Polymer 54 (2013) 3556-3565

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis and liquid crystalline behavior of 2,5-disubstituted styrenebased random copolymers: Effect of difference in length of the rigid core on the mesomorphic behavior of mesogen-jacketed liquid crystalline polymers

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ARTICLE INFO

Article history: Received 7 October 2012 Received in revised form 12 April 2013 Accepted 21 April 2013 Available online 14 May 2013

Keywords: Liquid crystalline polymer Random copolymerization Phase behavior

ABSTRACT

A series of binary copolymers, poly{2,5-bis[(4-octadecyloxyphenyl)oxycarbonyl]-styrene-*co*-2,5-bis[(4'-octadecyloxybiphenyl)oxycarbonyl]-styrene} (poly(M-OC18-*co*-M-C18)), were synthesized via free radical polymerization. The random nature of the copolymers was expected on the basis of the assumed similar reactivities because of the analogous monomers. A combination of differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide-angle X-ray diffraction (WAXD) demonstrated that phase behavior of this series of copolymers were strongly composition dependent. The P-OC18 formed smectic A phase, re-entrant isotropic phase and column nematic phase, while the P-C18 only exhibited the stable smectic A phase. The comparison between P-OC18 and P-C18 indicates that the length of the rigid core is crucial to determine the liquid crystalline (LC) structures. After copolymerization, the glass transition temperature and the phase transition temperature of the copolymers from smectic phase to isotropic phase both increased with the molar fraction of 2,5-bis[(4'-octadecylox-ybiphenyl)oxycarbonyl]-styrene (M-C18) in feed. In addition, when the feed was below 0.3, a column nematic phase was observed in high temperature. Namely, simply through copolymerization, we can greatly vary LC behavior of the mesogen-jacketed liquid crystalline polymers.

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1. Introduction

Phase structures and transitions of thermotropic liquid crystalline (LC) polymers have been one of the important topics to study in polymer chemistry and physics because LC polymers have a great potential in functional soft material [1–3]. Therefore, many researchers have investigated the structure–property relationship of side-chain liquid crystalline polymer (SCLCP) or main-chain liquid crystalline polymer (MCLCP) in order to understand the principles of structure formation and structure manipulation [4–17]. Depending on the position where the mesogens are linked to the backbone, the SCLCP can be categorized into either end-on SCLCPs or side-on SCLCPs. The former has mesogens linked at the end position, while another has mesogens linked at the waist or mass center position. For side-on SCLCPs, during the last 20 years, increasing interest has been devoted to mesogen-jacketed liquid crystalline polymers (MJLCPs) in which the rodlike mesogens are connected to every other carbon atom of polymer main chain at the waist position or mass center via a single covalent bond [18,19] because they display many thermotropic properties characterized by MCLCPs, although MJLCPs belong to SCLCPs chemically.

Since the concept of MJLCPs was proposed by Zhou et al., in order to understand the structure—property relationships of MJLCPs, containing glass transition, LC phase, clearing point, chain stiffness and conformation, one hand, the studies has been focused on the synthesis and characterization of new polymers with the type of mesogen and the length of flexible spacer linking the backbone and the side groups as well as the terminal substituent [20,21]. On the other hand, through atom transfer radical polymerization (ATRP) or reversible addition fragmentation chain transfer (RAFT), MJLCPs with different molecular weights or the block polymers in which polymer consisted of MJLCPs have been obtained [22–25]. The research shows that MJLCPs usually form columnar phase because of the strong steric effects, such as columnar nematic, hexagonal columnar, rectangular columnar [26]. Later, MJLCPs can display







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smectic A and smectic C, resulting from increasing the rigidity of the mesogen, H-bonding or electrostatic interaction [27–30].

