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Synthesis and characterization of side chain polymer with helical PLLA segments containing mesogenic end group

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ABSTRACT

Series of mesogenic biphenol derivatives HO6OPPOn ($n = 4,6,8$) were prepared by asymmetric reaction and purified. Then HOLAxO6OPPOn were prepared with controlled molecular weights by adjusting the feed ratios of HO6OPPOn, $SnOct_2$ catalyst and LLA by Ring-Opening Polymerization. **P-AOLAxO6OPPOn** materials were obtained in high yields by the free radical polymerization of polymerizable macromonomers of **AOLAxO6OPPOn** synthesized by esterization of HOLAxO6OPPOn with acrylic acid in the presence of DCC/DMAP. Their molecular weights were characterized by ^{1}H NMR and GPC. Differential Scanning Calorimeter method and Polarized Optical Microscopy method were used to study their thermal behaviors. Both **AOLAxO6OPPOn** and **P-AOLAxO6OPPOn** materials are found to form LCs with increased T_g, T_m and T_i with longer O-LLA segment length. Polymerization of **AOLAxO6OPPOn** also resulted in the increase of T_g, T_m and T_i. X-ray diffraction measurements revealed the presence of smectic phase in these materials. The O-LLA segments are in helical structure from CD spectra and this makes the resulting polymer materials good candidate of optical materials for huge optical rotation power.

1. Introduction

PolyLactide (PLA) is one of the most important bioactive polymers used as biodegradable and biocompatible materials [1–10]. It is also noticeable that L, L-Lactide or D, D-Lactide, as important two enantiomers of Lactide, can form interesting helical chiral polymers, Poly-L-Lactide (PLLA) or PDLA. Compared to those well studied racemeric PLAs used as biomaterials, PLLA and PDLA as optical pure chiral helical polymers are still not well studied [11–16].

Until now many papers have focused on the research of helical polymers [17–27], but extensive study on PLLA helical polymer as optically active polymers is still rare [28–31]. Helical PLLA polymers were expected to exhibit optical rotation power in solid state due to the asymmetric arrangement of atoms in helical main chain structure. Kobayashi [32] has processed and measured the huge intrinsic optical rotation power of PLLA in the fiber axis direction of uniaxial crystal, ρ, as large as 7200°/mm, 300 times larger than that of α-quartz. Also the measured response change in the amplitude of transmitted light was up to 10 MHz for fast light modulation [33]. This devotes PLLA as potential mateirals for optical elements and devices.

Kimura et al. [34] has prepared series of oligo(L-lactic acid) with an isopropoxyl end group. The ellipticity of oligo(L-lactic acid) (O-LLA) by Circular Dichroism (CD) increased with the increase of degree of polymerization and reached a maximal value at $n = 8$, indicating the completely built up of the helical structure in O-LLA, The ellipticity was keep almost constant for O-LLA with more repeating numbers but the ellipticity is a little lower than the maximal value. The better processability of O-LLAs than PLLAs is an advantage for large area flexible thin film optical devices.

Samuel I. Stupp et al. [35,36] has reported for the first observation of Liquid Crystal (LC) behavior of O-LLA with Cholesteryl groups attached at the end and studied the self-assembling property of Chol-(L-Lactic Acid)xOH as building blocks for self-assembling materials. Attachment of LC groups to form LC-LLA materials can be also a very good way of combining the self-organization property of LC group and the optical rotation power of helical O-LLA to get self-organized materials with huge optical rotation power. Considering that these self-assembling materials could be very good candidates as biomaterials and also good optical materials, the study of LC-OLLA materials is one of the very interesting areas of future.

This report presents the preparation, thermal and phase behaviors of series of side chain polymers with O-LLA as important helical chain segments, involving the preparation of molecular weight-controlled LC-OLLA materials HOLAxOmOPPOn, **AOLAx-OmOPPOn** and **P-AOLAxOmOPPOn** (Scheme 2 and Scheme 3).

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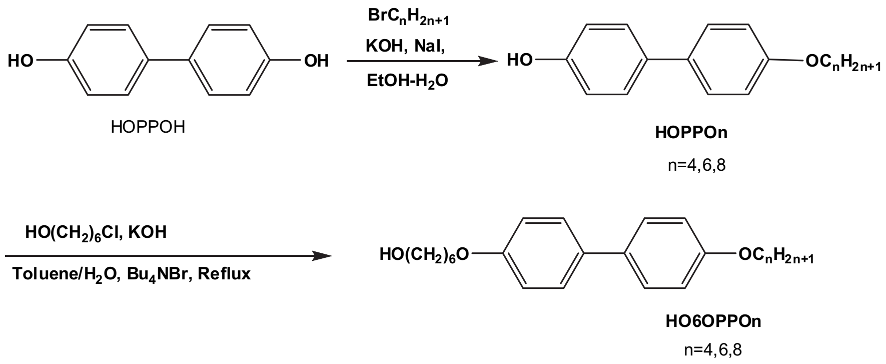


Scheme 1. Synthesis routine of the initiators.

2. Experimental sections

2.1. Materials

L-Lactide (LLA) was purified by recrystallization three times from toluene dried as following method. The polymerization of LLA was performed under Argon atmosphere. Toluene used for the ring-opening polymerization of L-Lactide as best solvent was dried on Sodium/potassium alloy Na/K (Benzophenone) and distilled off just before use and transferred with syringes.

Acrylic acid was distilled just before use. Azodiisobutyronitrile (AIBN) was recrystallized from ethanol and stored in refrigerator at 0 °C. Stannous octoate, $SnOct_2$, was redistilled three times first as reported in reference [37] and used by quantitatively transferring with syringe as toluene (Na/K dried) solution of known concentration. N, N′-Dicyclohexylcarbodiimide (DCC), 4-N, N′-dimethylamino- pyridine (DMAP) was vacuum dried before use. CH_2Cl_2 was dried over P_2O_5, when necessary. All the other materials are commercial available and used as received unless noted elsewhere.

