Polymer 50 (2009) 4813–4820

Contents lists available at ScienceDirect

Polymer

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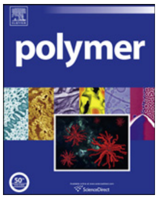

Synthesis and characterization of main-chain liquid crystalline copolyesters containing phosphaphenanthrene side-groups

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A R T I C L E I N F O

Article history:
Received 21 January 2009
Received in revised form
24 July 2009
Accepted 12 August 2009
Available online 14 August 2009

Keywords:
Main-chain liquid crystal polyesters
Phosphaphenathrene
Parallel side-groups

A B S T R A C T

A series of thermotropic main-chain liquid crystalline copolyesters P1–P5 containing 2-(6-oxide-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-dihydroxyphenylene (ODOPB) as non-mesogenic unit and 4,4′-dihydroxybiphenyl (DB) as mesogenic unit were prepared by polycondensation with sebacoyl chloride. The thermal and mesogenic properties were characterized by differential scanning calorimetry (DSC), polarizing optical micrography (POM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). It was found that introducing of ODOPB into polyester decreased the melting temperature (Tm) and the isotropic temperature (Ti). The copolyesters P1–P5 exhibited mesomorphic properties even when the molar ratio of the non-mesogenic monomer ODOPB to mesogenic monomer DB reached 6:4 in feed. For explaining the effect of DOPO group on the mesomorphic properties, the X-ray diffraction analysis of a low molecular weight modal compound containing ODOPB was carried out and the results show that the DOPO side-group is parallel with the most-adjacent benzene ring in the main-chain, which reveals the small effect of ODOPB on the mesogenic structure of polyesters. The thermal analysis showed that the incorporation of phosphorus-containing moieties increase the residual char of the formed liquid crystalline polymers. The thermal stability, however, decreases because the O=P–O bond is less stable than the common C–C bond.

1. Introduction

The main-chain thermotropic liquid crystalline polymers (MCLCPs) have still been attracting much attention owing to their scientific interests and numerous industrial applications [1–6]. The aromatic main-chain liquid crystalline polymers usually exhibit insoluble properties and high melting temperatures because of their rigid and symmetrical conformation. The structural modifications have been used to increase the solubility and reduce the melting point. Several approaches were reported including copolymerization of several aromatic monomers to obtain a more random backbone composition [7–9], introduction of lateral substituents to disrupt the chain symmetry [10–12], and introduction of non-mesogenic flexible spacers in the main-chain [13–16]. Incorporation of phosphorus in the polymers could increase the solubility, thermal stability and fire retardant properties, however, the studies on phosphorus-containing liquid crystalline polymers (LCPs) were mainly concentrated with phosphonate or phosphate groups in the main-chain [10,17–19]. Kannan et al synthesized LCPs containing phenylphosphonate segments in the main-chain along with different methylene groups [16]. The glass temperature of these phosphorus-containing polymers is much lower than that of non-phosphorus polymers.

As a novel retardant, 9,10-dihydro-9-oxa-10-phosphaphenathrene-10-oxide(DOPO) and its derivative ODOPB, which structures are shown in Scheme 1, have been extensively studied [20–29]. The research work, however, mainly focused on the characterization of retardant and other physical properties of materials by the introducing of them into polymers. Wang's group synthesized some kinds of phosphaphenathrene-containing wholly and partial aromatic thermotropic copolyesters with high flame retardancy (limiting oxygen index, up to 70%) and prepared in situ reinforced PET composites that have both better flame retardancy and mechanical properties than pure PET. The melt dripping behavior of PET was also improved [20–24].

In this study, we used ODOPB as a third component, 4,4′-dihydroxybiphenyl (DB) as mesogenic monomer [30–33] to synthesize a series of liquid crystalline copolyesters by polycondensation with sebacoyl chloride. We emphatically studied the influence of ODOPB on the thermotropic liquid crystalline behaviors and thermal

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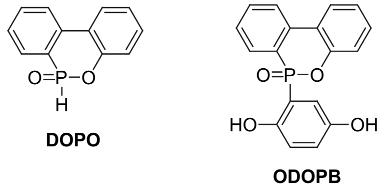
doi:10.1016/j.polymer.2009.08.016



Scheme 1. The molecular structures of DOPO and ODOPB.

properties of the DOPO-containing copolyesters. Moreover, we obtained a low molecular weight modal compound containing ODOPB (MD3) and modal polymer without DOPO as the side-group (PD1), as shown in Scheme 2, to distinguish the effect of side-group DOPO on the interaction of copolymer chains. Specially, we analyzed the single-crystal structure from MD3 to confirm the conformation of DOPO group, which could explain the effect of DOPO group on the mesomorphic properties. At present, our research group is focused on carrying out a more detailed mechanical properties related to the DOPO-containing polymers.

2. Experimental section

2.1. Materials

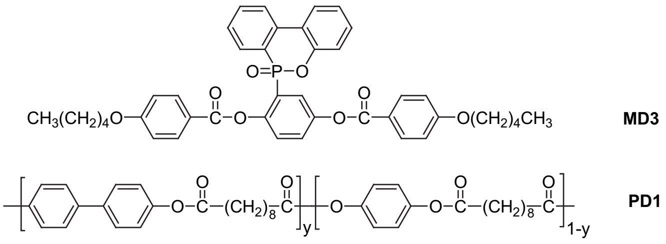
ODOPB and sebacoyl chloride (SC) were prepared in our laboratory according to the literatures [18,19]. MD3 was prepared by reaction of *p*-pentyloxybenzoyl chloride with 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-dihydroxybenzene in *o*-dichlorobenzene [34]. Other reagents were chemical pure and used as received.

