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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Niu, Langang , Nagarajan, Ramaswamy , Feng, Dingsong , Samuelson, Lynne A. and Kumar, Jayant(2006) 'Synthesis of Main-Chain Liquid-Crystalline Polyesters Containing Diphenyl Mesogens by Chemo-Enzymatic Route', Journal of Macromolecular Science, Part A, 43: 12, 1983 – 1990

To link to this Article: DOI: 10.1080/10601320600997781

URL: <http://dx.doi.org/10.1080/10601320600997781>

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Synthesis of Main-Chain Liquid-Crystalline Polyesters Containing Diphenyl Mesogens by Chemo-Enzymatic Route[†]

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Main-chain thermotropic liquid-crystalline polyesters containing rigid biphenyl mesogens and flexible spacers were synthesized by chemo-enzymatic route. The enzyme-catalyzed polymerization showed high regio- and chemo-selectivity, and is environmentally friendly. The resulting polyesters were characterized with ¹H-NMR, ¹³C-NMR, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and polarized light optical microscopy (POM).

Keywords liquid-crystalline polymers, biphenyl mesogens, enzymes

Introduction

In the last few years, main chain liquid-crystalline polyesters have been attracting much attention because of both scientific interest and numerous technological applications (1–6). Thermotropic main-chain liquid-crystalline polyesters are generally obtained by combining rigid mesogenic segments and flexible spacers in alternating succession (7). Such polymer melts exhibit mesomorphic phases of nematic or smectic order.

The first reported observation of thermotropic liquid-crystalline behavior in polymers was made by Roviello and Sirigu (8) and independently by Kuhfuss and Jackson (9). Since then, many research works have been focused on the synthesis of liquid-crystalline polymers. However, most of the synthesis is based on the conventional chemical reaction, and toxic catalysts and substrate are used in the synthesis of the polymers. Enzymes are efficient catalyst and their catalytic activity with unnatural substrate in organic reaction media is attracting considerable attention (10). Enzymatic synthesis has been proven to have a number of advantages and provide a good example to

[†]Dedicated to the memory of Professor Sukant K. Tripathy.

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achieve “green polymer chemistry” (11–13). The focus of this work is to exploit advances in both biotechnology and polymer science in order to synthesize main-chain liquid-crystalline polyester with biphenyl mesogen units. To our knowledge, the present communication is the first report of synthesis of main-chain liquid-crystalline polyesters using an enzymatic route.

Experimental

Materials

Novozyme-435, an immobilized enzyme, was purchased from Sigma. All other chemicals and solvents were of analytical grade and used as received unless otherwise noted. 4, 4'-Dihydroxybiphenyl, potassium carbonate, ethyl bromoacetate, 2-butanone, triethylene glycol, diethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol were purchased from Alfa Aesar, and polyethylene glycol dimethylether (Mw 1,000) was purchased from Aldrich.

Characterization

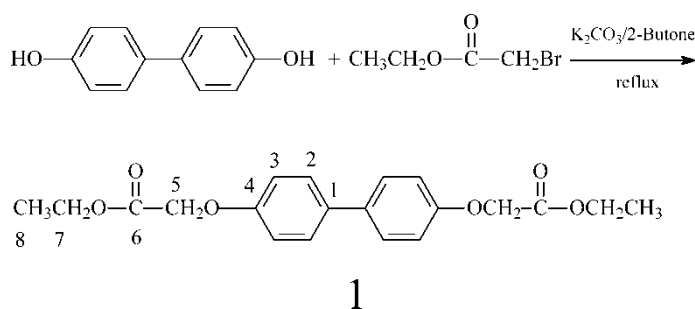
Gel permeation chromatography (GPC) was used to determine the molecular weights and the molecular weight distribution of the samples.

$^1\text{H-NMR}$, $^{13}\text{C-NMR}$ were recorded on a 200 MHz (Bruker ARX-200) spectrometer using CDCl_3 as solvent unless otherwise stated.