2.2. Synthesis

2.2.1. Synthesis of mono-substituted biphenol compounds

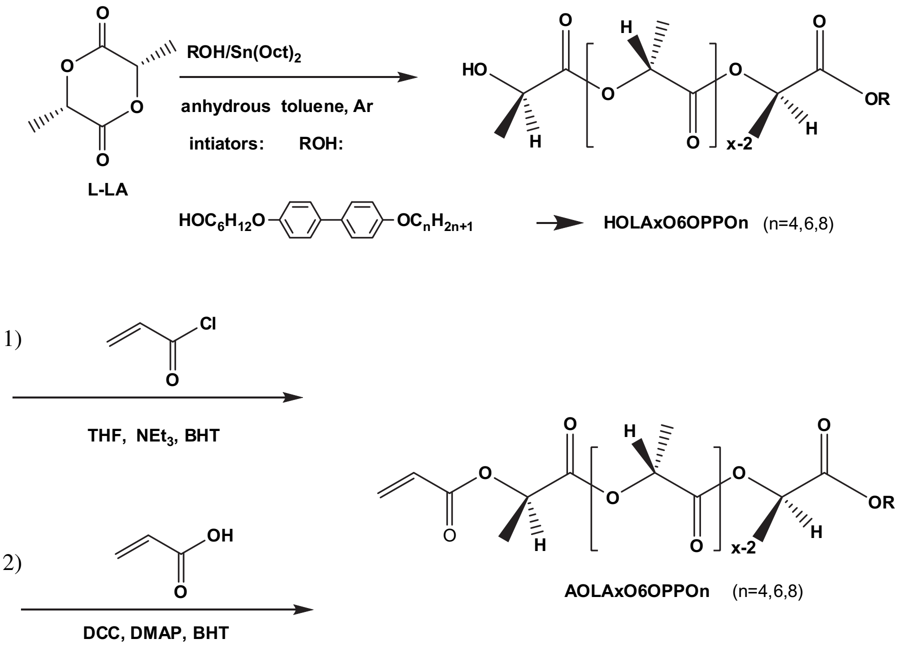
The synthesis procedure of the initiators was presented as Scheme 1.

The general operations were as following [38]: After biphenol (30 g, 0.16 mol) and KOH (40 g, 0.71 mol) forming a clear solution in 192 mL Ethanol/H_2O (v/v 2:1) solution at reflux by magnetic stirring, equimolar BrCnH2n + 1 (n = 4,6,8) in ethanol were added dropwisely under stirring and reflux for 12 h by Thin Layer Chromatography (TLC) monitor. The filtrates after filtering off nOPPOn solid were diluted with large amount of diluted sodium hydroxide water to recover the resultants by filtration as noted HOPPOn (n = 4,6,8) and recrystallized twice from ethanol.

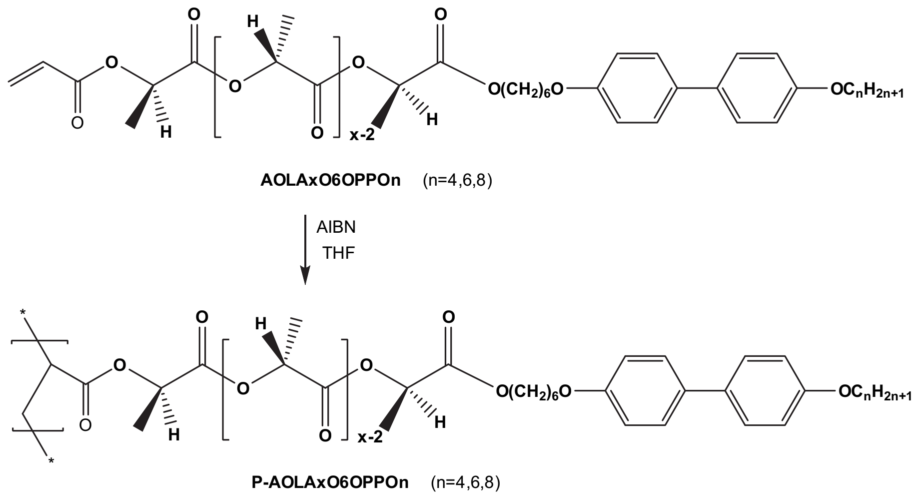
HOPPO4 yield 32.8%, $R_f = 0.46$ ($CHCl_3$:C_2H_5OH = 15:1)

HOPPO6 yield 23.3%, $R_f = 0.44$ ($CHCl_3$:C_2H_5OH = 15:1)

HOPPO8 yield 32.0%, $R_f = 0.46$ ($CHCl_3$:C_2H_5OH = 15:1)



Scheme 2. Ring-opening polymerization of LLA and the synthesis of the acrylic esters of the PLLA macromonomers.



Scheme 3. Radical polymerization of the acrylic ester macromonomers of O-LLAs.

2.2.2. Initiators HO6OPPOn (n = 4,6,8)

HOPPOn were reacted with NaOH, NaI, and $Cl(CH_2)_6OH$ in proper amount of solvent for 48 h with refluxing or by phase-transfer reaction in toluene with catalytic amount of Bu4NBr for 8 h, monitoring by TLC. HO6OPPOn were recovered by Rotary Evaporator and recrystallization from ethanol yielding white solid. HO6OPPOn were then recrystallized in toluene and dried for ROP reaction.

HO6OPPO4, yield 83.1%, $R_f = 0.35$ (CH_2Cl_2:C_2H_5O C_2H_5:$CH_3(CH_2)_4CH_3$ = 2:1:1)

HO6OPPO6, yield 60.6%, $R_f = 0.40$ (CH_2Cl_2:$C_2H_5OC_2H_5$:$CH_3(CH_2)_4CH_3$ = 2:1:1)

HO6OPPO8, yield 73.1%, $R_f = 0.35$ ($CHCl_3$:C_2H_5OH = 15:1)

2.2.3. Ring-opening polymerization of L-LA

A general procedure for the Ring-Opening Polymerization (ROP) of L-LA was shown in Scheme 2. The feed ratios of L-LA to HO6OPPOn and $SnOct_2$ were adjusted in order to get oligomers/polymers of different molecular weight. The procedure was briefly as following:

Proper amount of L-LA, HO6OPPOn were vacuum dried at near 50 °C for 3 h and then mixed with $SnOct_2$ (tridistilled) solution in toluene with typical ratio (x:1:1, x = 5,10,15,20) and toluene. After stirring for 10 h at 100 °C the viscous mixture was cooled and evaporated to dryness. Then the residual was dissolved with CH_2Cl_2 and washed with 1 M HCl aqueous and water, concentrated. The concentrated solution was then poured into ethanol or petroleum ether to precipitate. The final targeted polymer compounds were collected as white solid by filtration and dried (The H atoms marked for ^{1}H NMR measurement were shown as in Fig. 1).

