

Multiple Effects Tailoring the Self-organization Behaviors of Triphenylene Side-chain Liquid Crystalline Polymers *via* Changing the Spacer Length

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Abstract Long-alkyl tail triphenylene (TP) side-chain liquid crystalline polymers (SCLCPs) with different spacer length (P-*m*-TP, *m* = 2, 3, 4, 6, 8, which is the number of carbon atom in the flexible alkyl spacers) have been successfully synthesized *via* free radical polymerization. The differential scanning calorimetry (DSC), polarized light microscopy (POM), ultraviolet-visible spectroscopy (UV-Vis), wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) measurements were performed to investigate the influence of multiple effects on the self-organization behaviors of P-*m*-TP, including steric effect, decoupling effect and π - π stacking effect. The experimental results revealed that P-*m*-TP (*m* = 2, 3, 4) formed the columnar phase which was developed by the TP moieties and the main chain as a whole, suggesting that the side-chains had strong steric effect even though the number of spacer length (*m*) exceeded 4. In addition, the clearing points (*T*_{is}) of the polymers were above 300 °C. When *m* = 6 and 8, the polymers displayed hexagonal columnar phase and exhibited the low *T*_{is} (91 and 80 °C respectively), originating from the self-assembly of triphenylene due to the decoupling effect and π - π stacking effect. This work offers a viable and inspiring pathway to control the phase transition temperature and phase structure of TP SCLCPs *via* simply tailoring the spacer length and increasing the alkyl tail length of TP.

Keywords Polymer synthesis; Side-chain liquid crystalline polymers; Phase structure; Steric effect

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INTRODUCTION

Side-chain liquid crystalline polymers (SCLCPs) provide possibilities to construct high-performance liquid crystal materials, which is due to the combination of ordered structures of liquid crystals and excellent properties of polymers^[1–6]. Usually, SCLCPs comprise four parts, including main-chain, mesogen, spacer and tail *etc.* The phase behaviors and phase structures of SCLCPs can be tailored by changing the chemical structures to meet the practical demands. However, the investigation of mesogen units was mostly concentrated on calamitic mesogens, such as biphenyl, azobenzene, cholesterol derivatives and so on^[7–12]. In recent years, many other kinds of mesogens have been introduced to SCLCPs, for example, dendritic mesogens, hemiphasmidic mesogens and discotic mesogens^[13–19]. Among them, discotic SCLCPs have attracted great attention since discotic liquid crystals (DLCs) were firstly discovered by Chandrasekhar in 1977^[20–22]. Due to the large π -orbital overlap between adjacent molecules, DLCs can self-assemble into well-ordered supramolecular

structures and show excellent 1D charge-transport property with a high value of charge carrier mobility. It can be used as organic materials, such as organic photovoltaics and one-dimensional conductors^[23–28]. Compared with traditional calamitic SCLCPs, discotic SCLCPs exhibit unique phase behavior and phase structures^[29, 30]. Finkelmann *et al.* reported that the tendency of statistical chain conformation impeded the orientation of side-chains in the liquid state of polymer. Therefore, decoupling concept was proposed by Finkelmann, which indicated that the flexible spacers should be purposefully added to decouple the dynamics of the main-chain and the mesogenic side groups in order to obtain liquid crystalline phase^[31]. Recently, the increasing research results showed that decoupling concept was not appropriate to explain the unusual phenomenon in discotic SCLCPs systems. For instance, Chen *et al.* reported that the positive coupling effect (proper coupling between discotic side groups and main-chain) was meaningful to achieve well-organized ordered columnar mesophases^[29]. Therefore, it is necessary to further comprehend the structure-property relationship of discotic SCLCPs in order to provide the theoretical guidance for various promising applications^[32–35].

Similar to the mesogen jacketed liquid crystalline polymers (MJLCPs)^[36–43], the triphenylene (TP) SCLCPs possess the “jacket effect” because of the huge chemical

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structure volume resulting from the aromatic core and peripheral chains^[44, 45]. Yu *et al.* revealed that a variety of liquid crystalline polyacetylenes with TP mesogens linked by one or three alkyl spacer could adopt the columnar shaped structure owing to the side-chain of triphenylenes wrapped around the main-chain, which resulted in the formation of hexagonally packed columnar phase^[44]. Our group has studied the influence of main-chain on the phase structures and phase behaviors of long alkyl tail TP SCLCPs without flexible spacer^[46]. The experimental results indicated that all the polymers showed MJLCPs' properties, originating from the strong steric effect of long alkyl tail TP and the strong coupling effects between the main-chain and the TP mesogens.

According to the literature, TP SCLCPs can self-organize into well-ordered and self-healable supramolecular columns due to the π - π stacking of planar aromatic cores when the spacer length is long. However, when the spacer length is short, TP SCLCPs will form the variable liquid crystalline phase structure, which is attributed to the competition between " π - π stacking effect" and "steric effect". Nevertheless, there are few reports to systematically study the competitive effect on the phase structures of TP SCLCPs.

In this work, a series of long-alkyl TP SCLCPs with different spacer length ($m = 2, 3, 4, 6$ and 8), denoted as P- m -TP, were synthesized. The influence of spacer length on the steric effect, decoupling effect and π - π stacking effect was systematically investigated. To learn more information on the phase behaviors and phase structures of polymers, DSC, POM, 1D WXR and SAXS measurements were performed. The experimental results implied that the phase behaviors and structures of polymers were closely related to the spacer length. Firstly, TP side-chain presented the strong steric effect even though the spacer length was long. When $m = 2, 3$ and 4 , the polymers displayed a stable columnar phase with clearing point (T_i) above $300\text{ }^\circ\text{C}$. Secondly, when

$m = 2$ and 4 , the polymers exhibited two different phase structures with the increase of temperature. They formed rectangular column (Φ_R) phase at low temperature, while the nematic columnar (Φ_N) phase was observed at high temperature. For P-3-TP, it showed the nematic columnar (Φ_N) phase at whole LC temperature range. Lastly, P-6-TP and P-8-TP both formed hexagonal columnar (Φ_H) phase *via* the stacking of TP moieties. The T_i was 91 and $80\text{ }^\circ\text{C}$, respectively.

