviors of PMTS and confirmed that only the $T_{\rm g}$ can be detected for PMTS.²¹ As can be seen in Fig. 3, PMTS-CTA shows a single glass transition temperature, indicating that PMTS-CTA is homogeneous to PMTS, similar to mesogen-jacketed liquid crystalline polymers (MJLCPs).^{30,31} It illustrated that the liquid crystalline properties of PMTS-CTA were maintained after introducing a disulfide ester in the end group.

Polarized optical microscopy (POM) experiments further confirmed the DSC results. Thin films of the copolymers were prepared by the CH2Cl2 solution-cast method on clean cover glass, followed by drying slowly at room temperature. To maintain consistency with the DSC results, the samples were heated to the same high temperature (190 °C), and then slowly cooled to room temperature. The POM experimental results also show that PMTS-CTA is similar to PMTS,^{21,26-28} and forms a colorful LC texture at room temperature. When slowly heated to 80 °C, PMTS-CTA became soft and maintained the colorful LC texture (Fig. 4). During the heating procedure, the samples maintained zero birefringence until over 117 °C. During cooling from 117 °C, no LC textures were observed again at low temperature. This phenomenon was attributed to the fact that the backbone was compelled to stretch to a great extent, in order to minimize the torque arising from the rigid side chains of Tp DLCs. Thus the bulky side chain will be wrapped around the main chain.



Fig. 4 POM images of the texture of PMTS-CTA at 95 °C (200×).

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Fig. 5 1D WAXD patterns of PMTS-CTA during the second heating

We further performed the 1D WAXD thermal experiment of PMTS-CTA to verify the LC phase transitions, and the results are plotted in Fig. 5. 1D WAXD experimental results showed that at low temperature, for example, at 30 °C, only one sharp peak was in the low-angle region, $2\theta = 4.76^{\circ}$ (d = 1.86 nm), indicating the existence of an ordered structure, similar to PMTS, which can be identified as a Φ_N phase developed by the main chain and Tp as a whole.²⁶⁻²⁸ Meanwhile, in the wideangle region, two amorphous halos were found at 2θ values of $\sim 20.4^{\circ}$ (d = 0.44 nm) and $\sim 25.4^{\circ}$ (d = 0.35 nm) which represent the characteristic dimensions of the amorphous packing of the alkyl chains and the π - π stacking in a discotic LC column.³²⁻³⁴ On heating to 130 °C, two amorphous halos were formed located in the low-angle region near 5° and the wide-angle region around 22°, indicating that PMTS-CTA entered an amorphous state, which identified with the DSC and POM result.

Thermal and liquid crystalline properties of PMTS-b-PMT6S

The thermal stability and liquid crystalline properties of PMTSb-PMT6S were investigated by TGA, DSC and POM. The thermal stability is an important property for potential applications. As can be seen in Fig. 6, the TGA test results revealed that PMTS-CTA and PMTS-b-PMT6S showed good thermal stability, with almost no weight loss at temperatures as high as 375 °C. The dependence of the thermal transition temperatures on the



Fig. 6 TGA thermograms of PMTA-CTA and PMTS-b-PMT6S.



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Fig. 7 DSC curves of PMTS-b-PMT6S during the second heating process.

