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Polymer 48 (2007) 4252–4263

polymer

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Synthesis and mesophase behaviors of 2,5-disubstituted styrene-based random copolymers: Effect of difference in side-group length on liquid crystallinity

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Received 8 February 2007; received in revised form 14 April 2007; accepted 7 May 2007
Available online 18 May 2007

Abstract

Five series of binary copolymers, poly[2,5-di(ROOC)styrene-*co*-2,5-di(R′OOC)styrene]s ($R = n\text{-}C_3H_7$–, $R' = C_2H_5$–, $n\text{-}C_4H_9$–, and $n\text{-}C_5H_{11}$–; $R = n\text{-}C_6H_{13}$–, $R' = n\text{-}C_4H_9$–, and $n\text{-}C_5H_{11}$–), were synthesized via free radical polymerization. The random nature of the copolymers was expected on the basis of the assumed similar reactivities of the analogous monomers and proved by ^{13}C NMR analysis. It was also implied by the smoothly varying glass transition temperatures and further supported by the monotonous variation in *d* spacings for the liquid crystalline copolymers, where both corresponding homopolymers are liquid crystals. Subtle difference of R and R′ was found to have significant impact on the mesomorphic properties of the copolymers. When the pair of the corresponding homopolymers has the same mesogenic structure, a difference of one carbon atom in the alkyl chain can be tolerated over the whole copolymer composition range; however, the liquid crystalline structure soon disappears with the incorporation of a co-unit of an homopolymer that is not liquid crystal. For the copolymers with alkyl chain length differing by two carbon atoms, the liquid crystalline structure is lost with the incorporation of relatively low co-unit content despite the pair of corresponding homopolymers having the same mesogenic structure.

Keywords: Liquid crystallinity; Random copolymerization; Mesophase formation

1. Introduction

Copolymerization is a frequently employed method to modify the property of a homopolymer as desired by introducing a delicately chosen second repeating unit [1]. For liquid crystalline polymers (LCPs), the technique is originally applied in molecular designing of aromatic copolyesters to balance thermotropic liquid crystallinity and melt-processibility [2]. More recently, it has been extensively employed to manipulate the phase structures and phase transitions of side-chain LCPs [3]. The comonomer may either bear nonmesogenic or mesogenic structural unit. With the former case, due to the diluted mesogen concentration in copolymers, random copolymers lose mesomorphic properties below a minimum mesogen concentration, which depends on the nature of both monomer and comonomer [4–9]; whereas in alternating copolymerizations, the copolymers behave like liquid crystalline homopolymers since they contain a mesogenic group in each repeating unit [10]. With the latter case, a wide combination of mesogens, flexible linkages, and backbones has been employed to reveal the structure–property relationship [3,11–14].

Relatively few studies have focused on the effect of alkyl side-group length difference of monomer pairs on the mesomorphic behaviors of copolymers. Copoly[dialkylsiloxane]s with different side-chains are among the most systemically investigated copolymers thereof [15]. Poly[di(*n*-alkyl)siloxane]s

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doi:10.1016/j.polymer.2007.05.026

are capable of forming thermotropic hexagonal columnar mesophase, although no typical rod- or disk-like mesogenic moiety or amphiphilic group is present in the molecular structures [16,17]. In a series of poly[di(alkyl)siloxane/di(*n*-hexyl)siloxane]s containing either diethylsiloxane, di(*n*-butyl)siloxane, or di(*n*-pentyl)siloxane units, as reported by Möller and co-workers [15], a difference of one carbon atom can be accommodated within the 2D-ordered hexagonal columnar phase. When the alkyls differ by two carbon atoms or more in length, formation of stable mesophase cannot be displayed anymore because of the constitutional disorder in the polymer chain. However, all the di(*n*-alkyl)siloxane homopolymers concerned are of same mesophase and therefore the influence of the ability of the corresponding homopolymer to form a ordered structure on the mesomorphic behavior of the resultant copolymer remains unknown. Shaw and co-workers investigated the thermal behaviors of copoly(alkylisocyanate)s containing long aliphatic side groups (such as undecyl) with that containing shorter side groups (such as propyl) [18–20]. It was found that the introduction of an analogous comonomer differing only in alkyl side-chain length increased the temperature range of isotropic state. Unfortunately, the mesomorphic behaviors of the copolymers have not been discussed in detail.

Poly[2,5-di(alkoxycarbonyl)styrene]s with suitable alkyl length, similar to poly[di(alkyl)siloxane]s in containing no traditional mesogenic unit, are another type of interesting flexible thermotropic LCPs [21–23]. The glass transition temperatures (T_gs) of the polymers are much lower than polystyrene. Heating above T_g, the polymers enter isotropic state first and no birefringence can be observed. They form two-dimensional hexagonal columnar (Φ_H) phase at temperatures much higher than their glass transitions and the building blocks of the mesophase involve entire molecules having relatively extended conformation. The alkyl length plays an important role in mesophase formation. When the side group is methyl or ethyl, the polymer behaves like atatic polystyrene, i.e., only isotropic phase is observed in the heating and subsequent cooling process. Increasing the size of side group from *n*-propyl to *n*-pentyl leads to the formation of mesophase, which keeps stable upon subsequent cooling once it is formed. Hexagonal columnar phase can also be formed by the analogous polymer containing *n*-hexyl group at high temperature but disappears at low temperature, i.e., the polymer containing *n*-hexyl group shows an unusual reversible transition from isotropic to LC transition. In addition, the dimension of the mesomorphic phase increases with alkyl size.

In a recent publication, 2,5-di(*n*-butoxycarbonyl)styrene (C4) was employed to tailor the mesomorphic property of a mesogen-jacketed liquid crystalline polymer(MJLCP), poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PMPCS), by random radical polymerization [24,25]. All the resultant copolymers are able to form stable mesophase regardless of the compositions. When the molar fraction of 2,5-bis[(4′-methoxyphenyl)oxycarbonyl]styrene (MPCS) in feed (M_{MPCS}) is above 0.5, a hexatic columnar nematic ($\Phi^{\mathrm{I}}_{\mathrm{HN}}$) phase is formed with a constant *d* spacing value of 1.58 nm. When M_{MPCS} is below 0.1, a Φ_H phase is observed, and the corresponding *d* spacing is about 1.44 nm. In between $0.1 < M_{\mathrm{MPCS}} < 0.5$, another hexatic columnar nematic ($\Phi^{\mathrm{II}}_{\mathrm{HN}}$) phase can be recognized with tunable *d* spacing relying on the copolymer compositions. It is thought that the copolymers with dominant one component form mesophases since the irregularity induced by co-unit is not marked and can act as the corresponding homopolymers. For the copolymers with comparable quantity of MPCS and C4, the existence of mesophase is because MPCS and C4 cooperate to take cylindrical conformations, which are a prerequisite to ordered packing for such type LCPs. The variation in mesophase dimension is similar to main-chain liquid crystalline random copolymers whose bulk properties show a high sensitivity to relatively small changes in the chemical structure and proportions of the monomer components [26].