EXPERIMENTAL

General Considerations

Methacrylic acid, 1,2-dihydroxybenzene, 1-bromohexadecane, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane and 1,8-dibromooctane were purchased from Aladdin Shang Hai, China. 2,2-Azobisisobutyronitrile (AIBN) was refined by recrystallized from methanol. *N,N*-dimethylformamide (DMF), K_2CO_3 and KHCO_3 were obtained from related companies and were used without further purification.

Synthesis of Monomers

The chemical structures and synthetic procedures of monomers are demonstrated in Fig. 1. The monomers were synthesized by the similar method and were named as Mv- m -TP for convenience ($m = 2, 3, 4, 6, 8$), where m represented the spacer length of corresponding monomers. Taking Mv-6-TP as an example, the detailed synthetic procedure of monomers is given as follows.

2-(6-Bromohexyloxy)-3,6,7,10,11-pentakis(hexadecyloxy)triphenylene

2-Hydroxy-3,6,7,10,11-pentakis(hexadecyloxy)triphenylene (1.0 g , 0.69 mmol), K_2CO_3 (2.4 g , 2.76 mmol) and dried acetone (200 mL) were added into 500 mL round-bottom flask, and then the mixed solution was stirred at room temperature for 0.5 h . Next, 1,6-dibromohexane (10 mL) and

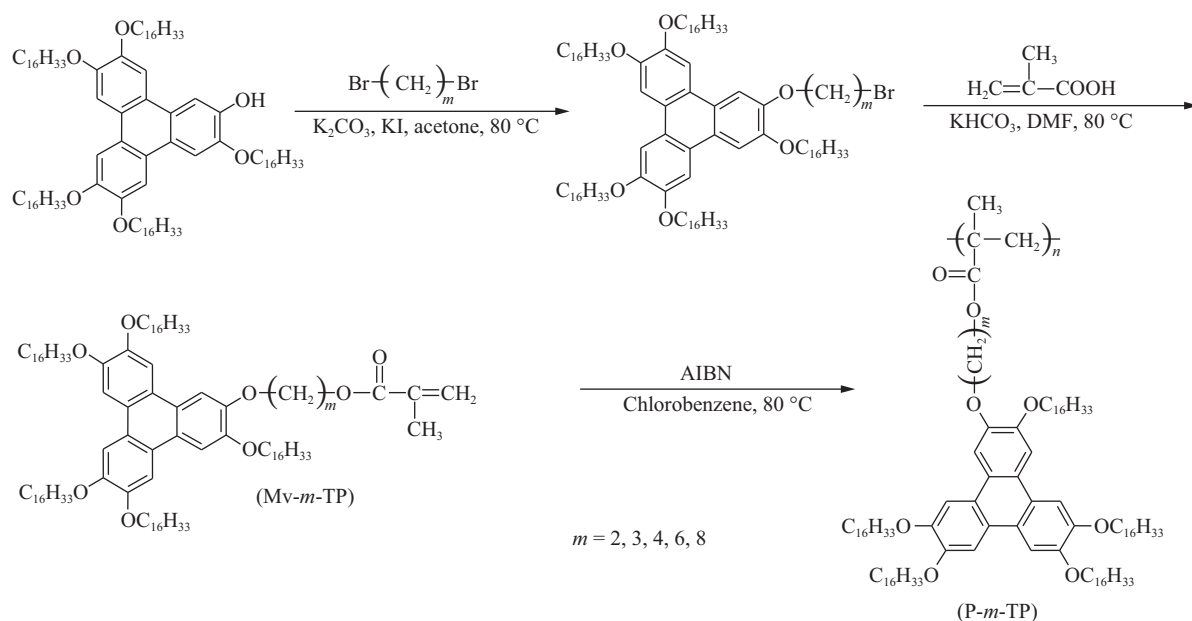


Fig. 1 Synthetic route to monomers (Mv- m -TP) and polymers (P- m -TP)

KI (0.3 g, 1.8 mmol) were slowly added into the solution. The reaction mixture was continually stirred at 80 °C for 12 h under nitrogen. After cooling to room temperature, the mixture was filtered to remove the insoluble salt. The product was purified by precipitation of the crude filtrate in 500 mL of methyl alcohol. The final product of 2-(6-bromohexyloxy)-3,6,7,10,11-pentakis(hexadecyloxy) triphenylene was obtained as a yellow solid.

6-[3,6,7,10,11-Pentakis(hexadecyloxy)-2-oxytriphenylene] hexyl methacrylate (Mv-6-TP)

Methacrylic acid (3 mL, 36 mmol) and KHCO₃ (3.6 g, 36 mmol) were dissolved in 100 mL of DMF and stirred for 0.5 h at room temperature. Then, 2-(6-bromohexyloxy)-3,6,7,10,11-pentakis(hexadecyloxy) triphenylene (0.8 g, 0.5 mmol) was added into the mixed solution. The solution was stirred for another 12 h under reflux at nitrogen atmosphere. The yellow crude product was obtained by filtration and purified by column chromatography on silica gel with ethyl acetate and petroleum ether ($V_1:V_2 = 7:500$) as an eluent. The characterization data of the monomer are given as follows (Fig. 2D). Yield: 52%. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 7.77 (d, 6H, Ar-H); 6.14 (s, 1H, =CH₂); 5.59 (s, 1H, =CH₂); 4.41–4.17 (m, 14H, –OCH₂–); 2.03–1.92 (m, 3H, =C–CH₃); 1.61 (m, 10H, –CH₂–); 1.58–1.25 (m, 136H, –CH₂–); 0.88 (t, 15H, –CH₃). Mass spectrometry (MS) (m/z) [M] Calcd. for C₁₀₈H₁₈₈O₇, 1613.34; Found, 1613.852.

m-[3,6,7,10,11-Pentakis(hexadecyloxy)-2-oxytriphenylene] alkyl methacrylate (Mv-m-TP) (m = 2, 3, 4, 8)

Other monomers were synthesized in a similar way. The characterization data of Mv-*m*-TP ($m = 2, 3, 4, 8$) are given as follows.