compositions of PMTS-b-PMT6S was studied by DSC experiments. Fig. 7 shows the second heating DSC curves of PMTS-b-PMT6S at a rate of 10 °C min⁻¹ under a nitrogen atmosphere after eliminating the thermal history. In our previous studies, the phase behaviors of PMTS and PMT6S had been particularly researched, and the experimental results showed that only $T_{\rm g}$ can be detected for PMTS. Meanwhile, both T_g and T_i can be detected from PMT6S. The values of transition temperatures of PMTS-b-PMT6S are summarized in Table 2. As can be seen in Fig. 7, each diblock copolymer showed a single glass transition temperature, indicating that the PMTS-b-PMT6S copolymers were homogeneous. From the transitional phenomenon of the diblock copolymers, PMTS-b-PMT6S could be divided into two types. The first type included PMTS-b-PMT6S-1 to PMTS-b-PMT6S-3, whose molar content of PMT6S (f_{PMT6S}) was below 64.2%. They were similar to PMTS, and showed only a glass-transition step but no endothermic peak correlating to a phase transition. Meanwhile, the second type included PMTS-b-PMT6S-4 and PMTS-b-PMT6S-5, whose molar content of PMT6S was above 64.2%. They were similar to PMT6S, where a glass-transition step and an endothermic peak were observed. From the combined POM and 1D WAXD results, this endothermic peak was attributed to transitions from LC phase to isotropic phase.³⁵ Meanwhile, with the increase in the molar content of PMT6S, the $T_{\rm g}$ decreased from 81 $^\circ {
m C}$ to 55 °C (see Table 2), indicating that the more flexible spacer (PMT6S) contained, the easier the formation of the" more stable hexagonal columnar phase.

Table 2 LC of PMTA-CTA and PMTS-b-PMT6S						
Sample	$T_{ m g}^{\ a}$ (°C)	T_{i}^{b} (°C)	$T_{\rm d}^{\ c} \left(^{\circ} {\rm C}\right)$	LC^b		
PMTS-CTA	117	186	378	Yes		
PMTS-b-PMT6S-1	81	116	379	Yes		
PMTS-b-PMT6S-2	70	94	377	Yes		
PMTS-b-PMT6S-3	64	91	380	Yes		
PMTS-b-PMT6S-4	56	88	379	Yes		
PMTS- <i>b</i> -PMT6S-5	55	87	382	Yes		

^a Evaluated by DSC during the second heating process at a rate of 10 °C min⁻¹ under a nitrogen atmosphere. ^{*b*} Evaluated by POM at a heating and cooling rate of 10 °C min⁻¹. ^{*c*} The temperatures at 5% weight loss of the samples under nitrogen $[T_d (N_2)]$ were measured by TGA heating experiments at a rate of 20 °C min-



Fig. 8 Representative POM images of the texture of PMTS-*b*-PMT6S-3 (a) and PMTS-*b*-PMT6S-5 (b) (200×).

Polarized optical microscopy (POM) experiments further confirmed the phase structures of PMTS-*b*-PMT6S and the DSC results. To be consistent with the DSC result (the second heating process), all the samples were heated to the same high temperature as in the DSC test, and then slowly cooled to room temperature. The POM test shows similar results to DSC in that PMTS-*b*-PMT6S could be divided into two different groups.

The first group comprised PMTS-*b*-PMT6S-1 to PMTS-*b*-PMT6S-3, with $f_{\rm PMT6S} \leq 58.1\%$, taking PMTS-*b*-PMT6S-3 as an example. As can be seen in Fig. 8a, PMTS-*b*-PMT6S-3 formed a colorful LC texture at room temperature. During the heating procedure, the diblock copolymer maintained zero birefringence until over 91 °C. During cooling from 91 °C to room temperature, no LC textures were observed again. This phenomenon was attributed to the following mechanism: when the molar content of PMT6S was below 58.1%, the diblock copolymer acted as PMTS forming a columnar nematic phase due to the strong coupling effect.

The second group comprised PMTS-b-PMT6S-4 and PMTS-b-PMT6S-5, with the $f_{PMT6S} \ge 64.2\%$, and showed similar results to PMT6S. Taking PMTS-b-PMT6S-5 as an example, as seen in Fig. 8b, PMTS-b-PMT6S-5 formed typical sand-shaped textures during slow heating, suggesting the formation of a columnar phase. Once the temperature reached 89 °C, the textures disappeared and the field of vision became dark, indicating that PMTS-b-PMT6S-5 entered into the isotropic state and a corresponding exothermic peak appeared in the DSC curve (Fig. 7). During cooling from 89 °C, the sandshaped textures were observed again at low temperature, and it was considered that the phase transitions of PMTS-b-PMT6S-5 followed the sequence of columnar phase \leftrightarrow isotropic phase. We attributed this phenomenon to the following: when the molar content of PMT6S was above 64.2%, the diblock copolymers showed the same properties as PMT6S, i.e., formed a hexagonal columnar phase owing to the decoupling and self-organization of the Tp moieties. The transition temperatures from LC phase to isotropic phase (measured by POM and DSC) are listed in Table 2. As can be seen in Fig. 9, the T_i and the T_g of the diblock copolymers decreased with the increase in the molar content of PMT6S.