For the phase behavior of the SCLCPs, it can be tailored not only by changing chemical structure, but also by changing the external conditions, such as, solvent, blends and copolymerization. For example, Kihara, H et al. have studied the thermodynamic phase behavior of LC copolymer/liquid crystal blends [31]. The results showed that the new type of phase diagram was obtained. Cui et al. have reported that the amorphous azopyridine polymer could easily be converted into LC polymers through self-assembly with a series of commercially available, aliphatic and aromatic carboxylic acids including the acetic acid [32]. Cheng et al. have researched the synthesis and phase structures of MJLCPs polyelectrolytes and their ionic complexes [29]. Authors found out that the complexes were amorphous when the MJLCPs were complexed with dodecyltrimethylammonium bromide (C12) because the alkyl tails were too short to induce the formation of ordered LC structures. However, by increasing the length of alkyl tails as in cetyltrimethylammonium bromide (C16) or by changing the shape of surfactant as in the fan-shaped amphiphilic molecule with three C12 tails (fan-shaped 3,4,5-tris(dodecyloxy)benzenamine), lamellar phases were observed for the complexes. For copolymerization, it represents one of the simplest synthetic techniques to effective control over the transition temperature and the phase structure and to widen their application range as high-performance materials. For example, when 2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrenes (MPCS) was copolymerized with non-liquidcrystalline vinyl monomers, such as styrene (St) and methyl methacrylate (MMA), mesophase can only be observed when the molar contents of MPCS in copolymers exceed about 89% and 84%, respectively [33]. It was speculated that the constitutional disorder, which diluted the concentration of mesogenic units and disrupted the interactions between backbone and side groups, was responsible for the destabilization of the mesophase. Tang et al. also have reported that 2,5-di(n-butoxycarbonyl)styrene was employed to tailor the mesomorphic property of PMPCS by random radical polymerization [34]. All the resultant copolymers were able to form stable mesophase regardless of the compositions. Moreover, the structure and dimension of the mesophase formed were manipulated through random copolymerization with nonmesogenic monomer in the whole composition range. Later, the author has researched that five series of binary copolymers, poly[2,5-di(ROOC) styrene-co-2,5-di(R'OOC)styrene]s, were synthesized via free radical polymerization [35]. The mesomorphic behaviors of the copolymers were found to be strongly affected by the presence of analogous comonomers differing in alkyl groups only, as

demonstrated by the increased glass transition temperatures, variation in phase dimensions, and the mesophase depression in certain copolymers.

This article presents the mediation of the LC properties of the random copolymers based on 2,5-bis[(4-octadecyloxyphenyl)oxycarbonyl]-styrene (M-OC18) and 2,5-bis[(4-octadecyloxybiphenyl) oxycarbonyl]-styrene (M-C18). In our previous studies, our group has proved that the P-OC18 formed the smectic A phase, re-entrant isotropic phase and columnar phases with the increasing of temperature [36]. The P-C18 presented the stable smectic A phase [37]. When M-OC18 was radically copolymerized with M-C18, the resultant copolymers displayed the interesting phase behaviors. The LC behaviors of this series of copolymers were investigated using DSC, POM and 1D WXRD experiments. This study provided a unique example of tuning the LC properties of MJLCPs by random copolymerization. Meantime, it can help us to understand the influence of thermotropic properties of the corresponding homopolymers on the mesomorphic properties of the copolymers.

2. Experimental section

2.1. Materials

The precursor 2-vinylterephthalic acid (VTA) was synthesized according to previous paper. The *p*-(*n*-octadecaoxyl)phenols were prepared as described by Klarmann et al. Chlorobenzene (Acros, 99%) was purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with distilled water, once with 5% sodium carbonate solution, and again with distilled water before being dried with anhydrous calcium chloride and then distilled. 4-(dimethylamino)pyridine (DMAP, 99%, ACROS), Hydroquinone and 4, 4'-Diphenol (98%, Alfa Aesar) and the corresponding octadecaoxyl bromides together with other reagents and solvents were used as received without further purification.

2.2. Synthesis of 4'-octadecyloxybiphenol

4,4'-biphenol (20 g, 0.1074 mol), octadecyl bromide (6 g, 0.0182 mol), K₂CO₃ (14.964 g, 0.1086 mol) and 200 ml were added into a 500 ml round-bottom flask. The mixture was heated for 12 h in 55 °C, next the reaction mixture poured into a large amount of water to precipitate products. The products were purified by precipitation in water from THF solution three times. At last, the crude products were purified by column chromatograph (silica gel, CH₂Cl₂). The final product of 4'-octadecyloxybiphenol was white



Fig. 1. Scheme of the synthesis of monomers M-OC18 and M-C18.