Mv-2-TP: Yield: 45%. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 7.95–7.83 (t, 6H, Ar-H); 6.17 (s, 1H, =CH₂); 5.57 (s, 1H, =CH₂); 4.62–4.21 (m, 14H, –OCH₂–); 2.17 (s, 3H, =C–CH₃); 1.96 (t, 10H, –CH₂–); 1.55 (m, 10H, –CH₂–); 1.41–1.23 (m, 120H, –CH₂–); 0.88 (t, 15H, –CH₃). Mass spectrometry (MS) (m/z) [M] Calcd. for C₁₀₄H₁₈₀O₇, 1557.34; Found, 1557.724.

Mv-3-TP: Yield: 40%. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 7.86 (d, 6H, Ar-H); 6.13 (s, 1H, =CH₂); 5.56 (s, 1H, =CH₂); 4.47–4.21 (m, 14H, –OCH₂–); 2.13 (s, 3H, =C–CH₃); 1.96 (t, 2H, –CH₂–); 1.54–1.26 (m, 140H, –CH₂–); 0.88 (t, 15H, –CH₃). Mass spectrometry (MS) (m/z) [M] Calcd. for C₁₀₅H₁₈₂O₇, 1572.34; Found, 1571.861.

Mv-4-TP: Yield: 58%. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 7.83 (s, 6H, Ar-H); 6.10 (s, 1H, =CH₂); 5.53 (s, 1H, =CH₂); 4.26–4.15 (m, 14H, –OCH₂–); 1.93 (m, 3H, =C–CH₃); 1.55 (m, 14H, –CH₂–); 1.41–1.23 (m, 130H, –CH₂–); 0.87 (t, 15H, –CH₃). Mass spectrometry (MS) (m/z) [M] Calcd. for C₁₀₆H₁₈₄O₇, 1586.34; Found, 1585.884.

Mv-8-TP: Yield: 52%. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 7.83 (s, 6H, Ar-H); 6.09 (s, 1H, =CH₂); 5.54 (s, 1H, =CH₂); 4.22–4.15 (m, 14H, –OCH₂–); 1.97–1.90 (m, 3H, =C–CH₃); 1.69–1.53 (m, 14H, –CH₂–); 1.41–1.25 (m, 138H, –CH₂–); 0.87 (t, 15H, –CH₃). Mass spectrometry (MS) (m/z) [M] Calcd. for C₁₁₀H₁₉₂O₇, 1641.34; Found, 1641.852.

Polymerization

As shown in Fig. 1, P-*m*-TP can be easily obtained by solution radical polymerization. Typical procedure for the polymerization is given as follows. Monomer Mv-6-TP, refined chlorobenzene (0.3 mL) and AIBN (molar ratio of $N_{\text{monomer}}:N_{\text{AIBN}} = 100:1$) were put into a dried reaction tube with a magnetic stirrer bar. After three freeze-pump-thaw cycles, the tube was sealed off under vacuum. Polymerization was carried out at 80 °C for 24 h. The reaction tube was open and the polymer solution was diluted with 10 mL of THF. Then the mixed solution was precipitated in warm acetone (~40 °C) for 3 times to obtain pure polymer samples. The polymers were dried under vacuum for 12 h.

Instruments and Measurements

¹H-NMR spectroscopy, GPC, TGA, DSC, POM, small-angle X-ray scattering (SAXS), one-dimensional wide-angle X-ray diffraction (1D WAXD) measurements were performed according to the procedures described in the literature previously^[46]. UV-Vis absorption spectra were recorded on an Agilent Cary600 spectrometer.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Polymers

The monomers TP SCLCPs with different spacer lengths (Mv-*m*-TP, $m = 2, 3, 4, 6, 8$) were synthesized. The synthetic route is illustrated in Fig. 1. At the end of each step, ¹H-NMR and high-resolution mass spectrometry were taken to confirm the chemical structure of resulting compound. The ¹H-NMR spectra (CDCl₃) of monomers are shown in Fig. 2. The results indicated that all the monomers were successfully synthesized because the chemical shifts and integrations of the proton resonances were matched with the theoretical values. All the polymers were obtained by free radical polymerization, and the respective characterization of polymers was carried out. The ¹H-NMR spectra (CDCl₃) of monomer M-8-TP and polymer P-8-TP are shown in Figs. 2(E) and 2(F) respectively. It can be seen that the protons corresponding to the vinyl group appear at 6.09 and 5.54 ppm (Fig. 2E), while they disappear completely after polymerization (Fig. 2F). In addition, all of the proton signals became broad because of the polymerization. To know the basic properties of polymers, GPC and TGA measurements were performed. The results are summarized in Table 1. The high M_n s of these polymers ranged from 2.05×10^5 g/mol to 4.35×10^5 g/mol with the polydispersity of 1.72–1.98, which could avoid possible influence of M_n on the LC behaviors. The T_d of these polymers was above 381 °C (see Fig. 3), indicating the polymers with good thermal stability.

Phase Transitions and Phase Structures of the Polymers

Phase transitions were investigated by the combination of DSC and POM measurements. To detect the morphological structures by POM, thin films of the polymers P-*m*-TP were prepared by the solution-cast method. The polymer solution was dropped on a piece of clean glass, dried at room temperature and sandwiched with a piece of cover glass. All