In this study, five series of binary copolymers, poly[2,5-di(ROOC)styrene-*co*-2,5-di(R′OOC)styrene]s ($\mathrm{R} = n\text{-}\mathrm{C_3H_7}-$, $\mathrm{R}' = \mathrm{C_2H_5}-$, $n\text{-}\mathrm{C_4H_9}-$, and $n\text{-}\mathrm{C_5H_{11}}-$; $\mathrm{R} = n\text{-}\mathrm{C_6H_{13}}-$, $\mathrm{R}' = n\text{-}\mathrm{C_4H_9}-$, and $n\text{-}\mathrm{C_5H_{11}}-$) were synthesized via free radical polymerization to investigate the influence of the constitutional disorder in the side groups, the composition, and the ability of the monomeric structural units to form a mesophase in the corresponding homopolymers on the mesomorphic behaviors of copolymers. Poly[2,5-di(*n*-propoxycarbonyl)-styrene] was chosen as a base polymer because it represents the lower limiting case that the homologous poly[2,5-di(alkoxycarbonyl)styrene]s form mesophase, while poly[2,5-di(*n*-hexoxycarbonyl)styrene] was chosen because of its unusual reversible transition from isotropic to LC transition. The present approach differs from our previous work by two facts. One fact is that either monomers or comonomers used in this work are nonmesogenic analogous vinyl compounds, which provide a convenient way to systematically investigate the effect of alkyl side-group length difference on the mesomorphic properties of the corresponding copolymers. Another fact is that the thermotropic properties of the homopolymers depend on the alkyl size of side group; delicately chosen monomer pairs would 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 monomers, 2,5-di(ethoxycarbonyl)styrene (C2), 2,5-di(*n*-propoxycarbonyl)styrene (C3), (C4), 2,5-di(*n*-pentoxycarbonyl)styrene (C5), and 2,5-di(*n*-hexoxycarbonyl)styrene (C6) were synthesized and purified following the procedures as described in the previous publication [21]. 2,2′-Azobis(isobutyronitrile) (AIBN, Beijing Chemical Co., 95%) was purified by recrystallization from ethanol (Beijing Chemical Co., A.R.) before use. Chlorobenzene (Beijing Chemical Co., A.R.) used as the polymerization solvent was washed successively with concentrated sulfuric acid (Beijing Chemical Co., 98%), aqueous solution of sodium bicarbonate (Beijing Chemical Co., A.R.), and deionized water and distilled out from calcium hydride (Beijing Chemical Co., A.R.) under an argon atmosphere. Tetrahydrofuran (THF, Beijing Chemical Co., A.R.) and methanol (Beijing Chemical Co., A.R.) employed as solvent and precipitant, respectively, were used as purchased. THF (Beijing Chemical Co., A.R.) distilled out from calcium hydride under an argon atmosphere was used in the size exclusion chromatography. Unless otherwise specified, all other solvents and reagents were purchased from Beijing Chemical Co. and used as received.

2.2. Copolymerization

Copolymerization was carried out in solution. In a typical run, C3 (0.14 g, 0.51 mmol), C5 (0.16 g, 0.49 mmol), AIBN (0.080 mg, 0.00050 mmol) and chlorobenzene (1.8 g, 16 mmol) were successively introduced into a reaction tube. After three freeze–pump–thaw cycles to remove any dissolved oxygen in the reaction mixture, the tube was sealed under vacuum and inserted into a thermostated oil bath at 60 °C. The polymerization was allowed to continue for 12 h. After the polymerization was terminated by breaking the tube, the reactant was diluted with 10 mL of THF and then precipitated in 200 mL of methanol. The dissolution in THF and precipitation in methanol were repeated three times to eliminate the unreacted monomers completely. The copolymers were dried at 40 °C under vacuum for 24 h before further characterizations were performed. The monomer conversion in weight was 36.4%. ^{1}H NMR (δ, ppm): 0.5–2.1 (broad peaks, $-CH_2CH-$ protons in the backbone, $-CH_2CH_3$ protons in the side groups of C3 units and $-CH_2CH_2CH_2CH_3$ protons in the side groups of C5 units), 2.8–4.2 (broad peaks, $-OCH_2$- protons in the two structural units), 6.8–7.8 (broad peaks, phenyl ring protons of the two structural units). ^{13}C NMR (δ, ppm): 165.4, 146.5, 133.9, 132.0, 129.2, 125.1, 66.1, 64.7, 34.8, 28.0, 22.3, 21.6, 13.9, 10.3.

2.3. Instruments and measurements

The number-average molecular weights (M_n), weight-average molecular weights (M_w) and polydispersity distribution index (PDI, M_w/M_n) of the resultant copolymers were estimated by a size exclusion chromatography instrument with a Waters 2410 refractive index detector. Three Waters Styragel columns with 10-μm bead size were connected in series. Their effective molecular weight ranges were 100–10,000 for Styragel HT2, 500–30,000 for Styragel HT3, and 5000–600,000 for Styragel HT4. The pore sizes were 50, 100, and 1000 nm for Styragel HT2, HT3, and HT4, respectively. THF was employed as the eluant at a flow rate of 1.0 mL min^{-1} at 35 °C, and the calibration curve was obtained with monodispersed polystyrenes as standards. All the announced molecular weights in this paper were in equivalent of standard polystyrenes. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer with $CDCl_3$ as solvent and TMS as an internal reference at 400 and 100 MHz, respectively.

The thermotropic transition of the copolymers was investigated with differential scanning calorimetry (DSC) on a TA Q100 calorimeter in a temperature range of −90 to 180 °C at a heating rate of 10 °C min^{-1} under continuous nitrogen flow. All the data were based on the second heating process after cooling at 10 °C min^{-1} from 180 °C. *n*-Octane (mp −56.8 °C) and indium (mp 156.8 °C) were used to calibrate the instrument. The average sample mass was about 3 mg, and the nitrogen flow rate was 50 mL min^{-1}. A TA Q600 instrument was used for thermogravimetric analysis of the copolymers. Generally, about 5 mg of sample was heated from 30 to 600 °C at a heating rate of 20 °C min^{-1} under nitrogen flow.

One-dimensional wide-angle X-ray diffraction (1D WAXD) experiments were performed on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as an X-ray source (Cu Kα radiation) and an X'celerator detector. A temperature control unit was utilized to study the structure evolution as a function of temperature changing at constant heating and cooling rates. Films with thickness of ~1 mm were cast on copper sheets from THF solution, and the diffraction patterns were collected by reflection mode. Background scattering pattern was recorded and subtracted from the patterns of the samples.

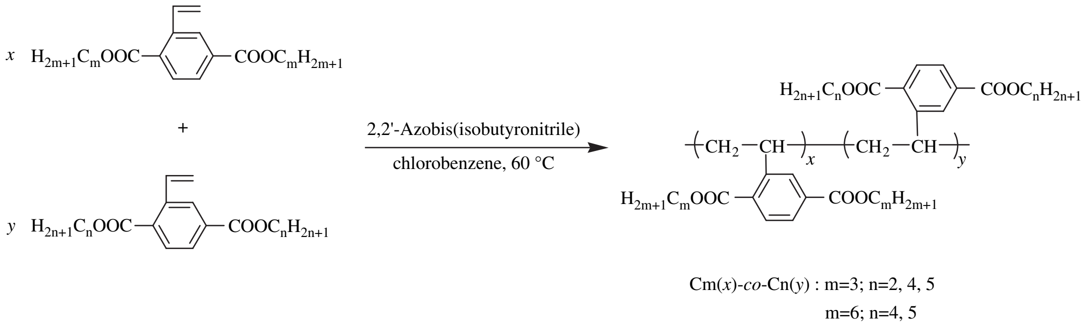
Two-dimensional wide-angle X-ray diffraction (2D WAXD) fiber patterns were obtained using a Bruker D8 Discover diffractometer with GADDS (general area detector diffraction system) as a detector. The two-dimensional diffraction patterns were recorded in transmission mode at room temperature. Fibers were drawn with stretching at a rate of about 1 m s^{-1} at 180 °C, isothermally annealed for 12 h, and quenched to room temperature before test. Background scattering pattern was recorded and subtracted from the patterns of the samples.

Phase morphology was identified via a Leica DML polarized light optical microscope (POM) with Mettler hot stage (FP 82 HT with a FP-90 central processor). The sample films were prepared by the solution-cast method, and the thicknesses were kept at several microns.