2.2. Synthesis of liquid crystalline copolyesters P0–P6 containing ODOPB

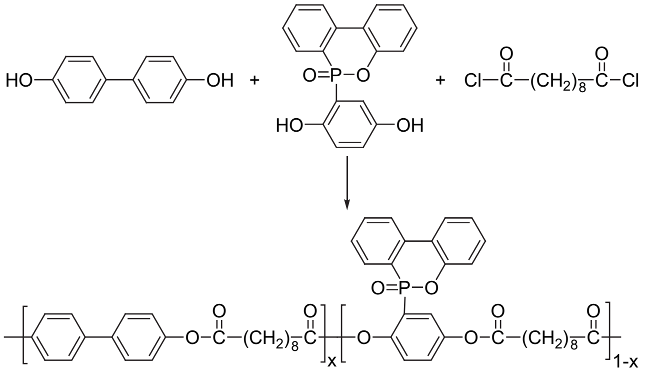
The synthetic route of P1 was chosen as standard procedure and shown in Scheme 3. ODOPB (0.648 g, 0.002 mol), 4,4′-dihydroxybiphenyl (3.654 g, 0.018 mol), sebacoyl chloride (4.78 g, 0.02 mol) and 50 mL of o-dichlorobenzene were mixed, stirred and heated at 80 °C for 30 min. And then the solution was stirred at 170 °C for 15 h. After cooling to room temperature, the solution was poured into 400 mL of petroleum ether. The precipitate was filtered and washed with 20 mL of ethanol, then dried under vacuum for 24 h. The P1 was obtained with about 95% yield. The other copolyesters P2–P5 and homopolyesters P0 and P6 were prepared by the similar procedure. The feed molar ratios were summarized in Table 1.

2.3. Synthesis of liquid crystal copolyester PD1

The copolyester PD1 was prepared by similar procedure with P1 as shown in Scheme 4. Hydroquinone (0.11 g, 0.001 mol), 4,4′-dihydroxybiphenyl (1.86 g, 0.009 mol) and sebacoyl chloride (2.39 g, 0.01 mol) were added into 25 mL of *o*-dichlorobenzene as solvent and reacted at 170 °C for 15 h. After cooling to room temperature, the solution was poured into 300 mL of petroleum ether. The precipitate was filtered and washed with 20 mL of ethanol, then dried under vacuum for 24 h. The PD1 was obtained with 95% yield.



Scheme 2. The molecular structures of MD3 and PD1.



Scheme 3. Synthesis of liquid crystalline copolyesters P0–P6 containing phosphaphenathrene side-groups.

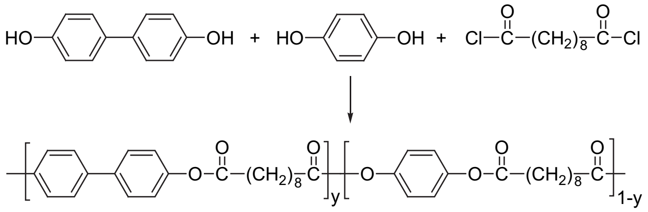
2.4. Characterizations

FT-IR spectra were determined on a Perkin–Elmer 2000 FTIR. DSC thermograms were recorded on a thermal analysis (TA) DSC-2100 at a heating rate of 10 °C/min from 0 °C to 300 °C under nitrogen. TGA spectra were performed with a TA TGA-2000 thermogravimetric analyzer with a heating rate of 15 °C/min in a nitrogen atmosphere from 50 °C to 600 °C. Optical microscopy was performed on a Leitz Laborlux-12 POM with Leitz-350 hot stage. The relative molecular weights of the polyesters were determined using a size-exclusion chromatograph (SEC) system equipped with a Waters 510 HPLC pump with linear polystyrene as standards and THF used as solvent. Wide-angle X-ray diffraction (WAXRD) patterns were recorded on a PANalytical X'pert Pro MPD × Powder X-ray diffractometer using 1.5418 Å Cu Kα wavelength at room temperature (scanning rate: 0.025 ^{o}/s). Small-angle X-ray diffraction (SAXRD) experiment was carried out using PANalytical Anton Paar SAXSess. The single-crystal X-ray diffraction was performed on a Quantum Design MPMS XL-5 SQUID system equipped with a horizontal rotator sample holder. The data were collected on a Nonius Kappa CCD with Mo KR radiation ($\lambda = 0.71073$ Å) at 293 K. Single crystal of MD3 was grown from acetonitrile aqueous solution. The structure was solved by direct methods and refined with full-matrix least-squares on *F*2 using the SHELX-97 program. All non-hydrogen atoms were refined anisotropically.

Table 1
The parameter of the synthesized liquid crystalline polyesters P0–P6.

Polyesters	Feed molar ratio of SC:ODOPB:DB	Yield/%	$\overline{Mw}$[a]	$\overline{Mw}/\overline{Mn}$[a]	The ratio of ODOPB to DB in polyester
P0	10:0:10	95	7600	1.31	0:10[c]
P1	10:1:9	95	5600	1.11	1.1:8.9[b]
P2	10:2:8	76	5800	1.15	2.5:7.5[b]
P3	10:3:7	69	5900	1.18	3.3:6.7[b]
P4	10:4:6	63	6800	1.22	4.9:5.1[b]
P5	10:6:4	62	5600	1.10	6.2:3.8[b]
P6	10:10:0	53	5100	1.11	10:0[c]

[a] Estimated by GPC in THF on the basis of a linear polystyrene calibration.
[b] Calculation from the area ratio of IR peak 750 cm^{-1} (P–O–Ph) to the sum of 2950 cm^{-1} and 2850 cm^{-1} (C–H).
[c] Calculation according to feed.



Scheme 4. Synthesis of liquid crystalline polyesters PD1.