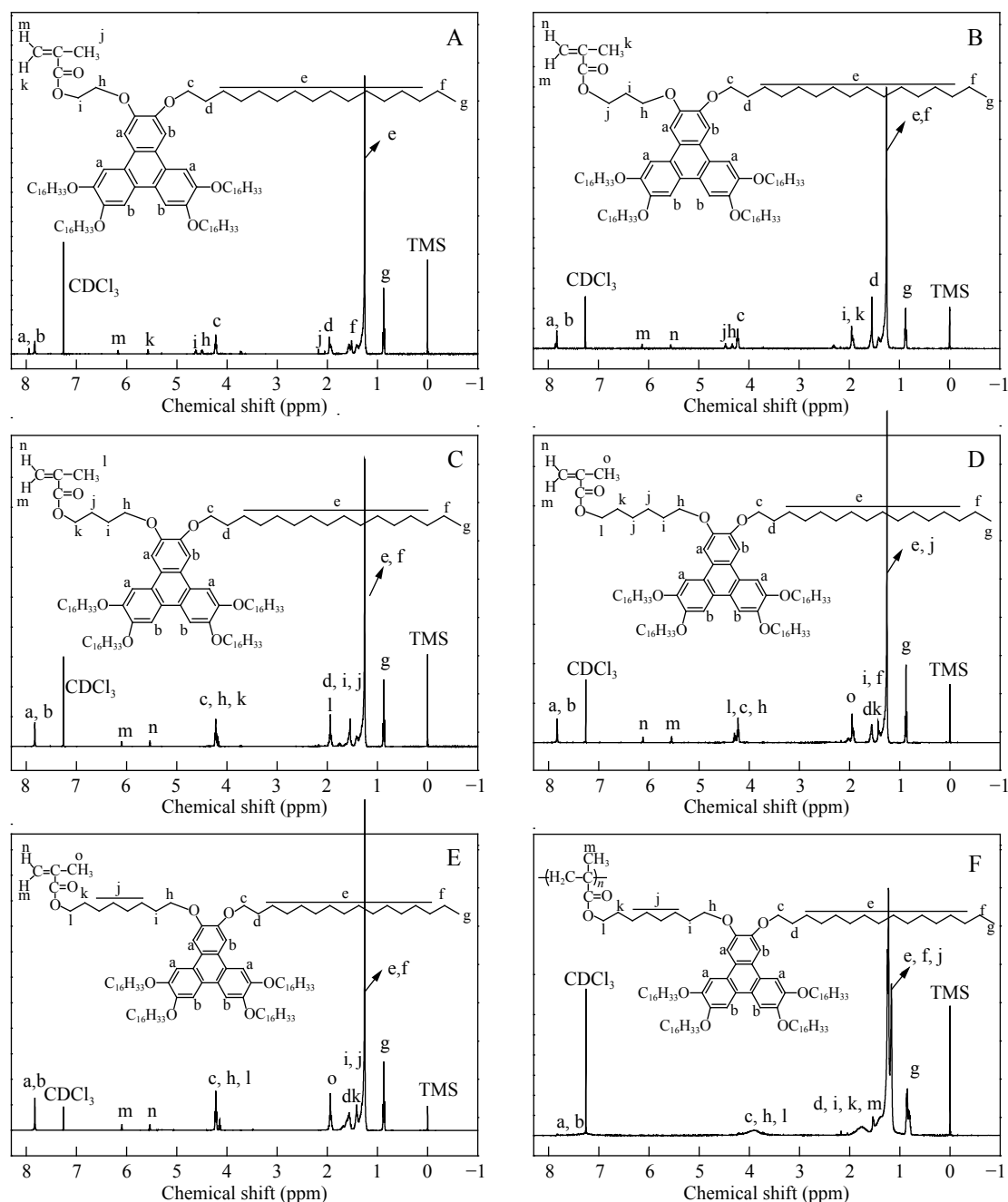


Fig. 2 ^1H -NMR spectra of monomers Mv-2-TP (A), Mv-3-TP (B), Mv-4-TP (C), Mv-6-TP (D), Mv-8-TP (E), and the polymer P-8-TP (F)

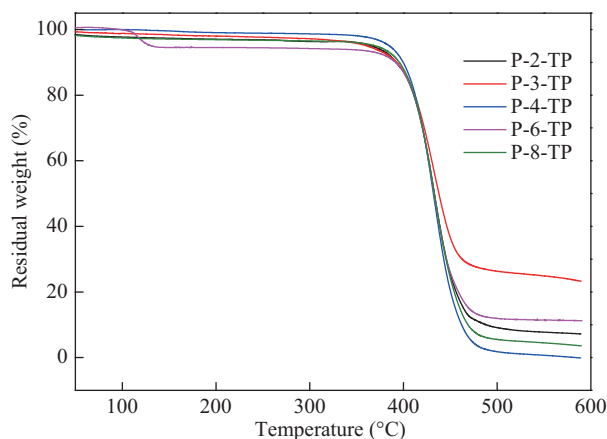
the polymers showed birefringence character but presented different clearing points (T_i) (Fig. 4, Table 1). For the samples with $m = 2, 3$ and 4, they still maintained the birefringence even by heating to 300 °C (Figs. 4a–4c). When the spacer length changed from 6 to 8, the obvious T_i s at 103 and 84 °C were detected and the colorful textures reappeared by slowly cooling the temperature from T_i . In order to eliminate the effect of thermal history, the samples were heated to 180 °C at 20 °C/min, cooled to –20 °C at 10 °C/min, and subsequently heated to 180 °C at 10 °C/min. The detail data are shown in Table 1. The DSC curves (Fig. 5) demonstrate that all the polymers have the crystallization or melting peaks at low temperature, which are attributed to the

long-alkyl tail. Interestingly, the degree of crystallinity of the alkyl tail increased with the increment of spacer length, suggesting the change of TP arrangement (see enthalpy change). With heating or cooling, a transition peak was detected for P-2-TP and P-4-TP at high temperature. The POM and X-ray diffraction results indicate the phase transition from one LC phase to another LC phase. When $m = 3$, no phase-transition peak was observed at high temperature in the DSC curve regarding of heating or cooling. For $m = 6$ and 8, endothermic peak appeared at 91 and 80 °C, respectively. This is corresponding to the transition from LC phase to isotropic phase. The results are consistent with the POM results. The POM and DSC results

Table 1 Molecular characteristics and properties of the polymers

Sample	$M_n^a \times 10^{-5}$ (g/mol)	PDI ^a	T_d^b (°C)	T_c^c (°C) (Enthalpy change)	T_1^d (°C)	T_i^e (°C)	I_{278}/I_{269} ratio ^g
P-2-TP	4.35	1.84	381	39.6 (36.7 J/g)	108	> 300	1.22
P-3-TP	2.84	1.84	383	26.4 (37.6 J/g)		> 300	0.96
P-4-TP	2.05	1.72	396	33.5 (38.1 J/g)	118	> 300	1.10
P-6-TP	3.16	1.73	386	35.5 (42.3 J/g)		103 (91 ^f)	1.80
P-8-TP	2.17	1.98	387	34.2 (40.3 J/g)		84 (80 ^f)	1.28