Fig. 2. ¹H NMR spectrums of the monomers M-OC18 and M-C18.

powder with a yield of 5 g. ¹H NMR (400 MHz, CDCl₃): δ = 0.86– 1.81 (m, 35, alkoxy H), 3.96–4.01 (t, 2H, –OCH₂–), 6.88–6.95 (m, 4H, *Ar*–*H*), 7.41–7.46(m, 4H, *Ar*–*H*).

2.3. Synthesis of 2,5-bis[(4-octadecyloxyphenyl)oxycarbonyl]styrene (M-OC18) and 2,5-bis[(4'-octadecyloxybiphenyl) oxycarbonyl]-styrene (M-C18) monomers

Both M-OC18 and M-C18 were synthesized with similar procedures. The synthetic routes of the monomers were outlined in Fig. 1.

The experimental details were described as follows using M-C18 as an example: VTA (5.2 mmol, 1 g) was added into 30 mL dried thionyl chloride in a 100 mL three-necked flask, and then the mixture was refluxed. After VTA was dissolved absolutely, the

excess thionyl chloride was removed under reduced pressure. The residue was washed with petroleum ether for three times. The petroleum ether was removed under the reduced pressure and afforded yellow liquid. This liquid was dissolved in dried THF to obtain solution A. 4'-octadecyloxybiphenol (13.0 mmol, 4.25 g) and DMAP (26.0 mmol, 3.18 g) were dissolved in 20 ml dried THF to obtain solution B. Under intense stirring at 0 °C, the solution A was slowly added into the solution B over a period of 2 h. The mixture was further stirred at room temperature for 12 h, and then most of the THF was distilled off by evaporation under reduced pressure. After water was added into the residue, the crude solid product was first collected by filtration and dried under vacuum, and then purified using column chromatography on silica gel with chloroform as eluant. The M-OC18 was synthesized according to our work [36]. The characterization data of these monomers were as follows and



Fig. 3. The constituent monomeric units of the poly (M-OC18-co-M-C18).

Fig. 2 gives the 1 H NMR spectra of the monomers M-C18 and M-OC18.

M-C18: ¹H NMR (400 MHz, CDCl₃): $\delta = 0.86-1.84$ (m, 70H, alkoxy H), 3.96–4.02 (t, 4H, $-OCH_2-$), 5.51–5.90 (2d, 2H, $=CH_2$), 6.91–7.00 (m, 4H, Ar–Ar'-H), 7.28–7.33(m, 4H, Ar-H-Ar'), 7.51–7.65 (m, 4H, Ar–Ar'-H and m, 4H, Ar-H-Ar' and 1H, -CH=), 8.23–8.50 (m, 3H, Ar-H). Mass Spectrometry (MS) (m/z) [M] Calcd for C₇₀H₉₆O₆, 1032.72; found, 1031.571 + 1.

M-OC18: ¹H NMR (CDCl₃): $\delta = 0.86-1.86$ (m, 70H, alkoxy H), 3.97–4.00 (t, 4H, -OCH₂-), 5.48–5.87 (2d, 2H, =*CH*₂), 6.95–7.17 (m, 8H, *Ar*-*H*), 7.53–7.60 (q, 1H, -*CH*=), 8.18–8.44 (m, 3H, *Ar*-*H*). Mass Spectrometry (MS) (*m*/*z*) [M] Calcd for C₅₈H₈₈O₆, 880.66; found, 879.465 + 1.

2.4. Synthesis of copolymers

Solution copolymerizations of M-OC18 with M-C18, with different feed compositions, were carried out in chlorobenzene at 65 °C using AIBN as initiator (0.05%, based on the total molar of monomers). Typical procedures of polymerization were as follows: An appropriate amount of AIBN, monomers and chlorobenzene were mixed in a reaction tube. After three freeze–pump–thaw cycles, the tube was sealed under vacuum and put into a 65 °C oil bath. Polymerization was carried out at 65 °C for several hours with constant stirring. After the tube was broken, the mixture was diluted with THF and then poured into a large amount of acetone to precipitate the polymer. The polymers were purified by precipitation in acetone from THF solution three times to eliminate the unreacted monomers completely, then, dried in a vacuum oven overnight at room temperature.