Phase structure identification of the diblock copolymers

Temperature dependent 1D WAXD experiments were conducted to study the mesomorphic structure of the diblock copolymers. In 1D WAXD experiments, the sample consisted of about 50 mg





of the polymer, which was added into an aluminum foil substrate. To be consistent with the DSC and POM results, the sample was heated to the same high temperature as in the DSC and POM test, and then slowly cooled to room temperature. Based on the 1D WAXD observations, the diblock copolymers could be divided into two different phase structures, consistent with the POM and DSC results.

The first group comprised PMTS-*b*-PMT6S-1 to PMTS-*b*-PMT6S-3, which to some extent were similar to PMTS, which formed a stable $\Phi_{\rm N}$ phase just like many MJLCPS.³⁶ Taking PMTS-*b*-PMT6S-3 as an example, the 1D WAXD powder patterns of PMTS-*b*-PMT6S-3 during the second heating step are shown in Fig. 10a. It shows only one peak in the low-angle region, $2\theta = 4.86^{\circ}$ (d = 1.82 nm), indicating the existence of an ordered structure, which can be identified as a $\Phi_{\rm N}$ phase developed by the main chain and Tp as a whole. However, in the wide-angle region, at room temperature, two amorphous halos were found at 2θ values of ~ 20° (d = 0.44 nm) and ~ 25° (d = 0.36 nm), which represent the characteristic dimensions of the amorphous packing of the alkyl chains and the π - π stacking in a discotic LC column, respectively.³³ The samples for PMTS-*b*-PMT6S-1 and PMTS-*b*-PMT6S-2 showed similar results to PMTS-*b*-PMT6S-3.

The second group included PMTS-*b*-PMT6S-4 and PMTS*b*-PMT6S-5. When the weight fraction of the PMT6S block increased to 64.2%, the molecular packing model was changed. Our previous work has proved that PMT6S formed stable $\Phi_{\rm H}$ phases, and thus, we will not discuss the experimental



Fig. 10 1D WAXD patterns of PMTS-*b*-PMT6S-3 (a) and PMTS-*b*-PMT6S-5 (b) during the second heating process.

results again. The 1D WAXD powder patterns of PMTS-b-PMT6S-5 during the second heating step are shown in Fig. 10b. As can be seen in Fig. 10b, only one peak at $2\theta = 4.73^{\circ}$ (d = 1.87 nm) is seen in the low-angle region below 50 °C, indicating the existence of an ordered structure, and was identified as a $\Phi_{\rm N}$ phase. After the temperature increased over 60 °C, two diffraction peaks in the low-angle region at $2\theta = 4.73^{\circ}$ (d = 1.87 nm) and 8.14° (d = 1.09 nm) were detected. The *d*-spacing values derived from these two peaks have the typical ratio of the q values of $1:3^{1/2}$ and the two peaks can be assigned to (100) and (110) diffractions, similar to PMT6S and demonstrating a long-range ordered hexagonal lattice ($\Phi_{\rm H}$) with a = b = 2.18 nm and $\gamma = 120^{\circ}$. Due to the thermal expansion, these two diffraction peak positions slightly shift to a low angle with the increase in temperature. Meanwhile, as with the first group, two peaks are found in the wide-angle region, because the two peaks belong to amorphous packing of the alkyl chains $(2\theta = 20^\circ)$ and π - π stacking of Tp $(2\theta = 25^{\circ})$. According to the previous work, we found PMT6S with a = b = 2.21 nm; however, the column diameter of the second group which includes PMTS-*b*-PMT6S-4 (a = b = 2.17 nm) and PMTS-*b*-PMT6S-5 (a = b = 2.18 nm) is smaller. This phenomenon was attributed to the fact that the activity of the PMT6S chain was limited after copolymerization, and thus, the Tp unit in the diblock copolymers was not as free as in PMT6S. Consequently, when the order structures reduced, the intensity of the diffraction peaks of the π - π stacking of Tp weakened, compared with PMT6S. Also, the 1D WAXD patterns (at room temperature) for diblock copolymers were used to calculate the diameter of the column, and the results are listed in Table 3. As can be seen in Table 3, with the increase in the molar content of PMT6S the diameter of the column increased from 1.76 nm to 1.84 nm.