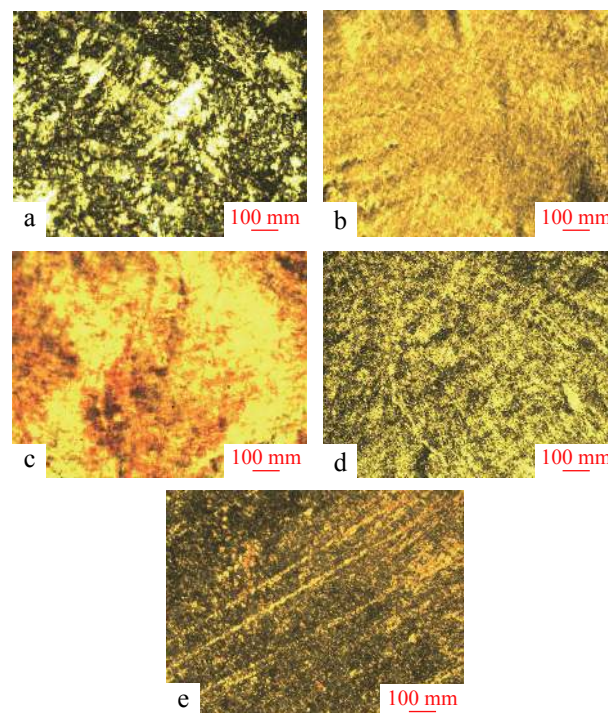
^a Determined by GPC in THF using PS standards; ^b Heating experiments were taken at a rate of 20 °C/min under nitrogen [T_d (N_2)]. The T_d was the temperatures at 5% weight loss of samples measured by TGA. ^c The crystallization temperatures (T_c) and enthalpy value were detected by DSC during the first cooling process at a rate of 10 °C/min under nitrogen atmosphere. ^d The phase transition temperature (T_1) from one LC phase to another LC phase was evaluated by DSC during the second heating process at a rate of 10 °C/min under nitrogen atmosphere. ^e Measured by POM at a heating rate of 10 °C/min. ^f Measured by DSC during the second heating process at a heating rate of 10 °C/min. ^g The intensity ratio of absorption at 278 and 269 nm was detected by UV-Vis spectra in the solution (8 μ mol/L in THF) at 25 °C.

**Fig. 3** TGA diagrams of samples in N_2 at a heating rate of 20 °C/min

prove that the phase structure of P- m -TP varies with different spacer lengths.

Phase Structure Identification of the Polymer

To learn more about the phase structure, all the samples were measured by the variable temperature 1D WAXD and SAXS. In order to be consistent with the DSC results, the samples were heated to 180 °C, and then slowly cooled to room temperature. The SAXS profiles of P-4-TP with different temperatures are shown in Fig. 6(a). With the increase of temperature, P-4-TP revealed two kinds of diffraction patterns. When the temperature was below 130 °C, five peaks could be detected (Fig. 6a) and the corresponding d -values were 4.55, 3.13, 2.67, 2.62 and 1.55 nm, which were assigned to (10), (01), (11), (20), (02), respectively. The schematic drawing of the molecular packing is shown in Fig. 6(d) and the polymer formed the rectangular column (Φ_R) phase with $a = 4.55$ nm, $b = 3.13$ nm and $\gamma = 90^\circ$. Considering that the ordered scale is much larger than the self-assembly of TP moieties, each cylinder may be attributed to a single oval polymer chain with the TP moieties distributed on opposite sides of the main chain. Therefore, the weak π - π stacking peak with $2\theta = 25^\circ$ (d -spacing = 0.36 nm) was found at the wide angle in the 1D WAXD profile below 120 °C (see Fig. 6b). When the temperature was above 150 °C, only one reflection peak was observed in low-angle region with d -value of 3.76 nm, meanwhile, the π - π stacking peak disappeared (see Fig. 6b). Combining the POM and DSC results, it is clear that the

**Fig. 4** POM images of the polymers (P- m -TP) with different spacer lengths $m = 2$ (a), $m = 3$ (b), $m = 4$ (c), $m = 6$ (d) and $m = 8$ (e) ($\times 200$)

polymer formed column nematic (Φ_N) phase in which the TP moieties distribute around the main chain in random. As shown in Fig. 6(c), SAXS results of P-2-TP were extremely similar with that of the P-4-TP. Below 150 °C, the d -values of three peaks belonging to rectangular column (Φ_R) phase were 4.30, 3.14, 2.15 nm respectively, which could be assigned as (10), (01), (20) diffraction of rectangular structure with $a = 4.30$ nm, $b = 3.14$ nm and $\gamma = 90^\circ$. When the sample was heated to 150 °C, only one peak with d -value of 3.56 nm appeared in low-angle region, suggesting the polymer entered into column nematic (Φ_N). The SAXS result of P-3-TP at room temperature is shown in Fig. 7(a). One diffraction peak with d -value of 3.65 nm was observed. The result of DSC showed no phase transition for P-3-TP, indicating that P-3-TP formed column nematic (Φ_N) phase with $a = 3.65$ nm. Fig. 7(b) shows the relationship between a -value of column nematic (Φ_N) phase scale and the spacer length. A gradual increase of a -value was observed from