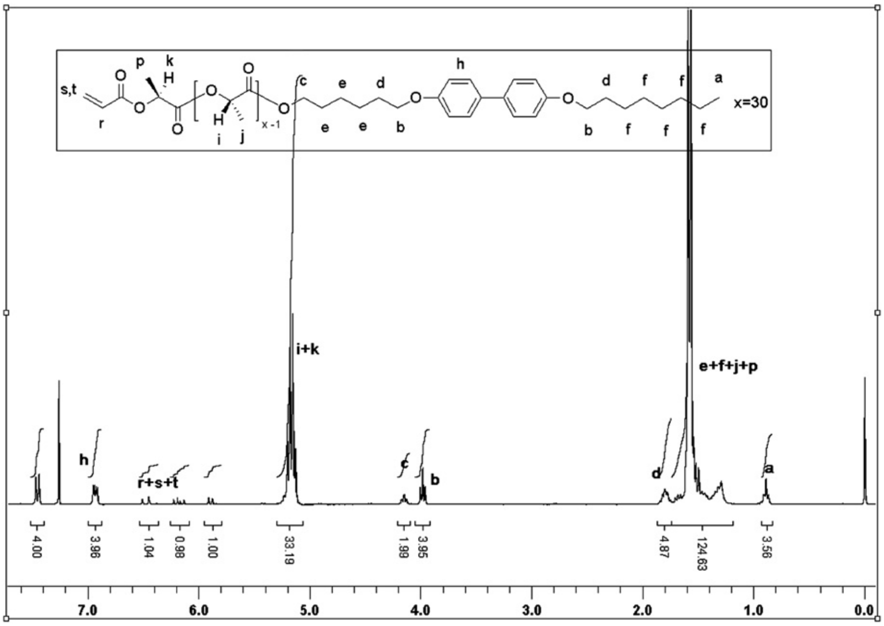


Fig. 1. A representative ^{1}H NMR spectral of $AOLA_xO6OPPOn$.

Table 1
Molecular weight and degree of polymerization and Degree of Polydispersity Index (DPI) of HOLAxO6OPPOn obtained by ^{1}H NMR and GPC methods.

	Theo.		^{1}H NMR		GPC		
	n	Mn	n	Mn	Mn	Mw	Mw/Mn
HOLA$_{10}$O6OPPO4	10	1063	10.8	1119	1944	2425	1.25
HOLA$_{20}$O6OPPO4	20	1783	19.9	1777	2880	3952	1.37
HOLA$_{30}$O6OPPO4	30	2504	29.1	2436	3633	5018	1.38
HOLA$_{40}$O6OPPO4	40	3225	39.6	3196	4328	6213	1.44
HOLA$_{10}$O6OPPO8	10	1119	9.9	1110	1924	2390	1.24
HOLA$_{20}$O6OPPO8	20	1839	19.5	1802	2827	3917	1.39
HOLA$_{30}$O6OPPO8	30	2560	29.1	2497	3681	5100	1.39
HOLA$_{40}$O6OPPO8	40	3281	37.6	3111	4932	6352	1.29

HOLAxO6OPPO4 ^{1}H NMR (300 MHz, CDCl$_3$): δ(ppm) = 0.986 (t, 3H, a); 1.406–1.706 (m, 3x + 8, e + f + j + p); 1.739–1.831 (m, 4H, d); 2.700 (b, 1H, q); 3.986 (t, 4H, b); 4.155 (t, 2H, c); 4.319–4.389 (m, 1H, k); 5.116–5.230 (m, n − 1, i); 6.913–7.469 (m, 8H, h).

HOLAxO6OPPO6 ^{1}H NMR (300 MHz, CDCl$_3$): δ(ppm) = 0.941 (t, 3H, a); 1.255–1.703 (m, 3x + 12, e + f + j + p); 1.749–1.842 (m, 4H, d); 2.700 (b, 1H, q); 3.984 (t, 4H, b); 4.156 (t, 2H, c); 4.323–4.392(m, 1H, k); 5.094–5.235 (m, n − 1, i); 6.914–7.470 (m, 8H, h).

HOLAxO6OPPO8 ^{1}H NMR (300 MHz, CDCl$_3$): δ(ppm) = 0.941 (t, 3H, a); 1.255–1.703 (m, 3x + 16, e + f + j + p); 1.749–1.842 (m, 4H, d); 2.700 (b, 1H, q); 3.984 (t, 4H, b); 4.156 (t, 2H, c); 4.323–4.392(m, 1H, k); 5.094–5.235 (m, n − 1, i); 6.914–7.470 (m, 8H, h).

2.2.4. Preparation of macromonomers

The preparation of the macromonomers was performed by the reactions either with excess amount of acryloyl chloride/triethylamine or acrylic acid/DCC/DMAP using 2,6-Di-tert-butyl-4-methylphenol (BHT) as inhibitor. Generally, the mixture of LC-OLLA-OH corresponding to macromonomer with BHT, DCC/DMAP, dissolved in CaH$_2$-dried CH$_2$Cl$_2$, was kept magnetic stirring for 60 h at room temperature and stopped with small amount of Ethanol/Acetic acid mixture. After filtration and concentration the residual was poured into cooled ethanol (−18 °C) and kept hours in refrigerator. White powder was collected by the filtration of the cooled ethanol solution and vacuum dried to get the polymerizable macromonomers in good yield.

AOLAxO6OPPO4 ^{1}H NMR (300 MHz, CDCl$_3$): δ(ppm) = 0.986 (t, 3H, a); 1.496–1.706 (m, 3x + 8, e + f + j + p); 1.739–1.827 (m, 4H, d); 3.962–4.016(m, 4H, b); 4.113–4.170 (m, 2H, c); 5.129–5.200 (m, nH, i + k); 5.878–5.913 6.135–6.227 6.451–6.507(m, 1H + 1H + 1H, r + s + t); 6.913–7.468 (m, 8H, h).

Table 3
Phase transition temperatures (°C) of macromonomers AOLA$_x$O6OPPOn.