3. Results and discussion

3.1. Synthesis of copolyesters

The feed ratios and results of copolyester were summarized in Table 1. The yields of P0–P6 gradually decrease from 95% to 53%, respectively. Meanwhile, weight-average molecular weights of copolyesters were also decreased from 7600 of P0 to 5100 of P6 with the feed ratio increase of the ODOPB. ODOPB groups can enhance the rigidity and polarity of polymeric chains due to containing a polar side-group DOPO, which can subsequently reduce the reactivity of functional end-groups and hindrance further propagation. The molecular weight distributions of all products were relative narrow (up to 1.3), which is attributed to the high-active monomers and the relative low-active rigid polyester chains.

3.2. IR characterization

Comparing with FT-IR spectra of homopolyesters P0 and P6, the absorptions at 750 cm^{-1} (P–O–Ph) and 1595 cm^{-1} (P–Ph) were observed in P3, as shown in Fig. 1, indicating that the copolyester containing ODOPB moieties was successfully produced. The peak absorption at 750 cm^{-1} is in proportion to the molar ratios of ODOPB in copolyesters. The peak absorption at 2926 and 2850 cm^{-1} (C–H) attributed to methylene groups in sebacoyl chloride should be constant. So the cumulative molar fractions of ODOPB in different copolyesters could be calculated through the ratios of the peak area at 750 cm^{-1} to that at 2926 and 2850 cm^{-1}, as shown in Fig. 2. The molar ratios of ODOPB to DB were 0:10 in P0 and 10:0 in P6, from which the results were calculated and summarized in Table 1. The cumulative ratio of ODOPB in copolymers is in proportion to the content of ODOPB monomer in feed, therefore the copolymerization was carried out completely.

The calculated equation of $R1$ is $R1 = \dfrac{[ODOPB]}{[ODOPB]+[DB]} = \dfrac{[ODOPB]}{[SC]}$;

The calculated equation of $R2$ is

$$R2 = \frac{[A_{750cm^{-1}}/(A_{2850cm^{-1}}+A_{2926cm^{-1}})]_{P1-P5}}{[A_{750cm^{-1}}/(A_{2850cm^{-1}}+A_{2926cm^{-1}})]_{P6}}$$

3.3. Thermal properties

ODOPB as a third monomer was copolymerized with 4, 4′-dihydroxybiphenyl (DB) and sebacoyl chloride to prepare DOPO-containing main-chain liquid crystalline copolyesters. The thermal transition behaviors of the ODOPB-containing copolyesters were examined by differential scanning calorimetry shown in Figs. 3 and 4. The DSC data were summarized in Table 2.

On the second heating cycle, three endothermic peaks are observed and attributed to the crystal-crystal transition temperature (Tc) [35–38], the melting temperature (Tm) and the isotropic temperature (Ti). Below the 3:7 molar ratio of ODOPB to DB, the three temperatures decrease slightly. The enthalpy values of the phase transitions both from crystalline to liquid crystalline and from liquid crystalline to liquid state decrease evidently. When the molar ratio of ODOPB/DB was higher than 3:7, Tm and Ti decrease quickly with increasing the value of ODOPB/DB. The corresponding enthalpy values also decrease.

These experimental results reveal that the mesogenic moities in the copolymers P0–P3 can basically keep the regular arrangement due to the lower amount of ODOPB, which makes Tm of the copolyesters to change little. The phosphathrene group of ODOPB as side substitute, however, increases the distance between polymeric chains and weakens the intermolecular interaction between mesogenic units, which leads to the decreasing of the enthalpy values of the melting phase transition. It also causes the mesophase to

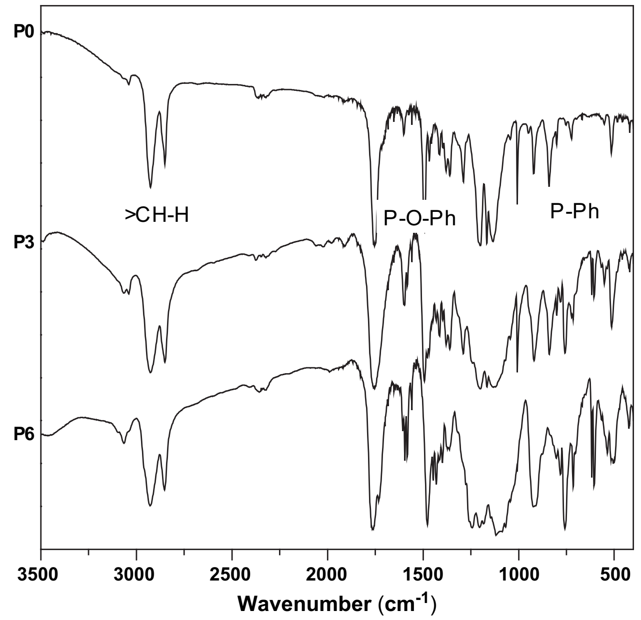


Fig. 1. The FT-IR spectra of P0, P3 and P6.

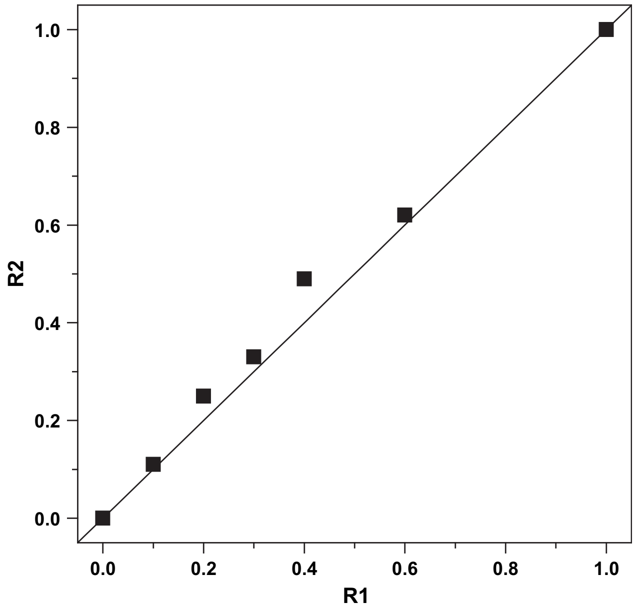


Fig. 2. The relationship of the cumulative molar fractions R2 of ODOPB segments in copolyesters via the feed molar ratios R1 of ODOPB in total dihydroxy monomers.