3. Results and discussion

3.1. Copolymerization

Random copolymerizations of 2,5-di(*n*-alkoxycarbonyl)styrenes were carried out in chlorobenzene at 60 °C using AIBN as an initiator (Scheme 1). The resultant copolymers are waxy solids or white powders at room temperature, which are soluble in a number of common organic solvents, such as chloroform, dichloromethane, THF, benzene, chlorobenzene and toluene. Tables 1–5 summarize the copolymerization results of the five series of copolymers, abbreviated as C3(*x*)-*co*-C4(*y*)s, C3(*x*)-*co*-C5(*y*)s, C3(*x*)-*co*-C2(*y*)s, C6(*x*)-*co*-C5(*y*)s, and C6(*x*)-*co*-C4(*y*)s, where *x* and *y* represent the molar contents of the two structural units in feed. To exclude the effect of the molecular weight on the thermotropic property, all the copolymers studied were obtained with high enough molecular weights by using rigorously purified monomers and solvent and relatively high monomer to initiator



Scheme 1. Synthesis and chemical structures of copoly[2,5-di(alkoxycarbonyl)styrene]s. C*m*(*x*)-*co*-C*n*(*y*)s are the abbreviation of copolymers with *m* and *n* indicating the lengths of alkyl groups, *x* and *y* represent the molar ratios of the two structural units in feed.

ratio. Because of the similarity in the structures of the monomers, the reactivities of the monomers were assumed to be equal. As a result, a random distribution of the two building units along the copolymer backbone was expected and the compositions of the copolymers were assumed to be the monomer to comonomer ratios in feed.

To confirm this assumption, ^{13}C NMR was employed to characterize the composition of the copolymers [15,27–29]. Fig. 1 represents the ^{13}C NMR spectra of C3(0.60)-*co*-C4(0.40) and C3(0.51)-*co*-C5(0.49), separately. From the relative intensities of $-CH_3$ (10.2–13.9 ppm), the partial molar proportions of C3 units in the copolymers could be calculated as 0.59 and 0.50. The values correspond well with the monomer fractions in feed, demonstrating the similar reactivities of C3/C4 and C3/C5 pairs.

3.2. DSC

DSC was first performed to study the thermotropic behaviors of the copolymers at a heating rate of 10 °C min^{-1}. Except for single glass transition, no other phase transition was discernible in the DSC thermograms. The glass transition temperatures (T_gs) of each series of copolymers are summarized in Tables 1–5. By increasing the content of one component, the T_gs of the copolymers varied monotonously. This continuous adjustment in T_g is another evidence of molecular-level homogeneity of monomer distribution in polymer main-chain [30].

Considering the possibility that the enthalpy of isotorpic-LC transition is too small to be detected by DSC when the sample amount is not enough, the weight of the sample and the scanning rate were increased to 20 mg and 20 °C min^{-1}, respectively. However, no other phase transition was observed too.

3.3. POM

To study morphological structures by POM, thin films (10–20 μm in thickness) of the copolymers were prepared by solution-cast method on clean cover glass, followed by slowly drying at ambient temperature. Under crossly polarized light

Table 1
Copolymerization results of 2,5-di(*n*-propoxycarbonyl)styrene and 2,5-di(*n*-butoxycarbonyl)styrene and thermotropic properties of the copolymers

Sample[a]	Yield (%)	M_n[b] (10^5)	PDI[b]	T_g[c] (°C)	Liquid crystallinity[d]	T_{LC} [d](°C)	*d* Spacing (nm)
C3(0.00)-*co*-C4(1.00)	29.6	2.8	1.46	−2.0	Yes	91	1.44
C3(0.06)-*co*-C4(0.94)	36.7	1.7	1.41	1.1	Yes	99	1.44
C3(0.10)-*co*-C4(0.90)	18.0	2.2	1.29	4.2	Yes	107	1.44
C3(0.15)-*co*-C4(0.85)	40.2	1.9	1.36	6.4	Yes	110	1.43
C3(0.19)-*co*-C4(0.81)	47.1	1.7	1.43	8.5	Yes	116	1.42
C3(0.26)-*co*-C4(0.74)	42.0	1.7	1.44	10.5	Yes	126	1.41
C3(0.30)-*co*-C4(0.70)	21.3	1.4	1.48	13.4	Yes	131	1.41
C3(0.40)-*co*-C4(0.60)	26.5	1.8	1.39	15.9	Yes	138	1.39
C3(0.51)-*co*-C4(0.49)	36.4	1.9	1.37	17.9	Yes	141	1.39
C3(0.60)-*co*-C4(0.40)	42.2	1.7	1.44	20.3	Yes	145	1.37
C3(0.71)-*co*-C4(0.29)	51.5	1.6	1.50	23.6	Yes	146	1.36
C3(0.75)-*co*-C4(0.25)	30.1	1.7	1.41	25.6	Yes	148	1.35
C3(0.80)-*co*-C4(0.20)	34.7	1.7	1.43	27.2	Yes	146	1.34
C3(0.85)-*co*-C4(0.15)	44.0	1.7	1.46	29.6	Yes	138	1.33
C3(0.89)-*co*-C4(0.11)	37.7	1.8	1.40	30.5	Yes	134	1.33
C3(0.94)-*co*-C4(0.06)	29.0	1.6	1.45	31.3	Yes	131	1.32
C3(1.00)-*co*-C4(0.00)	36.5	1.6	1.39	32.0	Yes	116	1.30

[a] Polymerization condition: chlorobenzene solution (20 wt%); temperature: 60 ± 0.5 °C; initiator: 2,2′-azobis(isobutyronitrile) (0.05%, based on total mole number of monomers).

[b] M_n: number-average molecular weight; M_w: weight-average molecular weight; PDI: polydispersity distribution index (M_w/M_n).

[c] T_g: glass transition temperature.

[d] T_{LC}: temperature at which the sample begins to show birefringent texture under polarized light optical microscope at a heating rate of 2 °C min^{-1}.

Table 2
Copolymerization results of 2,5-di(*n*-propoxycarbonyl)styrene and 2,5-di(*n*-pentoxycarbonyl)styrene and thermotropic properties of the copolymers

Sample[a]	Yield (%)	M_n[b] (10^5)	PDI[b]	T_g[c] (°C)	Liquid crystallinity[d]	T_{LC}[d] (°C)	*d* Spacing (nm)
C3(0.00)-*co*-C5(1.00)	42.1	1.7	1.48	−18.5	Yes	121	1.52
C3(0.06)-*co*-C5(0.94)	24.2	1.5	1.55	−17.3	Yes	143	1.51
C3(0.10)-*co*-C5(0.90)	22.3	1.6	1.50	−15.0	Yes	155	1.48
C3(0.15)-*co*-C5(0.85)	21.1	1.2	1.77	−12.0	Yes	167	1.48
C3(0.20)-*co*-C5(0.80)	17.3	1.3	1.62	−9.1	No	–	–
C3(0.26)-*co*-C5(0.74)	27.8	1.4	1.63	−8.5	No	–	–
C3(0.30)-*co*-C5(0.70)	50.1	1.4	1.61	−6.3	No	–	–
C3(0.40)-*co*-C5(0.60)	27.1	1.2	1.83	−0.0	No	–	–
C3(0.51)-*co*-C5(0.49)	31.1	1.4	1.62	2.9	No	–	–
C3(0.61)-*co*-C5(0.39)	28.5	1.5	1.62	7.7	No	–	–
C3(0.70)-*co*-C5(0.30)	47.0	1.4	1.64	13.1	No	–	–
C3(0.75)-*co*-C5(0.25)	54.4	1.2	1.69	16.9	No	–	–
C3(0.80)-*co*-C5(0.20)	45.6	1.2	1.74	19.2	No	–	–
C3(0.85)-*co*-C5(0.15)	43.3	1.2	1.76	22.1	No	–	–
C3(0.91)-*co*-C5(0.09)	22.2	0.9	1.78	25.8	No	–	–
C3(0.95)-*co*-C5(0.05)	27.7	1.3	1.68	27.8	Yes	148	1.33
C3(1.00)-*co*-C5(0.00)	36.5	1.6	1.39	32.0	Yes	116	1.30

[a] Polymerization condition: chlorobenzene solution (20 wt%); temperature: 60 ± 0.5 °C; initiator: 2,2′-azobis(isobutyronitrile) (0.05%, based on total mole number of monomers).