Samples	T_g	T_m	T_i
AOLA$_{10}$O6OPPO4	22.8	53.0	89.0
AOLA$_{20}$O6OPPO4	26.4	102.2	118.0
AOLA$_{30}$O6OPPO4	30.0	119.6	125.2
AOLA$_{40}$O6OPPO4	35.2	117.2	137.2
AOLA$_{10}$O6OPPO6	17.0	62.0	107.9
AOLA$_{20}$O6OPPO6	–	56.8	125.2
AOLA$_{30}$O6OPPO6	28.2	28.2	129.6
AOLA$_{40}$O6OPPO6	32.4	75.6	139.1
AOLA$_{10}$O6OPPO8	–	39.4	107.9
AOLA$_{20}$O6OPPO8	17.8	51.8	126.9
AOLA$_{30}$O6OPPO8	21.7	87.3	130.4
AOLA$_{40}$O6OPPO8	30.4	90.6	136.8

AOLAxO6OPPO6 ^{1}H NMR (300 MHz, CDCl3): δ(ppm) = 0.913 (t, 3H, a); 1.24–1.70 (m, 3x + 12H, j + p + e + f); 1.76–1.85 (m, 4H, d); 3.988 (t, 4H, b); 4.154 (m, 2H, c); 4.350 (m, 1H, k); 5.129–5.200 (m, nH, i + k); 5.892 (d, 1H, s); 6.180 (t, 1H, t); 6.44 (d, 1H, r); 6.913–7.468 (m, 8H, h).

AOLAxO6OPPO8 ^{1}H NMR (300 MHz, CDCl$_3$): δ(ppm) = 0.890 (t, 3H, a); 1.294–1.707 (m, 3x + 16H, e + f + j + p); 1.754–1.844 (m, 4H, d); 3.962–4.005(m, 4H, b); 4.125–4.177 (m, 2H, c); 5.129–5.200 (m, nH, i + k); 5.815–5.913 6.134–6.227 6.385–6.509 (m, 1H + 1H + 1H, r + s + t); 6.914–7.470 (m, 8H, h).

2.2.5. Polymerization of macromonomers

Side chain grafted comb-like polymers with biphenyl group and O-LLA segments were prepared by the radical polymerization of the macromonomers, **AOLAxO6OPPOn**, prepared above. General routine was as follows (**AOLA$_{10}$O6OPPO4** as an example): **AOLA$_{10}$O6OPPO4** (0.1069 g, 95.7 μmol) was placed in a 10 mL flask, and purged with dry Argon gas to remove oxygen before THF 3 mL and AIBN (46 μL AIBN/THF solution, 0.96 μmol) were added. The resulting mixture was kept for 10 h at 70 °C under magnetic stirring under Argon atmosphere. The targeted polymers were collected in good yield by filtration as white solid after poured the reaction mixture into petroleum ether to precipitate and then vacuum dry overnight for further characterization.

2.3. Measurements and characterization

^{1}H NMR was recorded on a AVANCE 300M/400M spectrometer (Bruker) in CDCl$_3$ or DMSO-D6 at room temperature. By ^{1}H NMR,

Table 2
Molecular weight and degree of polymerization and Degree of Polydispersity Index (DPI) of AOLAxO6OPPOn and P-AOLAxO6OPPOn obtained by ^{1}H NMR and GPC method.

Samples	M.W. of AOLAxO6OPPOn[a]			M.W. of P-AOLAxO6OPPOn By GPC			
	Theo.		^{1}H NMR[a]				
	x	Mn	O-LLA x/Mn	Mn × 10^{-3}	Mw × 10^{-3}	Mw/Mn	DP of PA[b]
P-AOLA$_{10}$O6OPPO4	10	1117	12/1261	21.2	23.2	1.09	17
P-AOLA$_{20}$O6OPPO4	20	1837	25/2137	24.5	26.7	1.09	11
P-AOLA$_{30}$O6OPPO4	30	2558	33/2774	28.7	31.7	1.11	10
P-AOLA$_{40}$O6OPPO4	40	3279	44/3567	38.5	47.7	1.24	11
P-AOLA$_{10}$O6OPPO6	10	1144	9/1072	11.6	14.6	1.26	11
P-AOLA$_{20}$O6OPPO6	20	1864	23/2070	12.5	15.2	1.22	7
P-AOLA$_{30}$O6OPPO6	30	2588	31/2660	20.3	30.7	1.51	8
P-AOLA$_{40}$O6OPPO6	40	3303	43/3519	21.9	28.1	1.28	6
P-AOLA$_{10}$O6OPPO8	10	1171	15/1531	15.9	17.5	1.1	10
P-AOLA$_{20}$O6OPPO8	20	1893	24/2181	23.3	27.3	1.17	11
P-AOLA$_{30}$O6OPPO8	30	2614	33/2830	33.1	37.2	1.13	12
P-AOLA$_{40}$O6OPPO8	40	3335	42/3479	33.6	39.5	1.18	10

[a] The theoretical molecular weight and degree of polymerization of macromonomers AOLAxO6OPPOn;
[b] The degree of polymerization of P-AOLLA determined based on the Mn of P-AOLLAs by GPC and Mw of macromonomers as repeat units as side chains.

Table 4
Phase transition temperatures (°C) and degree of crystallinity of P-AOLAxO6OPPOn.

Samples	T_g'[a]	T_g	T_m	T_i	ΔHm(J/g)	χ_c (%)[b]
P-AOLA$_{10}$O6OPPO4	−3.1	24.8	43.1	–	–	–
P-AOLA$_{20}$O6OPPO4	−3.8	39.8	106.4	120.5	14.32	15.28
P-AOLA$_{30}$O6OPPO4	−5.5	31.6	106.9	120.6	23.72	25.31
P-AOLA$_{40}$O6OPPO4	−5.1	41.1	106.9	127.9	33.08	35.30
P-AOLA$_{10}$O6OPPO6	−4.4	30.1	61.0	–	–	–
P-AOLA$_{20}$O6OPPO6	−4.7	24.5	107.9	131.9	22.17	24.36
P-AOLA$_{30}$O6OPPO6	−4.3	45.1	105.7	127.3	10.39	11.42
P-AOLA$_{40}$O6OPPO6	−4.5	20.1	107.2	132.3	12.65	13.90
P-AOLA$_{10}$O6OPPO8	−4.2	25.3	68.9	106.0	–	–
P-AOLA$_{20}$O6OPPO8	−4.2	44.2	106.0	137.6	31.70	33.80
P-AOLA$_{30}$O6OPPO8	−5.4	36.8	106.4	139.2	36.70	39.20
P-AOLA$_{40}$O6OPPO8	−5.5	41.4	106.8	130.3	40.10	42.80

[a] The $T_g's$ are the glass transition temperatures of the polyacrylate ester main chain parts;
[b] the ΔHm of complete crystal of PLLA is 93.7 J/g.

the DPs of O-LLAs, DP = $a + 1$, where the values of a were evaluated by comparing the proton peak areas of triple peak α-CH_{2-} of active −O-R at δ(ppm) = 4.15 with those of chiral -*CH− of PLLA at δ (ppm) = 5.17 (Fig. 1. where the H peaks were noted).