2.5. Instruments and measurements

¹NMR measurements were performed on a Bruker ARX400 MHz spectrometer using with CDCl₃ as solvent, tetramethylsilane (TMS) as the internal standard at room temperature.

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 at 38 °C. All the GPC data were calibrated with polystyrene standards.

DSC traces of all the polymers were obtained using a TA-Q10 DSC instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at a cooling and heating rates of 10 °C/min. Samples with a typical mass of about 5 mg were encapsulated in sealed aluminum pans.

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

One-dimensional (1D) wide-angle X-ray diffraction (WAXD) experiments were performed on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu K α) and an X'celerator detector. The sample stage was set horizontally. The reflection peak positions were calibrated with silicon powder ($2\theta > 15^{\circ}$) and silver behenate ($2\theta < 10^{\circ}$). A temperature control unit (Paar Physica TCU 100) in conjunction with the diffractometer was utilized to study the structure evolutions as a function of temperature.

3. Results and discussion

3.1. Copolymerization

The copolymerizations of M-OC18 with M-C18 in chlorobenzene were studied with different monomer to monomer ratios in the

Table 1

Summary of molecular weights (M_n) and polydispersities (PDI) of poly (M-OC18-*co*-M-C18) system.

Sample	$M_{M\text{-}OC18}\text{:}M_{M\text{-}C18}{}^a$	$M_n \times 10^{-5b} (g/mol)$	PDI ^b
P ₁	100:0	2.10	2.20
P ₂	95:5	2.00	2.10
P ₃	90:10	1.95	2.19
P ₄	80:20	1.50	2.25
P ₅	70:30	1.81	2.20
P ₆	60:40	2.10	2.32
P ₇	50:50	1.84	2.30
P ₈	40:60	2.15	2.51
P ₉	30:70	2.47	2.37
P ₁₀	20:80	2.12	2.32
P11	10:90	2.57	2.42
P ₁₂	0:100	2.13	2.12

 $^a~M_{M\text{-}OC18}$ is the mole fraction of M-OC18 to mole fraction of M-C18 ratios in the feed.

^b M_n and polydispersity (PDI) were measured by GPC using PS standards.





Fig. 4. DSC curves of copolymers during the first cooling scan (a) and the second heating scan (b) at a rate of 10 $^\circ\text{C}/\text{min}$ under a N_2 atmosphere.

Table 2
Thermotropic properties of poly (M-OC18-co-M-C18)

Sample	Tm ^a	Tg ^a	T1 ^b	T2 ^c
P ₁	48	91	115	217
P ₂	44	93	125	250
P ₃	44	105	132	270
P ₄	43	110	144	310
P ₅	47	118	168	330
P ₆	48	131	195	
P ₇	49	142	212	
P ₈	48	161	240	
P ₉	49	168	255	
P ₁₀	49	176	279	
P ₁₁	51	187	299	
P ₁₂	51	188	>350.0	

^a The melting temperatures of alkyl side chains (Tm) and the glass transition temperatures of copolymers (Tg) were measured by DSC at a heating rate of 10 °C/ min under nitrogen atmosphere during the second heating process.

 $^{\rm b}$ The transition temperature from smectic to isotropic phase (T1) measured by DSC at a heating rate of 10 °C/min under nitrogen atmosphere during the second heating process.

 $^{\rm c}$ The transition temperature from isotropic phase to liquid crystalline phase (T2) measured by POM at a heating rate of 10 $^{\circ}$ C/min.

feed. The constituent monomeric units of the copolymers are as shown in Fig. 3. GPC analysis was performed to determine M_n and molecular weight distributions of the polymers. To exclude the effect of the M_n on the LC behaviors, all copolymers were obtained with high enough M_n s by using rigorously purified monomers and solvent and relatively high monomer to initiator ratio. Because of the similarity in the structures of the monomers, the reactivity of the monomers was assumed to be equal. As a result, a random

distribution of the two building units along the copolymer backbone was expected. The copolymerization results of M-OC18 with M-C18 are summarized in Table 1 with the molar percentage of M-C18 in feed ranging from 0 to 1. From the Table 1, we can see that there are nearly the same M_n s and high M_n s for all samples.