[b] M_n: number-average molecular weight; M_w: weight-average molecular weight; PDI: polydispersity distribution index (M_w/M_n).

[c] T_g: glass transition temperature.

[d] T_{LC}: temperature at which the sample begins to show birefringent texture under polarized light optical microscope at a heating rate of 2 °C $\min^{-1}$.

Table 3
Copolymerization results of 2,5-di(*n*-propoxycarbonyl)styrene and 2,5-di(ethoxycarbonyl)styrene and thermotropic properties of the copolymers

Sample[a]	Yield (%)	M_n[b] (10^5)	PDI[b]	T_g[c] (°C)	Liquid crystallinity[d]	T_{LC}[d] (°C)	*d* Spacing(nm)
C3(0.00)-*co*-C2(1.00)	54.1	2.0	1.35	67.1	No	–	–
C3(0.11)-*co*-C2(0.89)	40.4	0.9	1.62	62.2	No	–	–
C3(0.24)-*co*-C2(0.76)	33.3	1.3	2.06	57.3	No	–	–
C3(0.39)-*co*-C2(0.61)	46.2	1.4	2.86	53.9	No	–	–
C3(0.46)-*co*-C2(0.54)	29.6	1.0	1.46	49.4	No	–	–
C3(0.60)-*co*-C2(0.40)	31.6	1.1	1.96	47.0	No	–	–
C3(0.67)-*co*-C2(0.33)	34.0	1.1	1.72	44.0	No	–	–
C3(0.72)-*co*-C2(0.28)	34.0	0.7	1.42	41.2	No	–	–
C3(0.76)-*co*-C2(0.24)	34.2	1.3	2.11	39.8	Yes	166	1.29
C3(0.86)-*co*-C2(0.14)	28.2	1.1	1.83	35.8	Yes	164	1.29
C3(0.90)-*co*-C2(0.10)	32.0	1.1	1.68	34.6	Yes	153	1.29
C3(0.94)-*co*-C2(0.06)	22.9	1.2	1.76	33.6	Yes	145	1.29
C3(1.00)-*co*-C2(0.00)	36.5	1.6	1.39	32.0	Yes	116	1.30

[a] Polymerization condition: chlorobenzene solution (20 wt%); temperature: 60 ± 0.5 °C; initiator: 2,2′-azobis(isobutyronitrile) (0.05%, based on total mole number of monomers).

[b] M_n: number-average molecular weight; M_w: weight-average molecular weight; PDI: polydispersity distribution index (M_w/M_n).

[c] T_g: glass transition temperature.

[d] T_{LC}: temperature at which the sample begins to show birefringent texture under polarized light optical microscope at a heating rate of 2 °C $\min^{-1}$.

Table 4
Copolymerization results of 2,5-di(*n*-hexoxycarbonyl)styrene and 2,5-di(*n*-pentoxycarbonyl)styrene and thermotropic properties of the copolymers

Sample[a]	Yield (%)	M_n[b] (10^5)	PDI[b]	T_g[c] (°C)	Liquid crystallinity[d]	T_{LC}[d] (°C)	*d* Spacing (nm)
C6(0.00)-*co*-C5(1.00)	42.1	1.7	1.48	−18.5	Yes	121	1.52
C6(0.16)-*co*-C5(0.84)	59.8	1.1	1.65	−19.8	Yes	132	1.53
C6(0.40)-*co*-C5(0.60)	48.2	2.5	1.83	−21.6	Yes	157	1.54
C6(0.52)-*co*-C5(0.48)	49.1	1.3	1.49	−23.2	Yes	164	1.55
C6(0.64)-*co*-C5(0.36)	67.9	1.8	1.66	−26.1	Yes	161	1.56
C6(0.84)-*co*-C5(0.16)	58.6	2.1	1.76	−27.9	Yes	148	1.59
C6(1.00)-*co*-C5(0.00)	49.6	1.5	1.54	−29.7	Yes	129	1.63

[a] Polymerization condition: chlorobenzene solution (20 wt%); temperature: 60 ± 0.5 °C; initiator: 2,2′-azobis(isobutyronitrile) (0.05%, based on total mole number of monomers).

[b] M_n: number-average molecular weight; M_w: weight-average molecular weight; PDI: polydispersity distribution index (M_w/M_n).

[c] T_g: glass transition temperature.

[d] T_{LC}: temperature at which the sample begins to show birefringent texture under polarized light optical microscope at a heating rate of 2 °C $\min^{-1}$.

Table 5
Copolymerization results of 2,5-di(*n*-hexoxycarbonyl)styrene and 2,5-di(*n*-butoxycarbonyl)styrene and thermotropic properties of the copolymers

Sample[a]	Yield (%)	M_n[b] (10^5)	PDI[b]	T_g[c] (°C)	Liquid crystallinity[d]	T_{LC}[d] (°C)	*d* Spacing (nm)
C6(0.00)-*co*-C4(1.00)	29.6	2.8	1.46	−2.0	Yes	91	1.44
C6(0.20)-*co*-C4(0.80)	62.1	2.2	1.44	−7.5	No	–	–
C6(0.39)-*co*-C4(0.61)	45.8	1.9	1.65	−9.9	No	–	–
C6(0.48)-*co*-C4(0.52)	46.6	2.0	1.49	−14.2	No	–	–
C6(0.62)-*co*-C4(0.38)	50.2	1.7	1.76	−17.8	No	–	–
C6(0.78)-*co*-C4(0.22)	39.8	1.6	1.79	−21.5	No	–	–
C6(1.00)-*co*-C4(0.00)	49.6	1.5	1.54	−29.7	Yes	129	1.63

[a] Polymerization condition: chlorobenzene solution (20 wt%); temperature: 60 ± 0.5 °C; initiator: 2,2′-azobis(isobutyronitrile) (0.05%, based on total mole number of monomers).

[b] M_n: number-average molecular weight; M_w: weight-average molecular weight; PDI: polydispersity distribution index (M_w/M_n).

[c] T_g: glass transition temperature.

[d] T_{LC}: temperature at which sample begins to show birefringent texture under polarized light optical microscope at a heating rate of 2 °C min^{-1}.

microscope, all the samples were colorless transparent solids and exhibited no discernible birefringence at ambient temperature. On raising the temperature, the copolymers behaved differently depending on the composition, the alkyl length difference, and the thermotropic behavior of the corresponding homopolymers of the structural units.