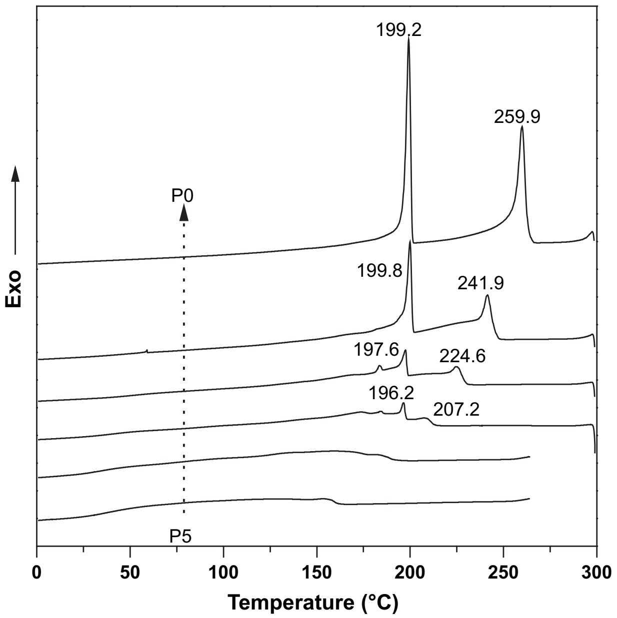


Fig. 3. The DSC curves of polyesters P0–P5 during the first cooling cycle (10 °C/min).

difficultly keep stability at higher temperature and the Ti accordingly decreases too. With introducing of more ODOPB into copolyesters, more and more non-mesogenic structure replaces liquid crystalline structure which makes the Tm and Ti of copolymers P4 and P5 decreasing largely. The analysis results of DSC data on the first cooling cycle are similar to those on the second heating cycle.

In order to further investigate the influence of phosphaphenathrene substitute on the mesormorphic properties, we designed and synthesized liquid crystalline copolyester PD1 without DOPO side-groups as model counterparts of P1. Fig. 5 shows the DSC curves of PD1 during the first cooling and second heating scans. The thermal analysis results were summarized in Table 2. Comparing with P1, Tm of PD1 decreases but Ti basically keeps constant, and ΔT(Ti–Tm)increase from 56 °C for P1 to 92 °C for PD1. It indicates that the phosphaphenathrene group as side substitute increases the distance between main-chains and decreases the interaction between them, which blocks the mesogenic units to form mesophase at a certain extent and makes the enthalpy values of whether Tm or Ti both decrease.

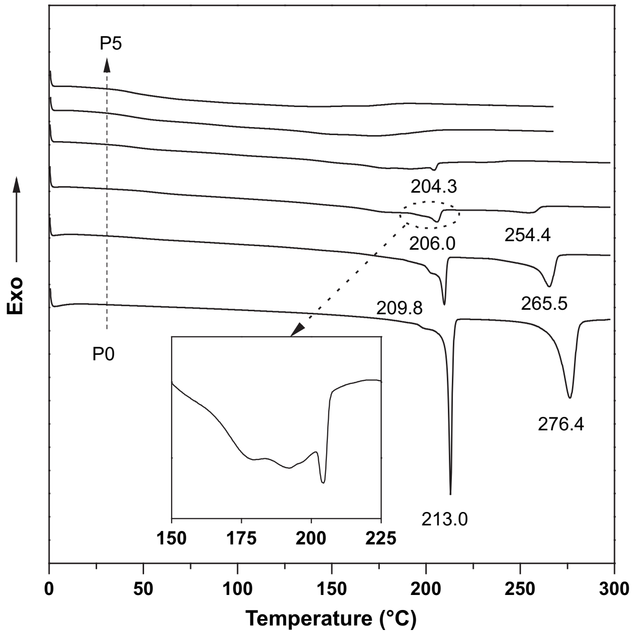


Fig. 4. The DSC curves of polyesters P0–P5 during the second heating cycle (10 °C/min).

Table 2
DSC results of the polyesters[a].

Polyester	T,°C(ΔH, J/g)	
	First cooling	Second heating
P0	i 259.9 (−38.8); S 199.2 (−35.8) k	k_1 198.3; k_2 213.0(34.9); S 276.4 (47.6) i
P1	i 241.9 (−6.9); S 199.8 (−17.8) k	k_1 191.2; k_2 209.8(12.4); S 265.5 (10.5) i
P2	i 224.6 (−4.5); S 197.6 (−3.7) k	k_1 177.8; k_2 206.0(5.4); S 254.4 (4.7) i
P3	i 207.2 (−1.7); N 196.2 (−1.7) k	k_1 177.2; k_2 192.4(–[b]); N 204.3(–[b]) i
P4	–[b]	k_1 148.6; k_2 172.8(–[b]); N 186.2(–[b]) i
P5	–[b]	k_1 –[b]; k_2 132.6(–[b]); N 168.7(–[b]) i
PD1	i 254.0 (−31.50); S 166.1 (−26.25) k	k 175.5(24.5); S 267.2 (41.1) i

[a] Data taken from the DSC thermograms recorded under nitrogen in the first cooling and second heating scans; abbreviations: k = semicrystalline state, S = smectic phase, N = nematic phase, i = isotropic state.
[b] It can not be distinguished clearly.

To the first peak Tc existed in Fig. 4, we noted that PD1 exhibits only two endothermic peaks corresponding to Tm and Ti and without the appearance of Tc. The phenomenon should be attributed to the introduction of phosphaphenathrene as side-group into main-chain, which induce the two kinds of regular arrangement between mesogenic units and fabricate the two crystal structures. The first crystal structure depended on biphenyl mesogenic moieties was studied in many articles. Now the second ones brought from ODOPB units is carefully carried out for the characterization.