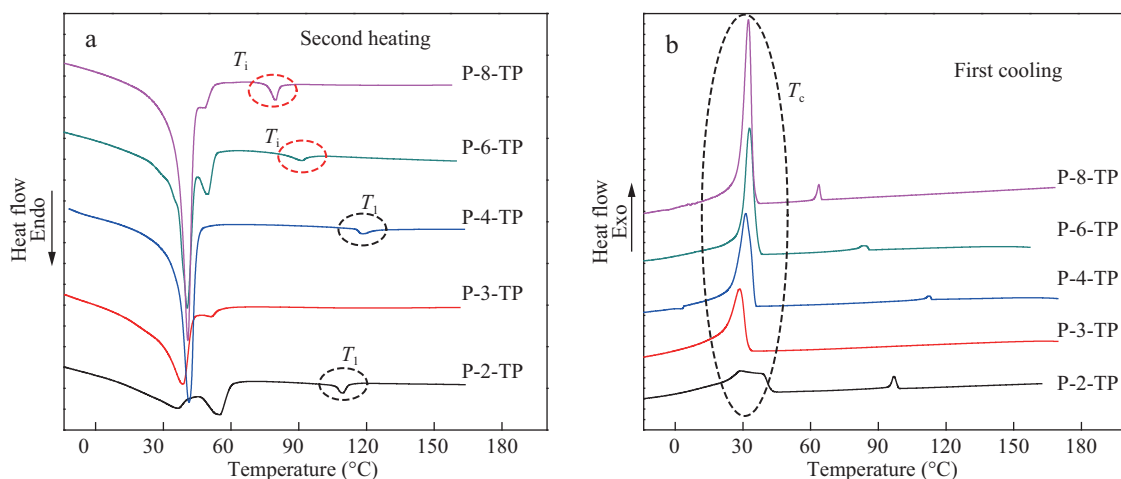


Fig. 5 DSC curves of P-*m*-TP in the second heating (a) and first cooling (b) at the rate of 10 °C/min

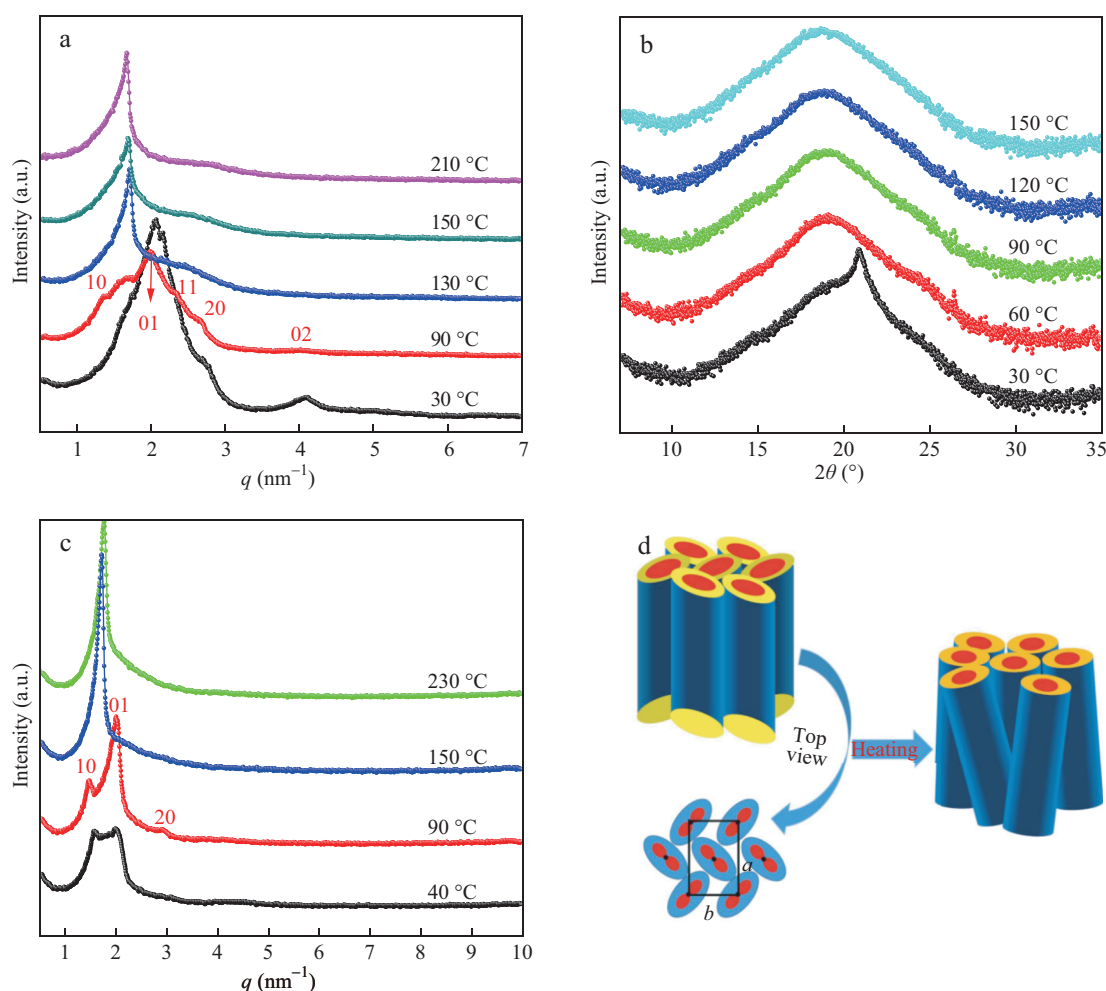


Fig. 6 The temperature dependent SAXS patterns of P-4-TP (a) and P-2-TP (c); The temperature dependent 1D WAXD profile of P-4-TP in high-angle region (b); The schematic drawing of the molecular packing for P-2-TP and P-4-TP from low temperature to high temperature (d)

3.56 nm to 3.76 nm with the increase of spacer length, implying that the diameter of the rod could be tuned by altering the spacer length.