From the DSC, POM and 1D WAXD test results, based on the study of the liquid crystal restricted behavior of PMTS-*b*-PMT6S, we found that the diblock copolymers exhibit two different stabilized phase structures. As shown in Fig. 11, the diblock copolymers showed similar properties to PMTS; when the weight fraction of the PMT6S block (f_{PMT6S}) was below 58.1%, PMTS-*b*-PMT6S-1 to PMTS-*b*-PMT6S-3 showed similar properties to PMTS. They had only a single glass transition temperature according to the DSC test. From this result, we considered that the movement of the PMT6S chain was limited by the rigid PMTS, when the diblock copolymers had a low weight fraction of the PMT6S block. Thus, the diblock copolymers acted as PMTS; the packing model of the columns and molecular dynamics simulation results of the diblock copolymers are shown in Fig. 11a. The polymethylacrylic acid main chain and

Table 3The 2θ d-spacing values of PMTS-b-PMT6S					
Sample	$2 heta^a (^\circ)$	d_{100}^{a} (nm)			
PMTS-b-PMT6S-1	4.99	1.76			
PMTS-b-PMT6S-2	4.94	1.78			
PMTS-b-PMT6S-3	4.86	1.82			
PMTS-b-PMT6S-4	4.80	1.84			
PMTS-b-PMT6S-5	4.73	1.87			

^a Obtained from one-dimensional WAXD experiments.



the Tp DLC side chains wrapped around the main chain to form stable $\Phi_{\rm N}$. When the weight fraction of the PMT6S block increased to 64.2%, PMTS-*b*-PMT6S-4 and PMTS-*b*-PMT6S-5 were similar to PMT6S, and formed stable $\Phi_{\rm H}$ based on the self-organization of Tp, as shown in Fig. 11b. Meanwhile, the column diameter was smaller than that of PMT6S, which was identified from all the test results. The reason for this phenomenon is unknown at the moment, but we suspect that it is attributed to the both intramolecular and intermolecular interactions.

Conclusions

This is the first time that a Tp based liquid crystalline diblock copolymer PMTS-b-PMT6S was designed and successfully synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. The phase behaviors of the PMTS-CTA and PMTS-b-PMT6S were studied by TGA, DSC, POM and 1D WAXD. The thermal analysis showed that all diblock copolymers had only a single glass transition temperature, indicating a homogeneous microstructure of the main chain. The phase behaviors of diblock copolymers were dependent on the weight fraction of PMT6S in diblock copolymers. When the weight fraction of PMT6S was below 58.1%, the diblock copolymers formed stable $\Phi_{\rm N}$, similar to PMTS. However, the diblock copolymers with a weight fraction of PMT6S above 64.2% were similar to PMT6S, presenting $\Phi_{\rm H}$ symmetry. It was considered that the formation mechanism of the two different phase behaviors depended on the quantity of the spacer. Meanwhile, the column diameter of PMTS-b-PMT6S-4 and PMTS-b-PMT6S-5 was smaller than that of PMT6S, suggesting that the diblock copolymers can provide new functional materials with fine-tuned ordered structures. The study of the phase behaviors of these novel Tp DLC diblock copolymers will be useful for fundamental research and real applications.

Conflicts of interest

There are no conflicts to declare.

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