3.4. *Mesomorphic structures*

Except for P6, copolyesters P1–P5 easily reveal the liquid crystalline textures observed by POM shown in Fig. 6 and their textures are different from P1 to P5. The mesomorphic texture of homopolyester P0 was observed only at higher temperature. But for

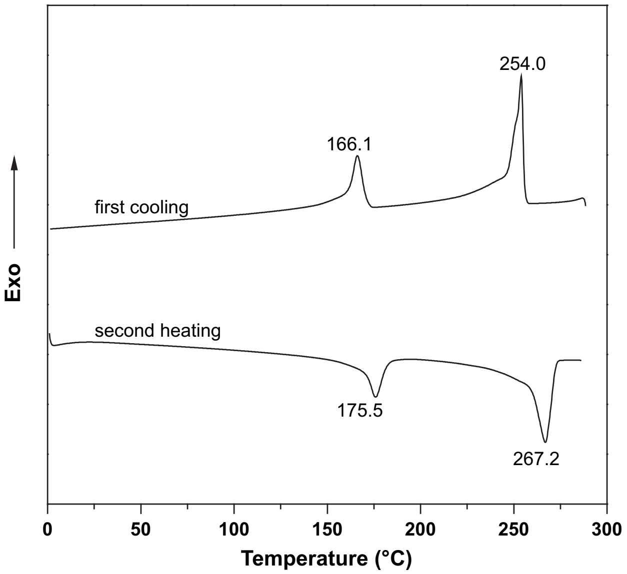


Fig. 5. DSC curves of polyester PD1.

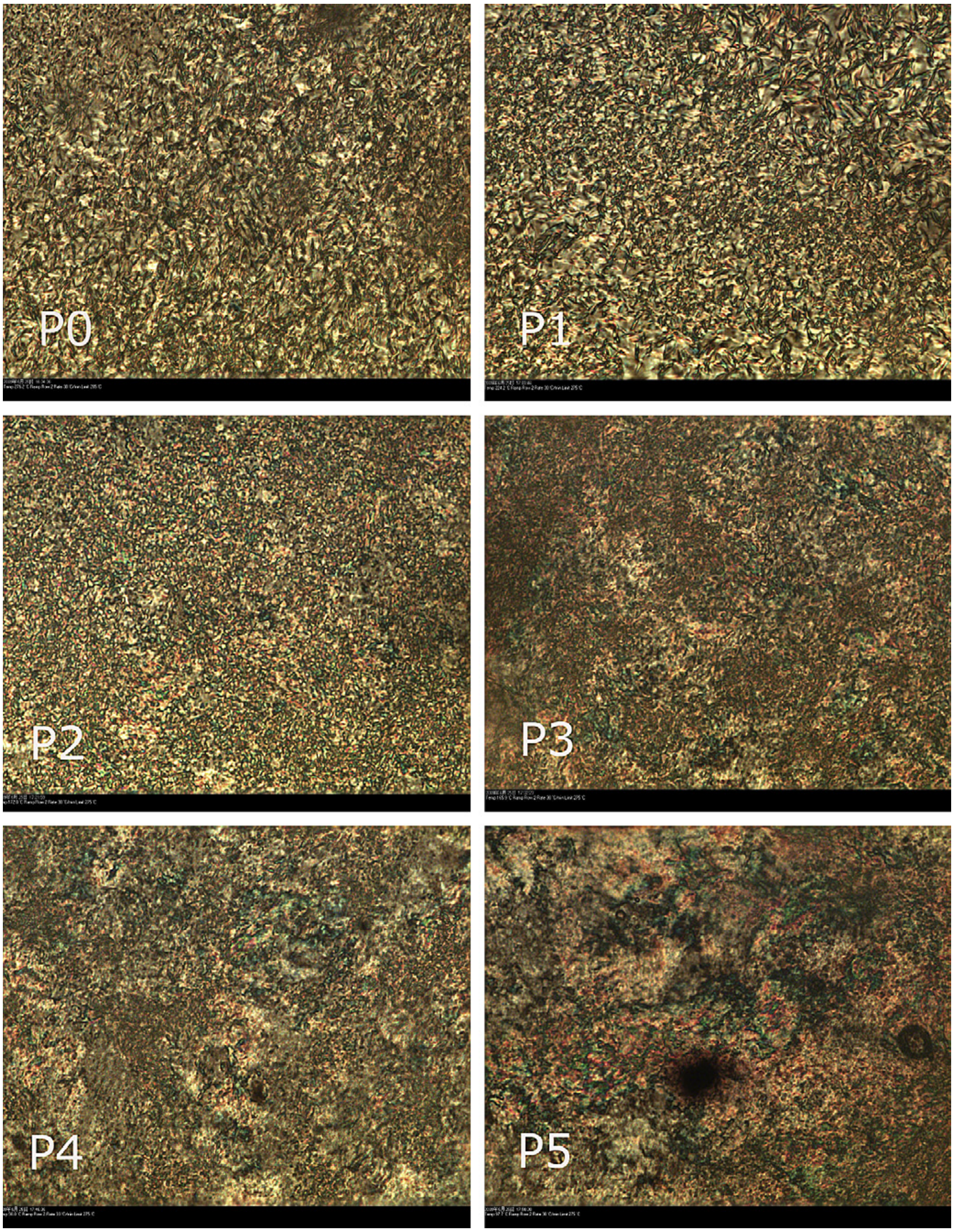


Fig. 6. POM images (4 × 100) of the P0–P5 at different temperatures during heating. (P0: 266 °C; P1: 224 °C; P2: 180 °C; P3: 166 °C; P4: cooled; P5: cooled).