3.2. Phase transitions and phase structures of copolymers

The dependence of the thermal transition temperatures on the compositions of copolymers poly (M-OC18-co-M-C18) was studied by DSC experiments. Fig. 4 shows the first cooling and the second heating DSC curves of copolymers at a rate of 10 °C/min under nitrogen atmosphere after eliminating the thermal history. Based on the second heating process, all phase transition temperatures of copolymers are shown in Table 2. First, as can be seen from Table 2, the melting temperatures of alkyl side chains (Tm) of P-OC18 and P-C18 are 48 °C and 50 °C, respectively. Second, a glass transition process can be observed in all these samples from Fig. 4(b). Moreover, only single glass transition was identified (see Fig. S1), indicating the monomers were placed randomly along the main chain and no phase separation occurred. The glass transition temperatures (Tg) of the copolymers increases from 91 °C to 188 °C with increasing the content of M-C18 in the feed. Contrast to the P-OC18, the Tg of P-C18 is higher presumably because of the difference length of the rigid core and the strong interactions between biphenyl. This continuous adjustment in Tg is evidence of molecular-level homogeneity of monomer distribution in polymer main-chain. Third, after Tg, the DSC traces contain one weak endothermic peak (except P₁₂). Combined the POM and 1D WAXD experiment results, this transition peak assigned as the transition



Fig. 5. Representative POM images of the texture of P₁ maintained at 115 °C (a), 145 °C (b), 250 °C (c) (Magnification: ×200).

temperature from smectic A phase to isotropic phase (T1). Meanwhile, with the increasing of the M-C18 fraction in feed from P₁ to P₁₁, the T1 increased from 115.1 °C to 299 °C, indicated that the more the longer rigid core (M-C18) copolymers contained, the more stable smectic A phase became. When cooling, this weak transition peak can also be seen in Fig. 4(a). Last, after T1, one transition peak appeared at 217 °C for P₁, which was caused by the phase transition from isotropic phase to column nematic phase (T2) [36]. For P₂–P₅, the T2 were difficultly detected by DSC because the thermal heat was small. However, they were detected by POM and increased from 250 °C to 330 °C (see Table 2).

To study morphological structures by POM, thin films of the copolymers were prepared by solution-cast method on clean cover glass, followed by slowly drying at ambient temperature. And then the samples were sandwiched in between two cover glasses and, therefore, were protected from direct contact with the air. On the basis of the POM observations, copolymers could be divided into two groups. The first group was P₁–P₅. Fig. 5 shows the observation for sample P_1 . When heating, the sample became soft above the Tg, then the granular LC texture (Fig. 5(a)) started to disappear when the temperature reached about 120 °C at which a corresponding endotherm appeared in DSC curve. Upon heating further, there was no birefringence to be seen (Fig. 5(b)). However, needle-like texture was formed when the temperature reached to 217 °C. Continue heating, no visible change of birefringence was observed before decomposition (see Fig. 5(c)). The POM results of the P_2-P_5 were same to P₁ and the representative POM images of them in high temperature are shown in Fig. 6(a), (b), (c) and (d), respectively. So, the phase transitions of P₁–P₅ followed the sequence of smectic A phase \leftrightarrow re-entrant isotropic phase \leftrightarrow columnar phase [36].

The second group was P_6-P_{12} . Taking the P_6 as an example, the sand-shape texture was observed when heating and is shown in Fig. 7(a), suggesting the formation of smectic phase. The texture disappeared when temperature reached 195 °C. It was consistent with the DSC result. Upon heating to 350 °C, there was no bire-fringence to be seen. After cooling, the sand-shape texture reappeared. For the copolymers P_7-P_{11} , the POM results were same to P_6 . The POM images of P_9 and P_{11} are shown in Fig. 7(b) and (c). For the POM results of P_{12} , the LC birefringence did not disappear before the polymer decomposed (Fig. 7(d)). So, the phase transitions of P_6-P_{11} followed the sequence of smectic A phase \leftrightarrow isotropic phase and P_{12} exhibited the stable smectic A phase [37].