GPC measurements were performed on an HPLC equipped with 515HPLC pump, Waters 2414 Refractive Index Detector and Ultra-vis detector and HR3/HR4/HR6 columns at 1.00 mL/min using THF as eluent under 40.0 °C with Polystyrene standard (Shodex Standard SL-105 , Japan). The samples were prepared by passing the THF solution through a short neutral Al_2O_3 to remove any metal cations and then pass 0.22 μm microfilter film.

UV and the Circular Dichroism (CD) spectra were recorded on J-810-150L Spectropolarimeter (Jasco, Japan) from 190 nm to 550 nm at scan rate 0.1 nm using acetonitrile solvent under inert N_2 at 20 L/min, cell length 0.5 mm, pure acetonitrile as blank. The [θ] value was only contributed LA part and thus calculated based on the O-LLA segments.

Differential Scanning Calorimeter (DSC) measurements were performed on a DSC-SP (Rheometric Scientific Inc., New Jersey, USA) from −50–200 °C under inert N_2 atmosphere with a scanning rate of 10 °C/min. Glass transition temperatures (T_g) were determined by the mid point of baseline shift. Polarized Optical Microscope observation was performed on a Olympus BX51p with a Linkam THMSE600 cold–hot stage (−196–600 °C) and photographed by a Q-imaging Micropublisher 5.0RTV (CCD). The thermal transition temperatures were determined combining the DSC measurement and POM observation.

The X-ray diffraction measurements were performed on a Rigaku D/Max-rB X-ray diffractometer equipment (Japan) with Cu–K ($\lambda = 1.54056$ Å), 40 KV* 100 mA and scanned from 0.5° to 5° at a scan rate of 2°/min and 3°–50° at 4°/min. The samples were spin-coated or melt-pressed into pellets and annealed at 80 °C for 12 h.

3. Results and discussions

3.1. Preparation of initiators

The preparation of mono-substituted derivatives, HOPPOn, is the most important step, while the resulting mixtures always contain three possible compounds HOPPOH, HOPPOn and nOPPOn because of the o-alkylation's selectivity of homo- and bis- substitutions biphenol, HOPPOH. Recrystallization only is not enough to separate. The pure HOPPOn were obtained by a two-step operation according to the different solubility in different solutions: HOPPOH is completely removed first by dissolving in alkaline solution and then nOPPOn can be removed as solid by filtration of the hot Ethanol/water alkaline solution. The HOPPOn could be recovered by neutralization of the resulting filtrate. Further twice recrystallization is enough to get pure HOPPOn free of HOPPOH and nOPPOn. Best for initiators could be achieved by phase-transfer reaction of HOPPOn with corresponding ω-HO-alkane bromide or chloride for ROP of L-LA.

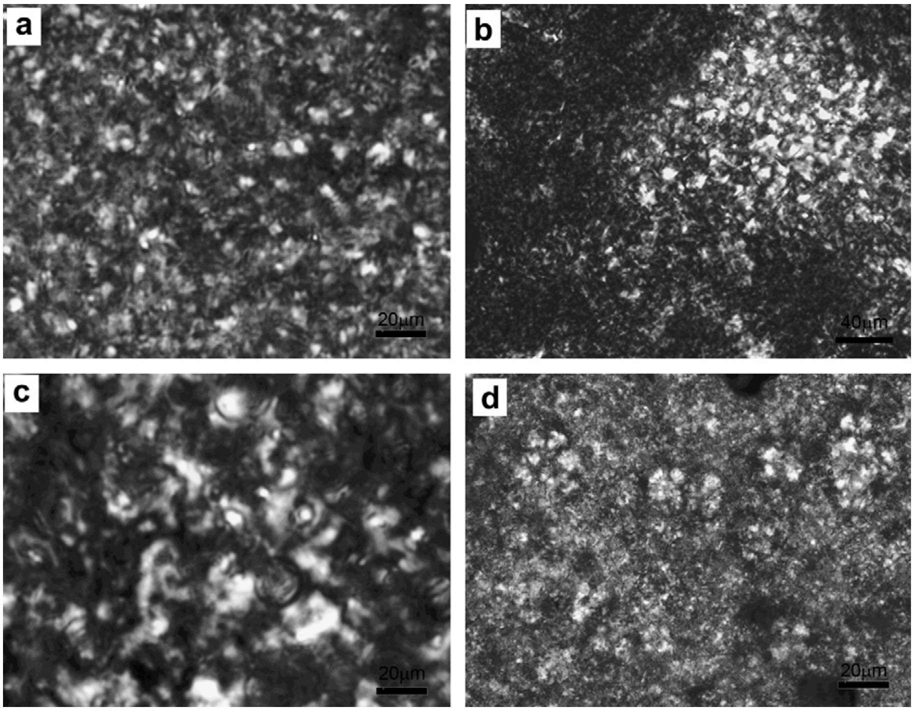


Fig. 2. POM textures of P-AOLAxO6OPPOn. a, P-AOLA$_{30}$O6OPPO4 at heating the original sample to 84 °C; b, P-AOLA$_{40}$O6OPPO6 heated to 104 °C; c, P-AOLA$_{20}$O6OPPO8 cooled to 111 °C; d, P-AOLA$_{40}$O6OPPO8 heated to 113 °C.

3.2. Preparation and characterization of AO-LAxO6OPPOn

3.2.1. ROP of L-LA

The HO-group of HO6OPPOn was sufficient active for the ROP of L-Lactide if $SnOct_2$ was used as catalyst but, for best results; need to be recrystallized with dry toluene just before use to remove any HO-containing molecules. Better control of the molecular weights of the resulting O-LLAs can be achieved when $SnOct_2$ was distilled under vacuum for three times or more just before use. It is also important that the L-LA solid were recrystallized with toluene (Na/K dry) three times or more and used just before use. Among the solvents used to recrystallize the L-LA, toluene is easy to purify and dry for the best results.