When the spacer included 6 and 8 methylene groups, the corresponding phase structures of P-6-TP and P-8-TP were

quite different from those of above samples. From the temperature dependent SAXS results of P-6-TP shown in Fig. 8(a), three peaks at $q = 2.38, 4.15$ and 4.73 nm^{-1} were observed in the low angle region and the reciprocal q -value ratio was $1:3^{1/2}:2$, indicating that P-6-TP displayed

hexagonal columnar (Φ_H) phase at low temperature with $a = 3.05$ nm. In Fig. 8(b), a strong peak with d -value = 0.36 nm was found at low temperature, demonstrating the presence of strong π - π stacking. The above results indicate that each cylinder of P-6-TP is constructed by the TP moieties. The

schematic drawing of the phase structures is shown in Fig. 8(d). When the sample was heated to 150 °C, the π - π stacking was destroyed and the polymer entered into isotropic phase. The SAXS pattern of P-8-TP was similar with that of P-6-TP (Fig. 8c). It also formed a hexagonal

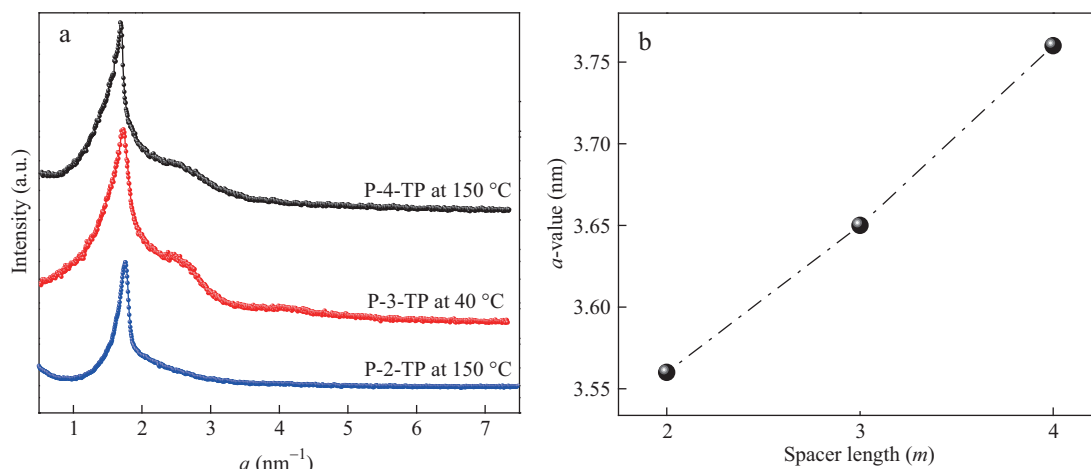


Fig. 7 SAXS patterns of P-2-TP, P-3-TP and P-4-TP with column nematic (Φ_N) phase (a); The relationship between a -value of column nematic (Φ_N) phase scale and the spacer length (b)

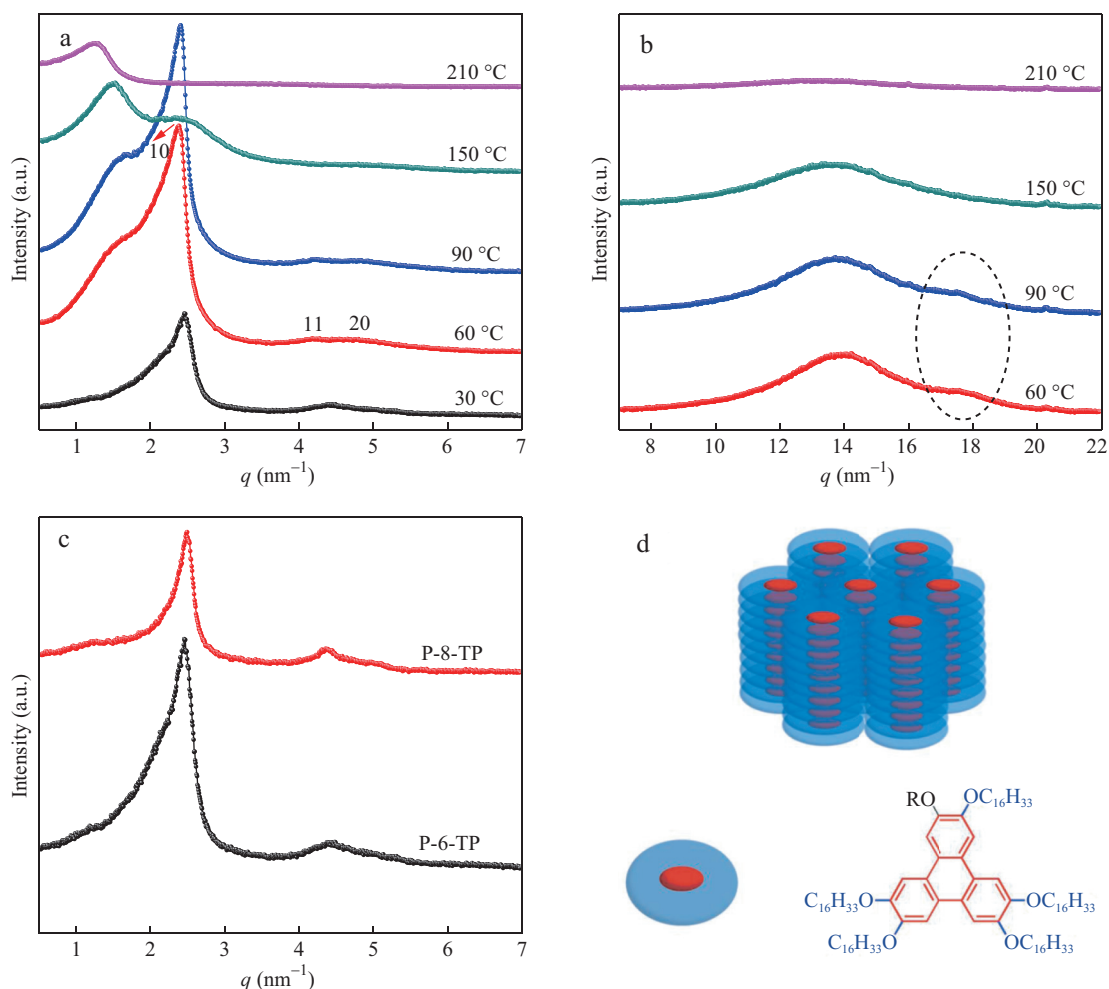


Fig. 8 The temperature dependent SAXS patterns of P-6-TP in low-angle region (a) and in high-angle region (b); SAXS patterns of P-6-TP, P-8-TP at room temperature (c); The schematic drawing of the molecular packing (d)

columnar (Φ_H) phase with $a = 2.91$ nm.