To get more insight into the phase transition temperature and phase structure, we performed reflection light intensity (birefringence) measurements. Fig. 7(a) shows the transition temperatures of P₂ which evaluated by DSC and Fig. 7(b) shows the recorded changes in reflection light intensity for P₂ by POM both at a rate of 10 °C/min. It can be seen from Fig. 7(b) that two transition peaks appear. For the former peak, it appeared at T1, which agreed well with the transition temperature of this copolymer on DSC. Around T1, the reflection light intensity sharply decreased to 2.9% from 47.9%, indicating a transition from ordered state to isotropic state. For another one, it was difficult to be detected by DSC, however, it was obvious to appear at 250 °C (T2) in which the reflection light intensity sharply increased to 48.2% from 2.9%, showing a transition from isotropic state to ordered state. The dynamic process of the heating and cooling on the texture of P₂ is shown in supporting information. Before, our group has researched the influence of the heating and cooling rates on the thermal transition temperature (T1) by DSC. The results showed that the value of T1 was



Fig. 6. Representative POM images of the texture of P₂ at 255 °C (a), P₃ at 275 °C (b), P₄ at 315 °C (c) and P₅ at 335 °C (d) (Magnification: ×200).



Fig. 7. Representative POM images of the texture of P₆ at 185 °C (a), P₉ at 220 °C (b), P₁₁ at 275 °C (c) and P₁₂ at 300 °C (d) (Magnification: ×200).

independent of them [39]. To further know the phase transition and information about various phases, the influence of the heating and cooling rates on the thermal transitions from isotropic phase to columnar phase were studied by POM. Taking the P₂ as an example, the reflection light intensity curves are shown in Fig. 3. First, for the transition temperature from isotropic phase to columnar phase (T2) or from columnar phase to isotropic phase, they were also independent of the change of heating or cooling rate and basically kept 250 °C and 210 °C, respectively. Second, when cooling, the

change of intensity was slower than heating process, indicating after the polymer formed columnar phase, the polymer could keep the order structure in some degree to reduce the influence of driving force of the entropy. For the T1 of all copolymers, they were detected by reflection light intensity measurements, and the results were shown in Fig. S2, which was consistent with the DSC results.



Fig. 8. (a) Heat flow at a heating rate 10 $^\circ C/min$ in DSC and (b) the change of reflection light intensity for P_2 at a heating rate 10 $^\circ C/min$ in POM.



Fig. 9. Reflection light intensity curves of heating and subsequent cooling of P_2 at different rates in POM.

The phase transitions of the polymers were further verified on the 1D WAXD instrument. In order to be consistent with the DSC result, all samples were heated to 250 °C, and then slowly cooled to the room temperature. Based on the 1D WAXD observations, copolymers were also divided into two groups. The first group was P_1-P_5 . Fig. 8 describes the structurally sensitive 1D WAXD patterns of the P_2 from 35 to 260 °C. Upon the second heating, in the low 2θ region of $1-3^\circ$ (as shown in Figs. 9 and 10(a)), one obvious diffraction peaks are observed about 1.98° (d = 4.48 nm), indicating a smectic structure of the sample although the second-order diffraction was absence.





The reason for the disappearance of the second-order reflections possibly lies in the electron density profiles normal to the layers tending to be sinusoidal, which would diminish the higher-order reflections [38]. When the sample was heated to 140 °C, the diffraction peaks disappeared and the scattering halo appeared, indicating that the sample becomes isotropic. Further increasing the temperature to 260 °C, one peaks appeared about 3.07° (d = 2.87 nm), indicating a transition from isotropic to columnar phase [36]. In the high 2 θ region of 10–35°, at lower temperature range the WAXD patterns only rendered one peaks (as shown in Fig. 10(b)), indicating the typical crystal formed by the long alkoxy tails.