The ROP reaction was almost complete around 12 h at 80 °C in toluene but best results were achieved for 10 h at 100 °C.

The $SnOct_2$ was removed by washing with cold HCl (0.5 M) aqueous solution and water. Generally, the O-LLA samples with lower feed ratios often have much lower yields due to the more apparent weight loss caused by water-dissolve of low molecular weight O-LLAs when washing with water.

3.2.2. Molecular weight of O-LLA segments

The molecular weights of O-LLAs were determined by ^1H NMR, GPC and listed in Table 1. The measured molecular weights of O-LLAs were in good agreement with the theoretical results and found to be well controlled by the feed molar ratios of the $SnOct_2$ catalyst, L-LA to HO6OPPOn ($n = 4,8$) providing enough $SnOct_2$ was used.

3.2.3. Preparation of macromonomers AOLAxO6OPPOn (AOLLA)

To form the polymerizable macromonomers, the acrylate esters of O-LLA segments, acrylic group was attached by reacting with HO-group of O-LLA. Considering that the HO-group percentages were very low in each HOLLAxO6OPPOn's, acrylic acid was used in excess amount and used in its activated state. The procedure involving the acrylic chloride, a highly active species, and triethylamine, proton absorbent, was fast but the products color are slight yellow and difficult to be avoided and removed. It changed much more when acrylic acid/DCC/DMAP was used instead. White powder samples were thus obtained from the later. However more acrylic acid was necessary to achieve better conversion of **HOLAxO6OPPOn** to **AOLAxO6OPPOn**. For example, here 10 times excess of acrylic acid was used in this paper. The appearance of the peaks of $CH_2 = CH-$ around 5.8 to 6.3 in ^1H NMR spectra and the proper amount of protons indicated the successful complete attachment of the acrylic group to the end of the O-LLA segments (as may have noted in Fig. 1, for example). Also a slightly increase of the average DP or the molecular weights of **AOLAxO6OPPOn** were observed from ^1H NMR, indicating the weight loss of AO-LLA molecules with lower DPs in the precipitation process due to their higher solubility in the cold ethanol solution. The weight loss of lower DPs also lead to the lower yields of **AOLAxO6OPPOn**, around 60% for $x = 10$ and above 90% for $x = 40$. The molecular weights of the resulting products **AOLAxO6OPPOn** were then determined by ^1H NMR and GPC measurements and listed in Table 1.

3.3. Preparation and characterization of Poly-AOLAxO6OPPOn

The macromonomers, as acrylate esters, can polymerize to form comb-like polymers with polyacrylate as main chain and O-LLA segments with mesogenic end group at the free end as side chains. As the DP of AO-LLA may be controlled by changing the initiator feed ratios, the resulting P-AOLLA will be formed with a distinct side chain length. The molecular weights of the polymers P-AOLLA characterized by GPC were listed in Table 2, together with the ^1H NMR results listed for the calculation of the DP of AO-LLA segments and the DP of P-AOLLA. The disappearance of the peaks in ^1H NMR spectra between 5.8 and 6.3, the acrylate part, is also distinct. The polymerization of AO-LLA can be again confirmed by the appearance of peaks at higher molecular weight region and the disappearance of the peak corresponding to a lower molecular weight of AO-LLA by GPC. The only single peak thus detected from each GPC was corresponding to the Mw/Mn of **P-AOLAxO6OPPOn** as listed in Table 2.

3.4. Thermal behavior of macromonomers AOLAxO6OPPOn and Poly-AOLAxO6OPPOn

The thermal behavior was evaluated by DSC measurements and transition temperatures were confirmed again with POM observations. One or two heat scans were performed for macromonomers (Table 3) and polymers (Table 4).

By POM observation on a hot stage with crossed polarizer all these materials showed distinct birefringent texture, characteristic

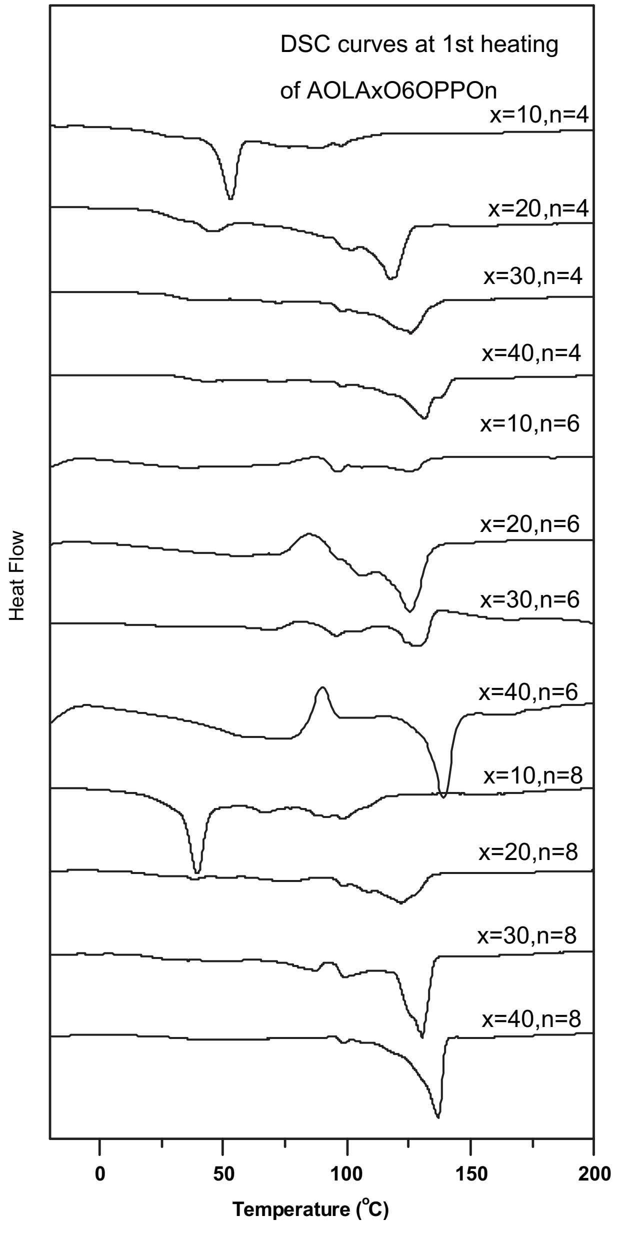


Fig. 3. DSC curves of $AOLA_xO6OPPOn$.

of layered smectic mesopahse, Fig. 2, until T_i was reached. Similar to what had been reported by Samuel I. Stupp, not only the T_m and T_i of both the **AOLAxO6OPPOn** and P-**AOLAxO6OPPOn** samples moved to higher temperature end, but also the LC phase ranges of higher regime liquid crystal phases were decreased with longer O-LLA segments length. Again, the T_m and T_i of the **AOLAxO6OPPOn** became higher after polymerized to P-**AOLAxO6OPPOn**. POM observations also give evidence that between T_g and T_m, POM textures also existed if only treated by proper cut or press to confirm, however the viscosity was relatively high compared to samples at higher temperatures. This means that LC phases may exist at these temperature ranges, as reported by Samuel I. Stupp.