For C3(*x*)-*co*-C4(*y*)s, no matter what were the molar ratios of the monomers, birefringence appeared gradually at the

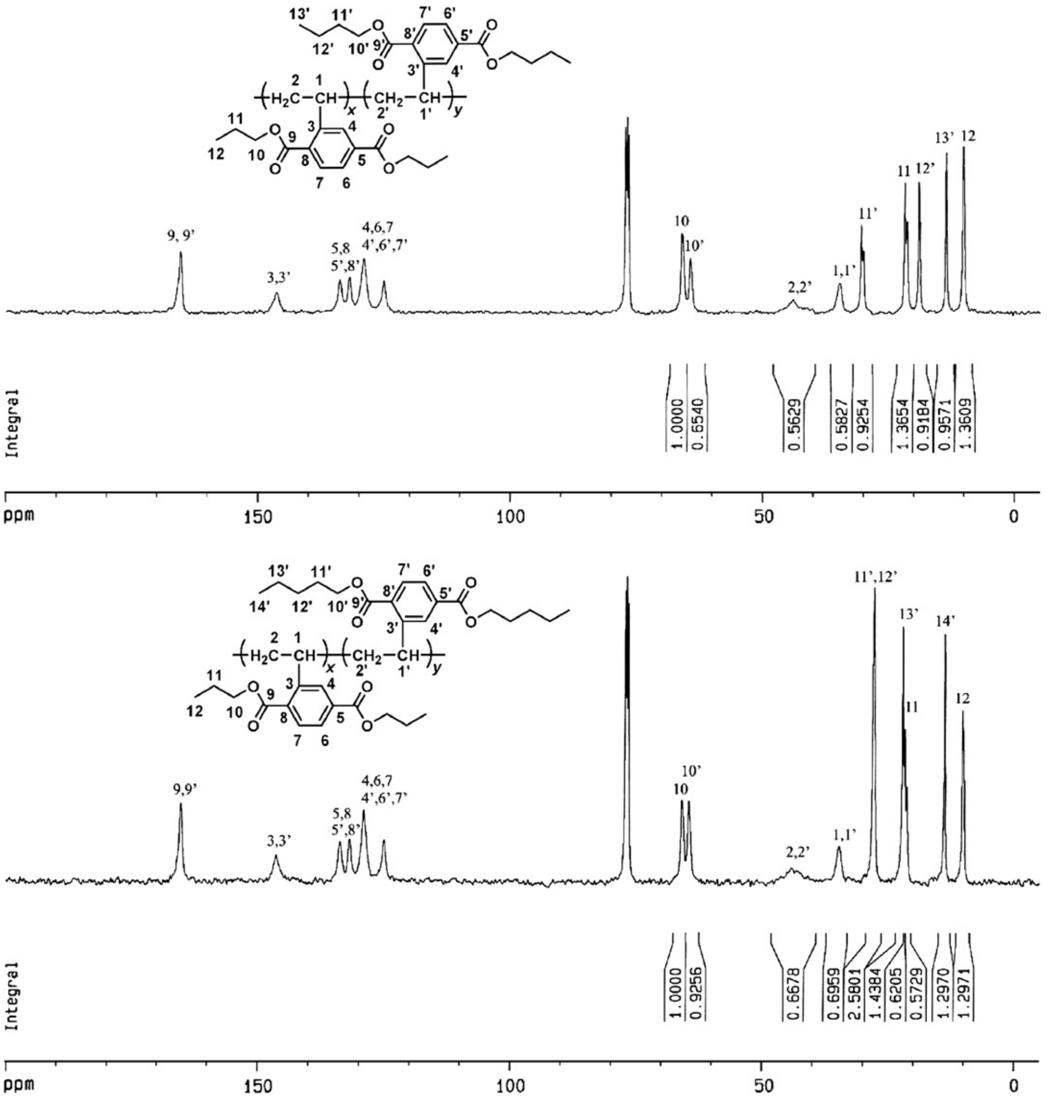


Fig. 1. ^{13}C NMR spectra of representative C3(0.60)-*co*-C4(0.40) (top) and C3(0.51)-*co*-C5(0.49) (bottom). (Bruker ARX 100 MHz, $CDCl_3$).

temperatures 100–140 °C higher than their T_gs, i.e., upon heating, C3(x)-*co*-C4(y)s entered isotropic melts first and then ordered into mesophase. Fig. 2a shows the representative focal-conic fan textures of C3(0.51)-*co*-C4(0.49) at 180 °C, which is one of the typical images of Φ_H phases [21,31]. Heating the samples further, no visible change was observed until thermal decomposition (onset temperature >300 °C). During the subsequent slowly cooling process, the textures underwent no obvious change. This suggests that the mesophase of the copolymers developed at high temperatures remains upon cooling, which is similar to the thermotropic behaviors of the corresponding homopolymers.

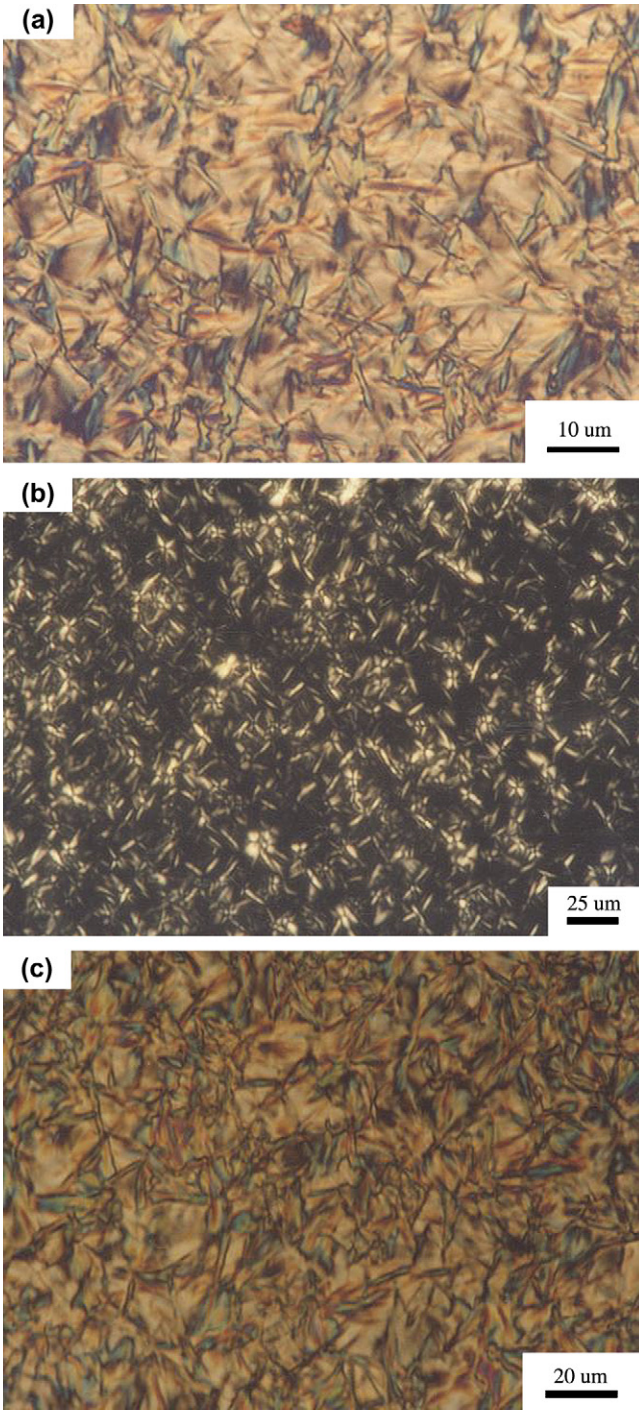


Fig. 2. Polarized light optical photographs of copolymers at 180 °C. (a) C3(0.51)-*co*-C4(0.49), (b) C3(0.10)-*co*-C5(0.90), and (c) C3(0.90)-*co*-C2(0.10).