The UV-Vis absorption of P-*m*-TP was recorded in the dilute THF solution (8 $\mu\text{mol/L}$) (Fig. 9). The peak in the ultraviolet region (277 nm) can be assigned to the π - π transition of TP groups^[47]. With the increase of spacer length, the intensity of this peak increases and the intensity ratio of P-*m*-TP' absorbance at 278 and 269 nm also increases (see Table 1), indicating the enhancement of π - π stacking. The UV-Vis absorption results are consistent with the XRD results.

Fig. 10 depicts the schematic drawing of P-*m*-TP phase structures at different temperatures. As seen, the polymers present the column nematic (Φ_N) phase which is built by the TP moieties and the main chain as a whole, showing that the side-chains exhibit strong steric effect even though the flexible spacer length over 4. However, for TP SCLCPs with 6 methylene alkyl tail (P*m*-n)^[29], the polymers form the well-organized columnar superlattices based on multicolumn bundle organization with "coordination number" from 2 to 6 through individual discogens or discrete columnar stack (DCS)-based intracolumnar stacking modes (the experiment results came from the Ref. [29]), resulting in a strong π - π stacking of TP discogens and the low T_i although the flexible

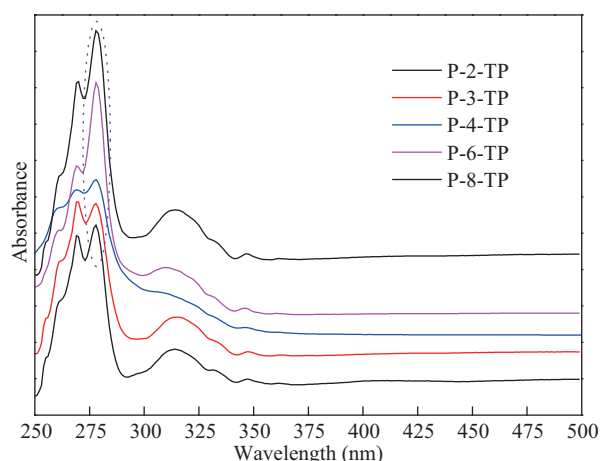


Fig. 9 UV-Vis spectra of polymers in the solution (8 $\mu\text{mol/L}$ in THF) at 25 $^{\circ}\text{C}$

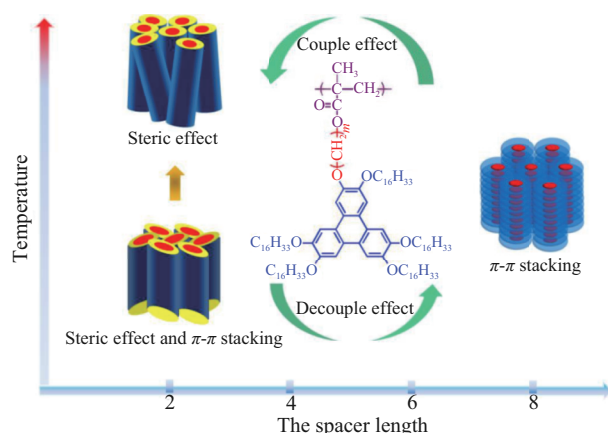


Fig. 10 Schematic drawing of the phase structures of P-*m*-TP at different temperatures

spacer length is below 2. The detailed experimental results are shown in Fig. 11, which suggest that the TP SCLCPs can form the stable LC phase when the alkyl tail length increases. On the other hand, further prolonging the spacer length, the P-*m*-TP ($m = 6$ and 8) presents a high symmetry Φ_H phase owing to the strong decoupling effect and self-organization of the TP moieties. It is interesting to notice that the T_i of P-*m*-TP ($m = 6$ and 8) is equal to the T_i of P*m*-n ($m = 6$ and 8), demonstrating that the alkyl tail length has little influence on the clearing transition temperature when the polymers exhibit LC phase by the π - π stacking of TP discogens.

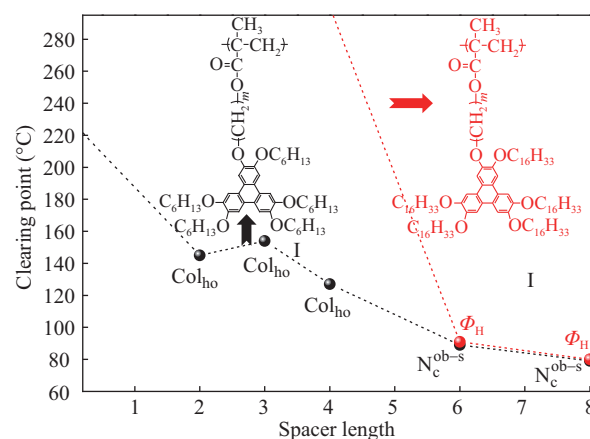


Fig. 11 Dependence of clearing temperatures (T_i) on the number of methylene groups (m) in the spacer for P*m*-n and P-*m*-TP Abbreviations: Col_{ho} = ordered hexagonal columnar lattice, N_c = proposed columnar nematic phase or columnar nematic phase with some superlattice order as indicated by a superscript^[29]. Φ_H = hexagonal columnar phase; I = isotropic phase.

CONCLUSIONS

In summary, a series of long-alkyl tail TP SCLCPs with different spacers (P-*m*-TP) were successfully synthesized via traditional solution radical polymerization. The M_n s of polymers were ranging from 2.05×10^5 g/mol to 4.15×10^5 g/mol. All the polymers had good thermal stability with T_d beyond 380 $^{\circ}\text{C}$. The phase behaviors and structures of polymers were studied by DSC, POM, 1D WAXD and SAXS. The results showed that the spacer length strongly influenced the couple effect, steric effect and π - π stacking effects, resulting in P-*m*-TPs with variable liquid crystalline phase structures. When $m = 2$ and 4, the polymers formed the column nematic (Φ_N) phase at high temperature, while at low temperature, they constructed an additional rectangular column (Φ_R) phase due to the strong steric effect and π - π interaction. When $m = 3$, the polymer exhibited column nematic (Φ_N) phase in the whole temperature range due to the odd-even effect. When $m = 6$ and 8, the polymers displayed hexagonal columnar (Φ_H) phase because of the strong decoupling effect and π - π stacking interaction. This work provided a new perspective to understand the structure-property relationship of SCLCPs.

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