P1–P5 the mesomorphic textures are easily observed below 270 °C. It is reasonable that the DOPO as side-group increases the distance between the chains and decreases copolymer's crystallinity to make copolymers easily into liquid crystalline states.

The WAXRD synchrotron profiles obtained for homopolyester P0 and copolyesters P1, P3, and P5 at room temperature and their separate liquid crystalline states were presented in Fig. 7 (a) and (b). The four narrow peaks in WAXRD diffractogram of P0 at 25 °C are located at 0.38, 0.41, 0.43 and 0.47 nm with the maximum value at 0.43 nm corresponding to the average intermolecular distances in the crystal state. It indicates that P0 has high crystalline degree and well-ordered crystal structure. However, there is only a broader peak at 0.42 nm in WAXRD diffractogram for P1, two peaks at 0.42 nm and 0.47 nm with the bigger value at 0.47 nm for P3 and P5. Those indicate that the introducing of DOPO as side-group into the main-chain of polyesters destroys the regularity between chains and decreases the crystalline degree. With the increasing of the content of ODOPB in copolymers the distances between chains increase. When the temperature was at 225 °C which is just over the Tm, the diffractograms of P0 and P1 are similar with only a narrow peak at 0.45 nm. But the peak slightly shifts to large chain distance at 0.49 nm for P3 and 0.48 nm for P5.

The SAXRD diffractograms of P1, P3 and P5 is presented in Fig. 7 (c) and (d). At room temperature, two peaks appear at 1.61 and 1.95 nm for P1, two peaks at 1.74 nm and 2.17 nm for P3, and broader peak between 1.5 nm and 2.5 nm for P5. Those demonstrate that with more ODOPB into the copolymers Bragg spacing turns to increase. When those copolymers were separately heated into liquid crystalline states, the SAXRD shows only one peak at 1.72 nm for P1, which are derived from the corresponding

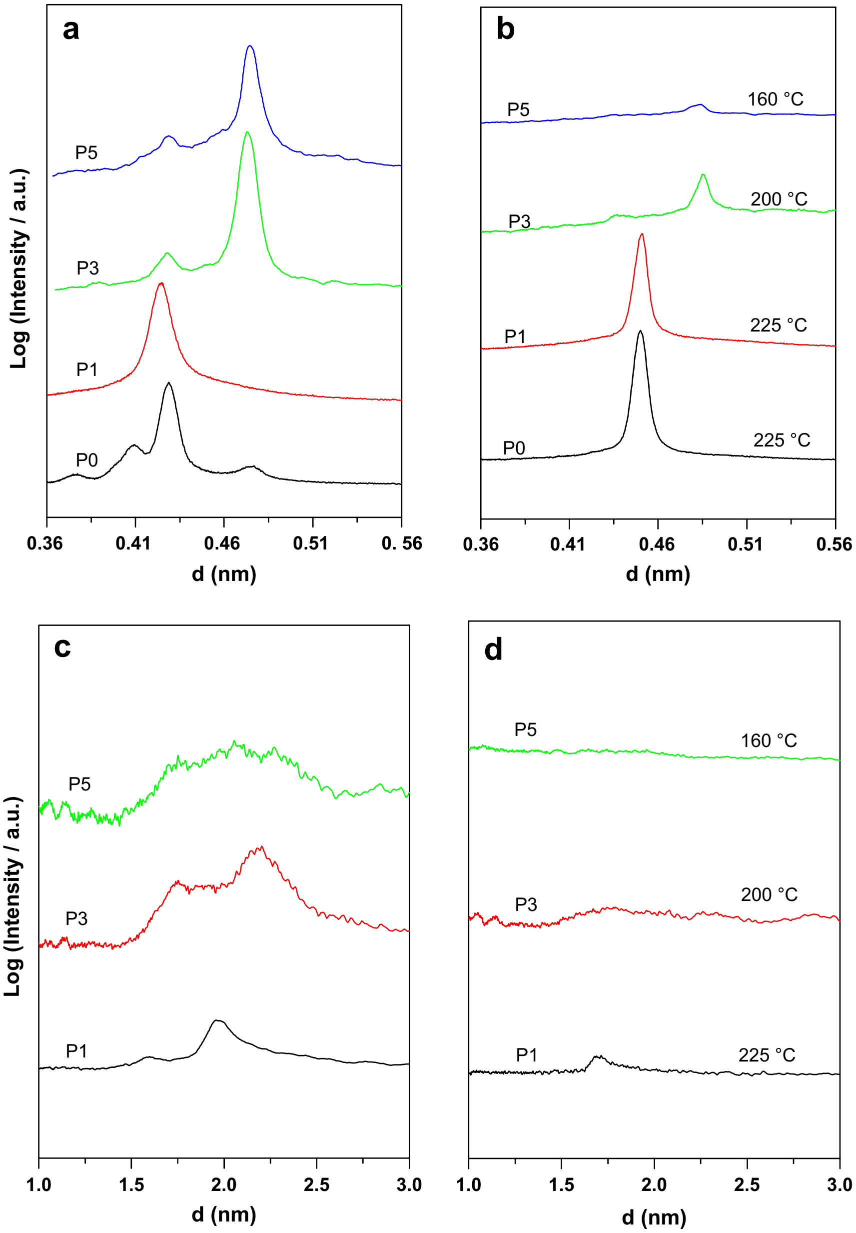


Fig. 7. (a) WAXRD of P0, P1, P3 and P5 heated at 25 °C; (b) WAXRD of P0, P1, P3 and P5 separately heated at 225 °C, 225 °C, 200 °C and 160 °C; (c) SAXRD of P1, P3 and P5 heated at 25 °C; (d) SAXRD of P1, P3 and P5 separately heated at 225 °C, 200 °C, and 160 °C.