From DSC curves, each macromonomer **AOLAxO6OPPOn** (Fig. 3) showed a distinct T_g around 30 °C and the T_g increased with the increase of the degree of polymerization, x, of O-LLA segments from x = 10 to 40. The fact that T_gs of **AOLAxO6OPPOn** and P-**AOLAxO6OPPOn** with x = 10, presented as distinct relative apparent endothermic peaks, not baseline shifts only as those samples with higher x values as shown in Fig. 4, indicates the melting behavior of PLLA segments but not a simple glass transition behavior.

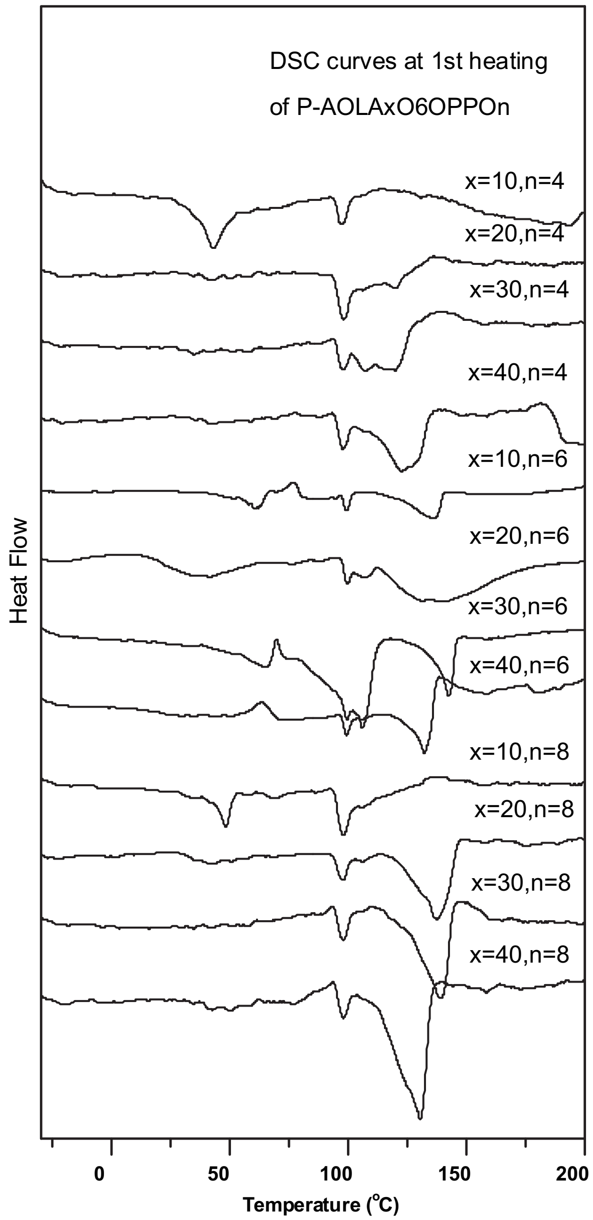


Fig. 4. DSC scans of P-AOLAxO6OPPOn.

For the P-**AOLAxO6OPPOn**s, compared with those corresponding macromonomers, **AOLAxO6OPPOn**s, T_gs moved to higher temperature ranges and another T'_g appeared distinctly at lower temperature range, around −4 ~ −5 °C, denoted to those of the polyacrylate ester main chains, and generally were more apparent at second scans. However they are still not distinguished more apparent at the second scans than those of T_g. The T'_gs baseline-shifted not large enough compared with the T_gs of O-LLA segment parts. This is apparently corresponding to the relative higher percentage of O-LLA segments and the lower percentage of acrylate parts in P-**AOLAxO6OPPOn**. The almost constant T'_gs are also the indication of the similarity DPs of P-**AOLAxO6OPPOns**, which were listed in Table 2, while those always increase of T_gs changed much from 20 to 40 °C for P-**AOLAxO6OPPOns** with the apparent increase of x, from x = 10 to x = 40. Anyway these values are still lower than 57 °C, the normal Tg of those of high molecular weight PLLA [39].

Low T_gs are good help for the movement of the O-LLA segments to form layered smectic phase which existed in both **AOLAxO6OPPOn** and P-**AOLAxO6OPPOn** samples. Generally, both types of compounds have more than one peak on DSC curves indicating the formation of mesophase at higher temperatures above T_g. Also listed in Table 4 are the degrees of crystallinity, χ_c, of the **P-AOLAxO6OPPOn** materials. Apparently the χ_c [40] values increased with the increase of LLA chain length, indicating a stronger crystallization tendency for higher molecular weight