The C3(x)-*co*-C5(y)s is distinguished from C3(x)-*co*-C4(y)s by the alkyl length difference of the monomer pairs. The alkyl length difference of the former is two, while that of the later is one. Owing to this small structural changes, C3(x)-*co*-C5(y)s displayed composition dependent thermotropic behaviors, and birefringence was observed only in the copolymers containing dominant C3 ($x > 0.95$) or C5 ($y > 0.85$). When the molar ratios of the two structural units were compared, $0.15 < x < 0.95$, no birefringence could be detected under POM in the temperature region studied irrespective of thermal history (such as heating, cooling, and isothermal annealing). Fig. 2b shows the typical optical polarizing micrograph of C3(0.10)-*co*-C5(0.90) at 180 °C. The birefringence appeared at about 150 °C, much higher than its T_g (−15 °C), and could be kept on the subsequent cooling run.

Above results suggest that for a series of homologous monomers that form mesogenic homopolymers, the copolymers formed from two neighboring monomers with only one carbon atom difference in their alkyl groups, e.g., C3(x)-*co*-C4(y)s, were all mesomorphic, but those copolymers formed from two every other monomers, e.g., C3(x)-*co*-C5(y)s, were mesomorphic only when one or the other monomer was dominant even though the two homopolymers were both mesomorphic. What if one of two monomers forms only nonmesogenic homopolymer?

Although the alkyl groups also differed by only one carbon atom, birefringence was only observed in C3(x)-*co*-C2(y)s containing more than 76 mol% of C3 units. Fig. 2c presents a representative focal-conic texture displayed by C3(0.90)-*co*-C2(0.10) at 180 °C.

The influence of the thermotropic properties of the corresponding homopolymers was also demonstrated in the POM observations of C6(x)-*co*-C5(y)s. For all C6(x)-*co*-C5(y)s, birefringence was formed at the temperatures 160–190 °C above their T_gs. However, the mesophase stability showed composition dependence. When x was above 0.52, the batonnet texture developed at high temperatures disappeared during the subsequent cooling process, which was similar to C6 homopolymer, otherwise the texture remained. It meant that the thermotropic behaviors of the corresponding homopolymers had a remarkable influence on the liquid crystallinities of the copolymers.

As to C6(x)-*co*-C4(y)s, similar to C3(x)-*co*-C5(y)s, no birefringence could be identified in the copolymers with x ranging from 0.20 to 0.78, again indicating the effect of length difference in the alkyl groups on the mesophase depression of the copolymers. When $x > 0.78$, the copolymer behaved like C6 homopolymer.

3.4. WAXD

The mesomorphic structures of the copolymers were further investigated with 1D and 2D WAXD experiments.

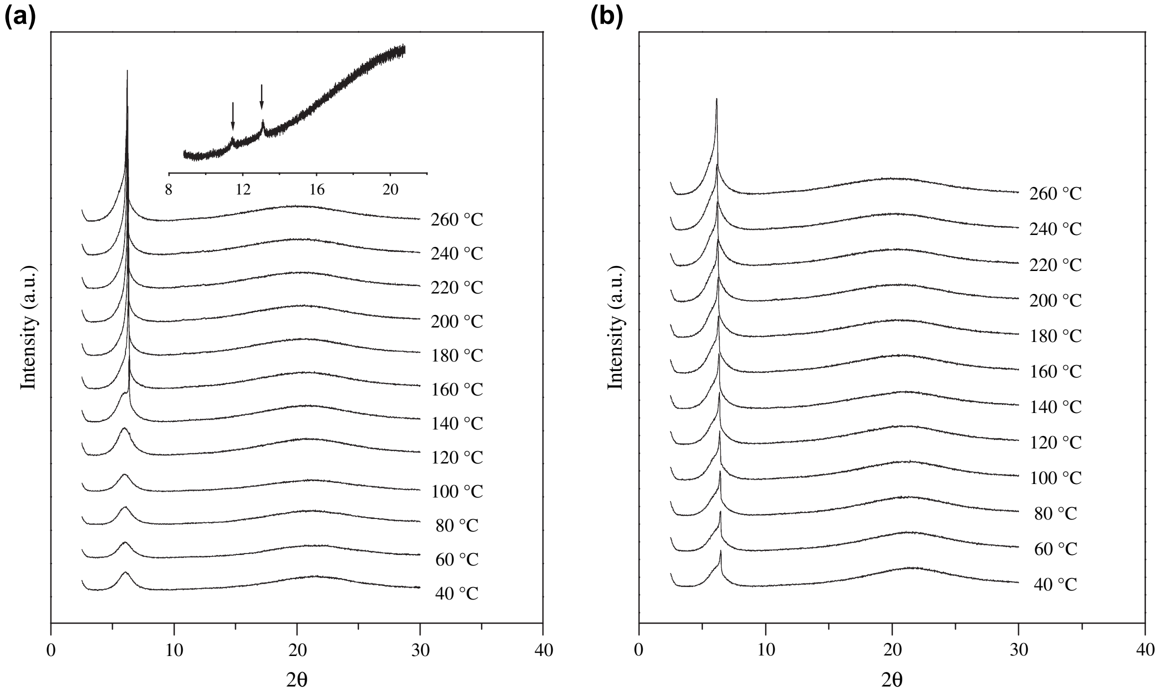


Fig. 3. One-dimensional wide-angle X-ray diffraction powder patterns of C3(0.51)-*co*-C4(0.49) during the first heating (a), the subsequent cooling course (b). The inset is the WAXD pattern obtained from sample annealed at 180 °C for 2 h.

Fig. 3 illustrates the temperature variable 1D WAXD patterns of C3(0.51)-*co*-C4(0.49) recorded during the first heating and the subsequent cooling runs. In the temperature interval 40–140 °C, scattering halos at ∼6° and ∼22° were present, indicating the existence of a disordered phase. Above 140 °C, a narrow reflection peak developed from the right shoulder of the scattering halo which centered at 6.4° (*d* spacing of 1.38 nm) was identified. Raising temperature further led to a substantial enhancement of the reflection peak intensity, and the peaks shifted slightly to lower angle region due to the thermal expansion. On decreasing the temperature gradually from 260 °C, the reflection peaks decreased in intensity but still exist even when the sample was cooled to 40 °C. It indicated that the mesophase formed at higher temperature was kept upon cooling, which was consistent with the POM observation.

The WAXD pattern obtained from C3(0.51)-*co*-C4(0.49) annealed at 180 °C for 2 h is shown in the inset of Fig. 3a and two weak reflection peaks at 11.4° (*d* spacing of 0.78 nm) and 13.1° (*d* spacing of 0.68 nm) are identified. The scattering vector ratio of the two diffraction peaks together with the strong peak at about 6.4° followed $1:3^{1/2}:4^{1/2}$, demonstrating a long-range ordered hexagonal lattice.

On the other hand, the high angle scattering halo ($2\theta - 22°$) retained the same shape in the temperature variable experiment, which coincided with that observed for the amorphous phase in semi-crystalline polyethylene [32]. It indicated that no long-range order was developed in the sub-nanometer length scale during the process.

Fig. 4 shows the 2D WAXD pattern of the oriented C3(0.51)-*co*-C4(0.49) sample with the X-ray incident beam parallel (Fig. 4a) and perpendicular to the fiber axis (Fig. 4b). A six-fold symmetry of the diffractions at about 6.4° was exhibited. The corresponding azimuthal intensity profile which exhibits six maxima with an angle of 60° between two adjacent diffraction maxima is shown in Fig. 4c. And two additional diffraction arcs along the meridian direction can be observed at about 11.4° and 13.1° in Fig. 4b. These three diffraction arcs can be assigned to be the (100), (110), and (200) planes indicating a long-range periodic hexagonal packing along the lateral direction perpendicular to the fiber axis. It demonstrated that a Φ_H phase was formed in C3(0.51)-*co*-C4(0.49), which was similar to the mesomorphic structure of C3 or C4 homopolymers. The mesomorphic structures of other copolymers in this series were also studied by the same way and were similar to that of C3(0.51)-*co*-C4(0.49).