Fig. 11. 1D WAXD patterns of the P-C18 (P_{12}) during the second heating process of the as-cast film ((a) in the low 2 and (b) in the high 2θ).



Fig. 12. 1D WAXD patterns of the $P_7(a)$ and $P_9(b)$ during the second heating process of the as-cast film ((a) in the low 2θ and (b) in the high 2θ).

Table 31D WAXD results of the polymers at 50 °C.

Sample	d-spacing (nm)	
P ₁	4.01	
P ₂	4.48	
P ₇	4.85	
P ₉	5.09	
P ₁₂	5.56	

The second group was P_6-P_{12} . Before, our group has proved that P-C18 (P12) formed the stable SA phase, herein we wouldn't discuss the experiment results again (see Fig. 11) [37]. Fig. 12(a) and (b) describe the structurally sensitive 1D WAXD patterns of P₇ and P₉ from 50 to 265 °C in the 2θ region from 2.5° to 30°. The 1D WAXD experiment results of them were similar to the P₁₂, and the only difference was that the sharp diffractions in low angle disappeared at 220 °C and 265 °C, respectively for P7 and P9, indicating the polymers entered into isotropic phase from smectic phase, which was consistent with the POM and DSC results. In addition, as can be seen from Fig. 12(b), the ratios of the lower diffraction peak angle (2θ) with respect to the higher angle are 1:2, further indicating a smectic structure of the copolymer. On the basis of the 1D WAXD studies, the d-spacing values measured at 50 °C are summarized in Table 3. The d-spacing value of mesophase increased from 4.21 nm to 5.56 nm, indicating that the more the longer side groups copolymers contained, the larger the d-spacing values was.

3.3. Roles governing mesophase formation of copolymers

Based on DSC, POM and 1D WAXD experiments results, all copolymers showed the smectic phase. The schematic drawing of the layer structure of copolymers is shown in Fig. 13. Comparing with the phase behavior of P-OC18, P-C18 exhibited the different phase behaviors although there was only minute difference in structure between M-OC18 and M-C18. Combined the microphase separation with the driving force of the entropy, the P-OC18 can form smectic A phase, re-entrant isotropic and column nematic phase. The P-C18 can exhibit a stable smectic phase because of the long symmetry mesogenic core and strong interactions between biphenyls. After copolymerization, the copolymers presented the interesting phase behavior. Phase transition behaviors of poly (M-OC18-co-M-C18) are shown in Fig. 14. As can be seen, all copolymers presented the smectic phase although the smectic phase formation mechanism of P-OC18 was different P-C18. Meanwhile, the T1 increased with the increasing of M-C18 fraction in feed. However, it was hard for the copolymers to form the column nematic phase. When the feed was above 0.3, the copolymers just have exhibited the smectic phase. According to Self-Compacting Chain Model, the entropy gain of the side groups obtained from liquid-mesophase transition of the copolymer would be less than that of the homopolymer, resulting in a less tendency for a copolymer to form a mesomorphic state [35,36,40].



Fig. 13. Schematic drawing of the layer structure of the polymers.



Fig. 14. Phase transition behaviors of the copolymers poly (M-OC18-*co*-M-C18). (G: glassy, I: isotropic phase, C: column phase).

4. Conclusions

Copolymers of the poly (M-OC18-*co*-M-C18) system were prepared with AIBN as initiator at 65 °C. Thermal analysis showed that all copolymers had only single glass transition, indicating a statistical microstructure of the main chain. The LC behavior of copolymers was dependent on the content of M-C18 in copolymers. The transition temperature of copolymers from the smectic phase to isotropic phase (T1) increased with the increasing of the molar fraction of M-C18 in feed. In addition, when the feed was below 0.3, the copolymers formed a re-entrant isotropic phase. The present work provides useful data for the discovery and application of new materials based on copolymers of M-OC18 with M-C18.

Acknowledgment

This research was financially supported by the Innovation Platform Open Foundation of University of Hunan Province (10k067), the National Nature Science Foundation of China (51073131, 21174117, 21104062). The authors thank Prof. Chen Er-Qiang and Chen Xiao-Fang of Peking University for their help with 1D WAXD experiments measurements.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.04.056.

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