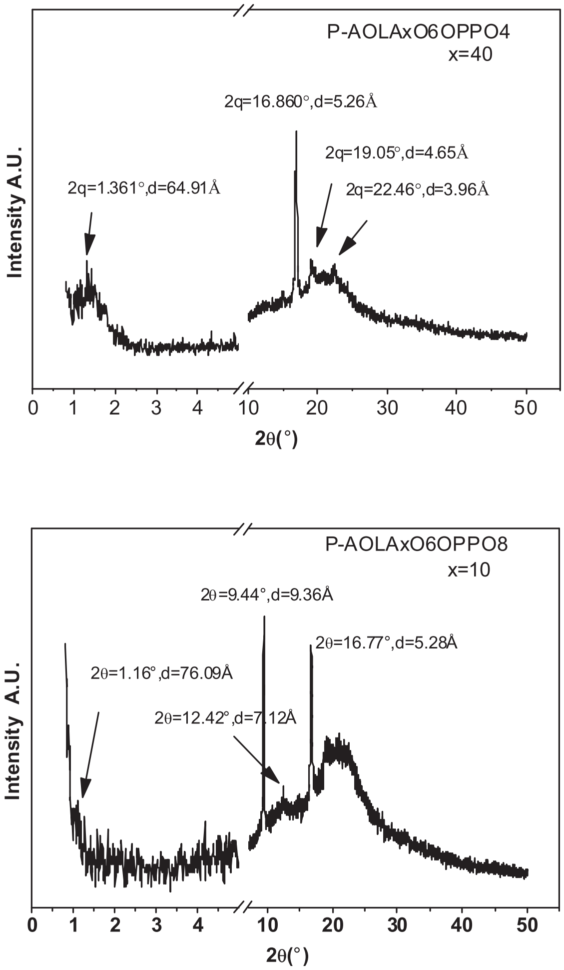


Fig. 5. XRD scans of P-AOLA$_{40}$O6OPPO4 at 80 °C and P-AOLA$_{10}$O6OPPO8 at 80 °C.

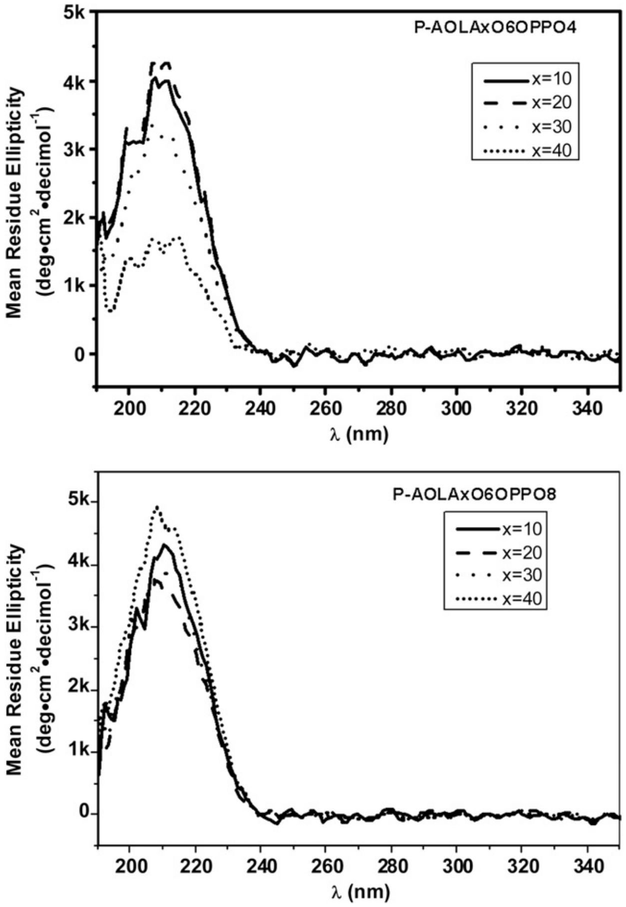


Fig. 6. Typical CD spectra of P-AOLAxO6OPPO4 and P-AOLAxO6OPPO8.

PLLA. The χ_c values are important for the preparation of layered phase, because the crystals of PLLA are often spherulites.

3.5. Phase behaviors of P-AOLAxO6OPPOn

X-Ray diffraction characterizations were performed to confirm the LC phase structure which may exist in **P-AOLAxO6OPPOn** and several were listed in Fig. 5. Peaks in the wide angle region, strong one at $2\theta = 16.86°$ and those weak peaks at $2\theta = 19.05°$, $22.46°$ (corresponding to $d = 5.26$ Å, 4.65 Å, 3.96 Å), were found to be the (110), (100), (203), (205) diffractions of α-form crystal of PLLA as have been reported by Miyata [41,42]. This is rational result for PLLA materials which formed α-crystal from solution and bulk. This implies that the LC phase of **P-AOLAxO6OPPOn** was apparently formed from the melting of PLLA α-crystals. Unfortunately, no obvious peaks of layered structure were found by temperature variable X-ray diffraction measurements without or with only short time annealing, while samples after overnight annealing have peaks appeared in small angle region. Because of the high molecular weight, the chemical bonding attachment at both ends of PLLA segments and the higher viscosity of **P-AOLAxO6OPPOns**, the ordering of the PLLA segments to form mesophases was much slower than those of common side chain Liquid Crystal Polymers and also chol-LAxOH samples. Thus reasonable frozen mesophases should exist after annealing overnight long and quenching to ice-cold metal plate and be observed by X-Ray Diffraction measurements. The weak peaks found at $d = 6.49$ nm for **P-AOLA$_{40}$O6OPPO4** annealing at 80 °C overnight and that at $d = 7.61$ nm for **P-AOLA$_{10}$O6OPPO8** annealing at 80 °C overnight indicating the presence of the layered structures for **P-AOLAxO6OPPOn** polymers (Fig. 5). This is in good agreement with cholesterol initiated O-LLA materials, which form layered phase reported by Samuel I. Stupp.

3.6. CD spectra of P-AOLAxO6OPPOn

All the CD spectra of **P-AOLAxO6OPPOn** materials showed typical positive cotton effect, a peak can be observed for each polymer around 210 nm, the absorption of C=O groups of O-LLA segments, with $[\theta] = 4000–5000$ deg*cm^2 decimol^{-1} (Fig. 6.). This indicated that stable helical structure has formed for these polymers because the [θ] value is comparative with any high Mw PLLA materials with good helical structure. The CD spectra give clear evidence that the **P-AOLAxO6OPPOn** materials may show strong optical rotation power if they are proper treated to form ordered films. Considering that LC materials can self-organized easily to form ordered materials, the study of **P-AOLAxO6OPPOn** may be used as optical materials in the future.

4. Conclusions

Series of mesogenic biphenol derivatives with active HO-group have been used as initiators successively to form Oligomeric L-LA materials with controlled molecular weight by adjusting the feed ratios by Ring-Opening Polymerization of LLA with SnOct$_2$ catalyst. Main Chain polymers **P-AOLAxO6OPPOn** were finally prepared by free radical polymerization of these polymerizable macromonomers esters that obtained by attaching acrylic group to these Oligomeric L-LA materials correspondingly. These macromolecules can be prepared with a controlled LLA length confirmed by ^{1}H NMR and GPC. All these materials can form good LC smectic phase from α-crystal. The O-LLA segments are in helical structure and this makes the resulting polymer materials good candidate of optical materials.

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