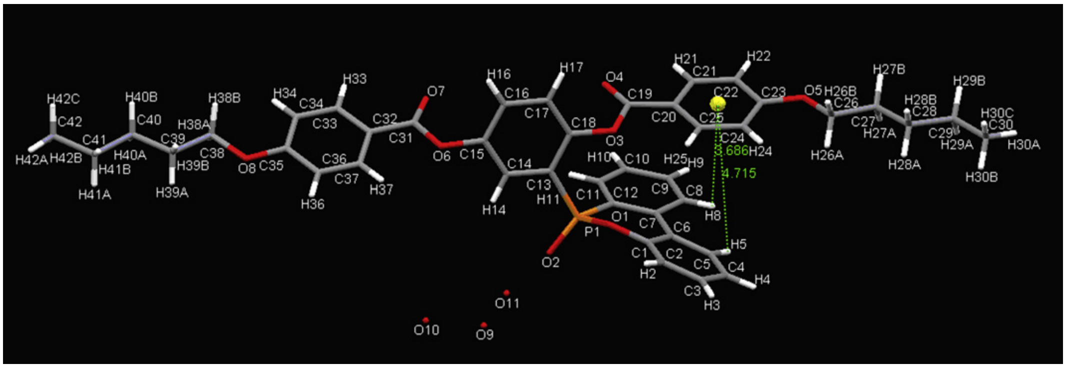


Fig. 8. The schematic intramolecular interaction between phosphaphenathrene group and the most-adjacent benzene ring in the MD3.

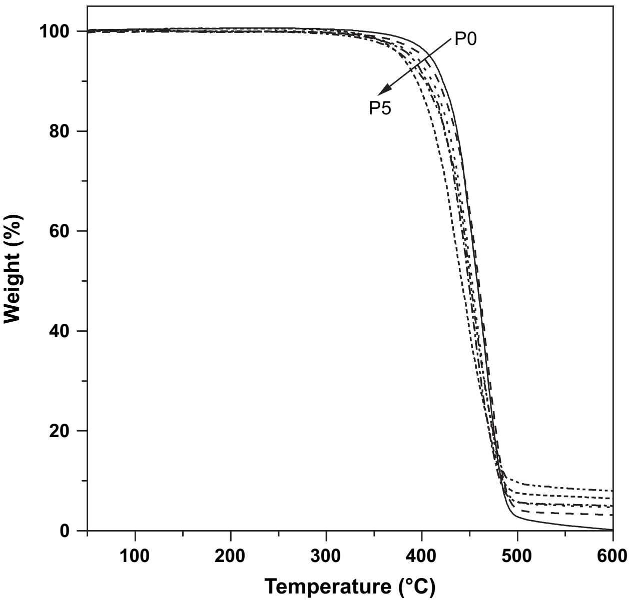


Fig. 9. TGA thermograms of polyesters P0–P5.

d-spacing of smectic orientations of the mesogens and very close to that of P0 [39]. However there are no peaks for P3 and P5, their liquid crystalline textures are nematic phases.

In order to get the detailed structure information with DOPO as side-group, a model compound MD3 was synthesized. The single crystal of MD3 was grown during the slow crystallizaton in mixture solvent of acetonitrile and water. Crystal size of 0.37 mm × 0.20 mm × 0.17 mm was used for X-ray structure determination. The results demonstrate that the crystal of MD3 belong to monoclinic system with space group P 2(1)/c [Mw = 758.77 g/mol, $a = 1.14097$ (4) nm, $b = 2.70219$ (10) nm, $c = 1.35331$ (6) nm, $\alpha = 90^\circ$, $\beta = 103.72^\circ$ (14), $\gamma = 90^\circ$ where Dc = 1.243 g/cm^3 for $Z = 4$ and $V = 4.0534$ (3) nm^3]. The plane of DOPO ring in MD3 (shown in Fig. 8) is parallel with the most-adjacent benzene ring because the distance and the angle of C–H–π center between H8 and C–H–π center are 0.3636 nm and 84.56°, and those between H5 and C–H–π center are 0.4715 nm and 89.20°, respectively. Thus regular arrangement between the mesogenic units in the presence of DOPO has no obvious difference with that in the absence of DOPO. The analysis result explains that the liquid crystal properties are maintained even in the molar ratio of ODOPB/DB to be 6:4.

3.5. *Thermal stability*

The thermal stability of synthesized polyesters was characterized with TGA as shown in Fig. 9. The temperatures of 5% weight loss ($T_{5\%}$) and char yields at 600 °C were summarized in Table 3. This series of copolymers decompose in only one-stage weight loss process due to more aliphatic moieties in the structure [40] and their lower molecular weights.

Table 3
Temperature of 5% weight loss ($T_{5\%}$) and char yields at 600 °C of the polyesters.

	Polyesters							
	P0	P1	P2	P3	P4	P5	P6	PD1
$T_{5\%}$/°C	408	400	396	386	380	375	378	410
Char yields at 600 °C/%	0.2	3.1	4.5	5.0	7.9	6.5	4.7	0.1

With the increase of ODOPB in feed, $T_{5\%}$ decreases from 408 °C for P0 to 378 °C for P6. As the counterpart copolyester P1, $T_{5\%}$ of PD1 is 410 °C, which is 10 °C higher than that of P1. The results indicate that the introduction of ODOPB decrease the thermal stability of polyesters because the O=P–O bond is less stable than the common C–C bond.

Polymers P0 and PD1 without DOPO groups have lower char yields at 600 °C down to 0.2 *wt%* and 0.1 *wt%*. The char yields firstly increase from 3.1 *wt%* for P1 to 7.9 *wt%* for P4, and then decrease to 4.7 *wt%* for P6 with the increase of ODOPB content in copolymers. These results demonstrate that ODOPB could improve the ability of copolymers to form char.