One-dimensional WAXD experiments of C3(x)-*co*-C5(y)s and C3(x)-*co*-C2(y)s were carried out under the same conditions. Typical hexagonal lattice were observed in C3(x)-*co*-C5(y)s when $x > 0.95$ or $x < 0.15$. In the composition range of $0.15 < x < 0.95$, broad scattering halos in the low 2θ angle region were present in the temperature region studied, indicating no long-range ordered structures. As to C3(x)-*co*-C2(y)s, the hexagonal ordered structure existed only when $x > 0.76$.

The investigation of thermotropic behaviors of C6(x)-*co*-C5(y)s also demonstrated the formation of Φ_H phase in all the copolymers with tunable supramolecular dimensions. However, since reversible transition from isotropic to LC transition is observed in poly[2,5-di(*n*-hexoxycarbonyl)styrene], while the mesophase in poly[2,5-di(*n*-pentoxycarbonyl)-styrene] retains upon cooling, the mesophase stability of

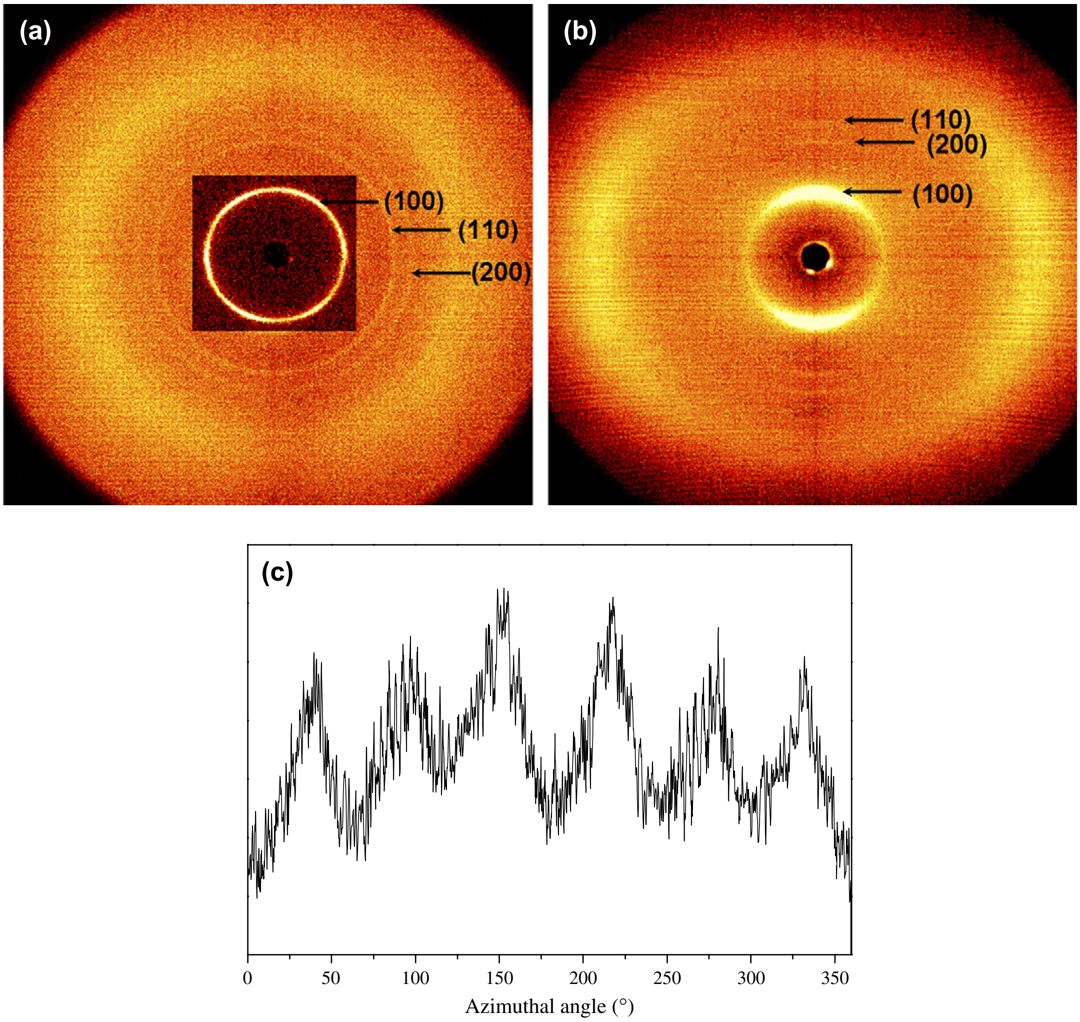


Fig. 4. Two-dimensional wide-angle X-ray diffraction fiber patterns of C3(0.51)-*co*-C4(0.49) with an X-ray incident beam parallel (a) and perpendicular to the fiber axis (b). The corresponding azimuthal intensity profile from a (c).

C6(x)-*co*-C5(y)s upon cooling showed composition dependent. Fig. 5 presents the temperature variable 1D WAXD patterns of C6(0.16)-*co*-C5(0.84) and C6(0.84)-*co*-C5(0.16) during the first cooling run. The narrow reflection peaks which centered at 5.8° (d spacing of 1.52 nm) and 5.6° (d spacing of 1.58 nm) were identified. Particularly, the diffraction peaks developed in C6(0.16)-*co*-C5(0.84) remained upon cooling while those of C6(0.84)-*co*-C5(0.16) diminished at lower temperatures, similar to the corresponding homopolymers. It agreed well with POM observations.

Fig. 6 represents the d spacings of the hexagonal ordered structures from 1D WAXD patterns at 180 °C as functions of molar ratios of C3 in feed (x) for C3(x)-*co*-C2(y)s, C3(x)-*co*-C4(y)s, and C3(x)-*co*-C5(y)s. The phase dimensions of C3(x)-*co*-C4(y)s decrease continuously with increasing C4 content within the whole composition. When C3(x)-*co*-C5(y)s are in Φ_H phases, i.e., $x > 0.95$ or $x < 0.15$, the d spacings also decrease with an increase in C3 content. In the case of C3(x)-*co*-C2(y)s, when $x > 0.76$, Φ_H phases are displayed, but the mesomorphic dimension is invariable regardless of the compositions.

3.5. Roles governing mesophase formation of copolymers

The thermotropic properties of poly[2,5-di(alkoxycarbonyl)styrene]s and the related copolymers might be rationalized by Self-Compacting Chain Model [33], which was developed by Allegra and Meille to explain the phase behaviors of flexible liquid crystalline polymers free of conventional ‘rod’- or ‘disk’-like mesogens, such as symmetrically substituted poly-[di(n-alkyl)siloxane]s [17,34], poly[di(n-alkyl)silylene]s [35], and poly[di(n-alkoxy)phosphazene]s [36,37]. As indicated in the previous section, certain poly[2,5-di(alkoxycarbonyl)-styrene]s and the related copolymers underwent isotropic-mesomorphic phase transition without accompanying enthalpy change upon heating, indicating a entropy-driven process. According to Self-Compacting Chain Model, the optimization of the organization of the side groups and the polymer main-chains leads to an overall extended conformation of the macromolecules in mesomorphic state. The entropy loss due to the straight-chain arrangement is overcompensated by the reduction of steric conflicts within the side groups by suppression of main-chain bending. Therefore, the mesophase achieves

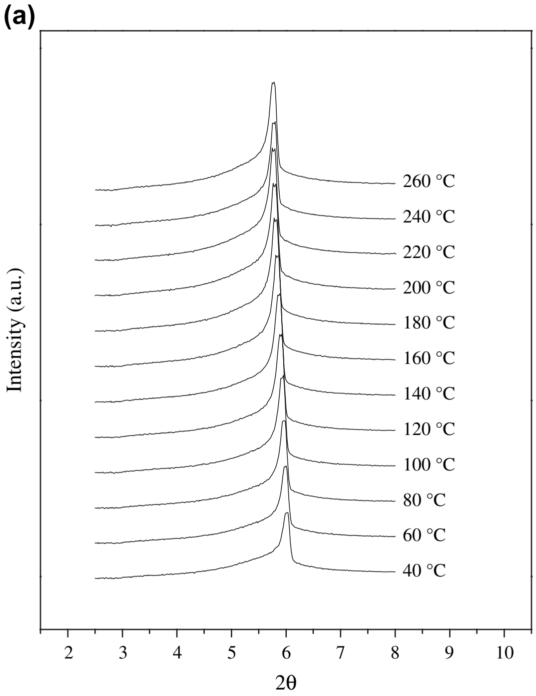


Fig. 5. One-dimensional wide-angle X-ray diffraction powder patterns in the low 2θ angle region of C6(0.16)-*co*-C5(0.84) (a) and C6(0.84)-*co*-C5(0.16) (b) during the first cooling course.

entropy stabilization as the side groups of each chain have a wider conformational freedom in liquid crystalline state than in isotropic state. It means that, despite the higher apparent order in the mesomorphic state, poly[2,5-di(alkoxycarbonyl)styrene]s with suitable length alkyl side groups may attain a larger entropy than in the liquid state. It also states that the larger the freedom difference of the side-groups between in ordered state and in disordered state, the stronger tendency of the polymer to develop into mesophase. The copolymerization of analogous monomers like 2,5-di(alkoxycarbonyl)styrenes leads to the co-existence of alkyl side groups with different lengths in the same main-chain. This should entail a decrease in the repulsive interactions between side groups and a larger conformational freedom of side groups than in homopolymers for a given degree of bending of polymer backbones. 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.

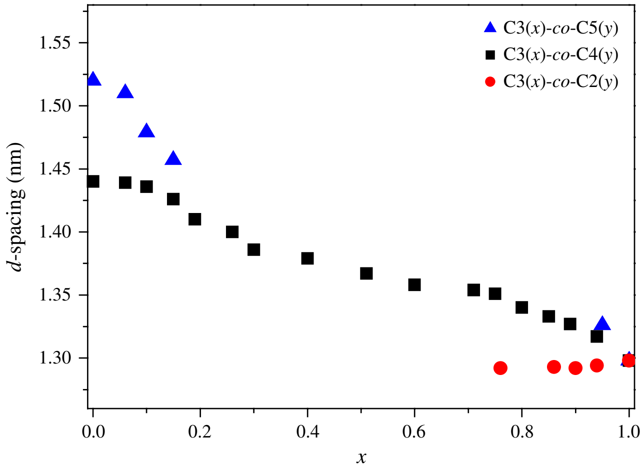


Fig. 6. *d* Spacing data of copoly[di(alkoxycarbonyl)styrene]s in low 2θ angle region as functions of the molar ratio of 2,5-di(*n*-propoxycarbonyl)styrene (*x*) at 180 °C.

In the case of C3(*x*)-*co*-C4(*y*)s and C6(*x*)-*co*-C5(*y*)s, where the alkyl side groups differ in only one carbon atom, the entropy increase (ΔS_S) of the side groups in liquid-mesophase transition can still overcompensate the entropy loss (ΔS_M) of the main-chains and Φ_H phases are achieved at all compositions. In the case of C3(*x*)-*co*-C5(*y*)s and C6(*x*)-*co*-C4(*y*)s, where the difference in *n*-alkyl side groups is two carbon atoms, the release of the steric conflicts of the side groups should be even stronger for a given degree of bending of main-chains. As a result, the mesophase formation would depend on the copolymer composition. When one component is dominant, ΔS_S is still more than ΔS_M and the same mesomorphic structures with that of the homopolymer of the dominating unit are formed. When the two components are comparative in the copolymers, ΔS_S is less than ΔS_M and mesophase depression is observed.

For the above four copolymers, the *d* spacings vary monotonously with the compositions. It reflects that both structural units cooperate to take cylindrical conformation, which is a prerequisite to ordered packing for such type LCPs. Such variation in mesophase dimension is similar to main-chain liquid crystalline random copolymers whose bulk properties show a high sensitivity to relatively small changes in the chemical structure and the compositions [26].

Poly[2,5-di(ethoxycarbonyl)styrene] is not a liquid crystalline probably because its side group is so short that the increase of conformational entropy value of ethyl side groups cannot balance the entropy loss of the main-chain. Due to the same reason, when C2 exceeding a certain amount is incorporated into the copolymers C3(*x*)-*co*-C2(*y*)s, no mesophase can be formed. When the molar content of C2 in the copolymers is less than 24%, the entropic balance between main-chain freedom and steric crowding of the side groups favor the copolymer backbones to adopt a cylindrical shape and hexagonal columnar phase is formed to maximize overall conformational entropy. The mesomorphic dimension of C3(*x*)-*co*-C2(*y*)s was consistent with that of C3 homopolymer regardless of copolymer compositions since poly[2,5-di(ethoxycarbonyl)styrene] is not liquid crystalline and small amount C2 units can't interrupt the mesomorphic structure of C3 homopolymer. The invariable mesomorphic behavior phenomenon is also observed in the copolymers based on MPCS and St or MMA when the monomer ratios of MPCS exceed certain values [38]. For the copolymers based on C4 and MPCS, when M_{MPCS} is above 0.5 or below 0.1, constant *d* spacing values of 1.58 nm for the former case and 1.44 nm for the latter case are also obtained regardless of the copolymer compositions [24]. The authors attribute it to the difference of mesomorphic structures of C4 (Φ_{H} phase) and MPCS (Φ_{HN} phase) homopolymers. When one structural unit is dominant, the copolymer molecules form the same ordered packing with the corresponding homopolymer.

4. Conclusion

Five series of binary random poly[2,5-di(ROOC)styrene-*co*-2,5-di(R′OOC)styrene]s were designed and synthesized via free radical polymerization. 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. For the copolymers made up of the monomers, the homopolymer of which is mesogenic, to form mesophases within the whole composition, the alkyl group length difference can't be more than one carbon atom. Changing the copolymer composition has the effect to tune the glass transition temperature and mesophase dimensions. Examples of which include C3(*x*)-*co*-C4(*y*)s and C6(*x*)-*co*-C5(*y*)s. When the length difference of alkyl groups is two carbon atoms, as in C3(*x*)-*co*-C5(*y*)s and C6(*x*)-*co*-C4(*y*)s, mesophase formation is depressed when the molar ratios of two monomer pairs are comparative and hexagonal columnar phase can only be observed in copolymers with dominant content of one co-unit. The mesomorphic dimension also depends on the copolymer composition. Additionally, in the case that the molar ratio of C6 is dominant, the copolymers show reversible transition from isotropic to hexagonal columnar phase, which is similar to poly[2,5-di(*n*-hexoxycarbonyl)styrene].

For the copolymers C3(*x*)-*co*-C2(*y*)s, where one comonomer C2 differs others by the fact that its homopolymer is non-mesogenic, the hexagonal columnar phase is only displayed in the copolymers containing more than 76 mol% of C3. The mesophases are stable once formed and the *d* spacing in the WAXD pattern is independent of the variation of the copolymer compositions.

Acknowledgements

The financial support from the National Natural Science Foundation of China (Grants 20674001 and 20634010) and National Distinguished Young Scholar Fund (Grant 20325415) is gratefully acknowledged.

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