4. Conclusions

A series of thermotropic main-chain liquid crystal copolyesters (P1–P5) containing 2-(6-oxide-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-dihydroxyphenylene (ODOPB) as non-mesogenic unit and 4,4′-dihydroxybiphenyl (DB) as mesogenic unit were prepared by solution polycondensation with sebacoyl chloride. The X-ray single crystal diffraction results of a small molecular model compound containing DOPO (MD3) showed that arrangement of DOPO groups is parallel with the most-adjacent benzene rings in the main-chain. Thus regular arrangement between the mesogenic units in the presence of DOPO has no obvious difference with that in the absence of DOPO. The DSC and XRD results of copolymers were consistent with above analysis. Copolyester P1 exhibits smectic mesomorphic phase and is very similar to P0 without ODOPB, however, P3–P5 exhibit nematic phases. Though the O=P–O bond in ODOPB is less stable than the common C–C bond, the temperatures of 5% weight loss of all copolyesters prepared are above 375 °C because of strong polar and big π-conjugated structure of ODOPB segments. The char yield of synthesized liquid crystalline polymers at 600 °C gradually increases with the increase of the content of ODOPB segment in the copolyesters due to the incorporation of phosphorus-containing groups.

Acknowledgements

This research was supported by the basic research found of Beijing Institute of Technology (20070442004). Authors are grateful to Prof. Zhang Fei, Sun Lin and Pan Wei (College of Chemistry and Molecular Engineering, Peking University) for using the apparatus in determination of DSC and POM.

References

[1] Niu LG, Nagarajan R, Feng DS, Samuelson LA, Kumar J. J Macromol Sci Part A Pure Appl Chem 2006;43:1983–90.
[2] Tan A, Altinok E, Yerlikaya Z, Aksoy S. J Macromol Sci Part A Pure Appl Chem 2007;44:425–31.
[3] Patil HP, Liao J, Hedden RC. Macromolecules 2007;40:6206–16.
[4] Fernandez-Blazquez JP, Bello A, Perez E. Macromolecules 2007;40:703–9.
[5] Fernandez-Blazquez JP, Bello A, Perez E. Macromol Chem Phys 2007;208:520–8.
[6] Bhowmik PK, Kamatam S, Han H, Nedeltchev AK. Polymer 2008;49:1748–60.
[7] Ciferri A, Krigbaum WR, Meyer RB. Polymer liquid crystals. New York: Academic Press; 1982.
[8] Isayev AI, Kyu T, Cheng SZD. Liquid–crystalline polymer systems: technological advances. In: ACS symposium series, vol. 632. Washington, DC: ACS; 1996.
[9] Lettieri M, Guadagno L, Vittoria V. Polymer 1998;39:2557–61.
[10] Zhao YB, Zou JH, Shi WF. Micropor Mesopor Mater 2006;92:251–8.
[11] Tsuwi J, Hartmann L, Kremer F. Polymer 2006;47:7189–97.
[12] Chung SJ, Kim KK, Jin JI. Polymer 1999;4:1943–53.
[13] Alcon MJ, Espinosa M, Galia M. Macromol Rapid Commun 2001;22:1265–71.
[14] Chang SJ, Chang FC. J Appl Polym Sci 1999;72:109–22.
[15] Cheng YB. J Appl Polym Sci 2004;91:1233–53.
[16] Senthil S, Kannan P. Polymer 2004;45:3609–14.
[17] Bello A, Perez E, Marugan MM, Perena JM. Macromolecules 1990;23:905–7.
[18] Wang XD, Zhang Q. Eur Polym J 2004;40:385–95.

[19] Suna YM, Wang CS. Polymer 2001;42:1035–45.
[20] Chen XT, Tang XD, Wang YZ. Chem J Chinese Univ 2002;23:508–23510.
[21] Wang YZ, Chen XT, Tang XD. J Appl Polym Sci 2002;86:1278–84.
[22] Wang YZ, Chen XT, Tang XD, Du XH. J Mater Chem 2003;13:1248–9.
[23] Chen L, Huang HZ, Wang YZ, Jow J, Su K. Acta Polym Sinica 2009;5:493–8.
[24] Du XH, Wang YZ, Chen XT. Polym Degrad Stab 2005;88:52–6.
[25] Wang CS, Lin CH, Chen CY. J Polym Sci Part A Polym Chem 1998;36:3051–61.
[26] Wang CS, Shieh JY, Sun YM. J Appl Polym Sci 1998;70:1959–64.
[27] Wang CS, Lin CH. Polymer 1999;40:747–57.
[28] Liu YL, Wu CS, Hsu KY, Chang TC. J Polym Sci Part A Polym Chem 2002;40:2329–39.
[29] Canadell J, Mantecon A, Cadiz V. J Polym Sci Part A Polym Chem 2007;45:1980–92.
[30] Watanabe J, Hayashi M, Nakata Y, Niori T, Tokita M. Prog Polym Sci 1997;22:1053–87.
[31] Watanabe J, Hayashi M. Macromolecules 1988;21:278–80.
[32] Watanabe J, Hayashi M. Macromolecules 1989;22:4083–8.
[33] Krigbaum WR, Asrar J, Toriumi H, Ciferri A, Preston J. J Polym Sci Polym Lett Ed 1982; 20:109–15.
[34] Wang CS, Lin CH. Polymer 1999;40:4387–98.
[35] Tokita M, Osada K, Yamada M, Watanabe JJ. Macromolecules 1998;31:8590–4.
[36] Cheng SZD. Macromolecules 1988;21:2475–84.
[37] Li C, Xie X, Cao S. Polym Adv Technol 2002;13:178–87.
[38] Schneggenburger LA, Osenar P, Economy J. Macromolecules 1997;30:3754–8.
[39] Krigbaum WR, Watanabe J, Ishikawai T. Macromolecules 1983;16:1271–9.
[40] Balabanovich AI, Pospiech D, Korwitz A, Haußer L, Harnisch C. Polym Degrad Stabil 2009;94:355–64.