The DSC measurements were carried out using a TA Instruments DSC 2910. A scan rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ was used. Samples were tested under a nitrogen atmosphere and sample sizes were between 3–8 mg.

Synthesis of Monomer 1

Diester monomer 1 was prepared by the reaction of 4,4'-dihydroxybiphenyl (9.3 g, 50 mmol) with ethyl bromoacetate (25 g, 150 mmol) in 2-butanone (100 ml) under reflux for 8 h, and potassium carbonate (27.6 g, 200 mmol) was used as catalyst (Scheme 1). After the reaction, the crude product was recrystallized from 50% (v/v) ethanol aqueous solution to give white crystals, and the yield was 85%. The final product was a white crystal with a melting point at $127\text{--}129^\circ\text{C}$. $^1\text{H-NMR}$ Data



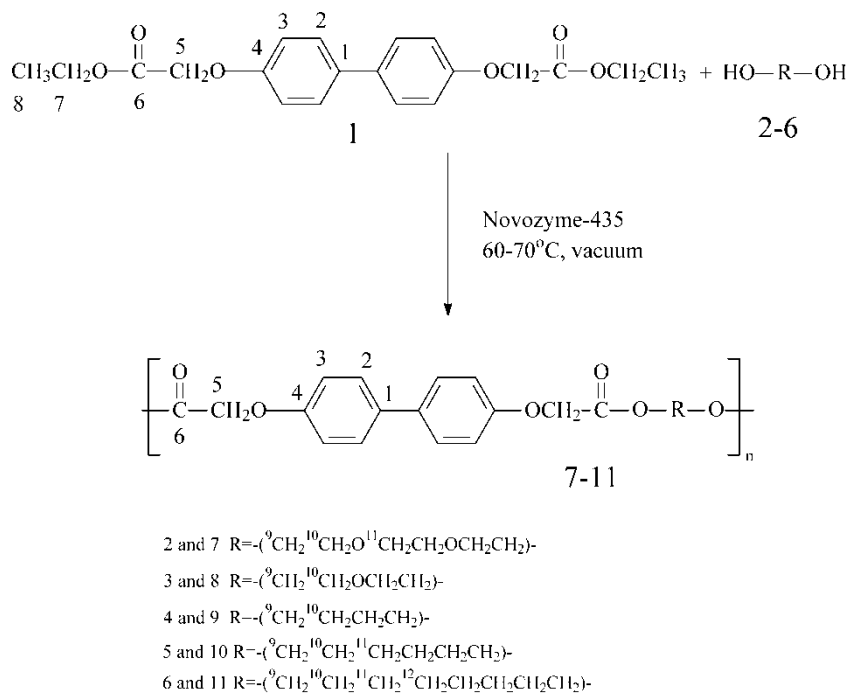
Scheme 1. Synthesis of diester monomer 1.

(DMSO): $\delta = 1.24$ (m, C-8H), 4.19 (m, C-7H), 4.83 (m, C-5H), 7.03 (m, C-3H), 7.54 (m, C-2H). ^{13}C -NMR Data (DMSO): $\delta = 15.01$ (C-8), 61.56 (C-7), 65.66 (C-5), 115.8 (C-3), 128.32 (C-2), 133.77 (C-1), 157.71 (C-4), 169.73 (C-6).

General Polymerization Procedure

In a typical experiment, equimolar amounts of diester monomer **1** and diols monomers **2–6** were taken into a round-bottom flask, 10 wt% of novozyme-435 and 400 wt% of poly(ethylene glycol) dimethylether (with respect to the weight of monomers) was added (Scheme 2). Poly(ethylene glycol) dimethylether was used as solvent in the polymerization. The resulting mixture was kept at 60–70°C for 48 h under reduced pressure. After the reaction, 1,4-dioxane was added and the enzyme was filtered off to quench the reaction. The polymer solution was poured in a methanol solution to get the polymer. The polymer was resolubilized in hot 1,4-dioxane and the resulting solution was precipitated in methanol to recover the polymer. This procedure was repeated several times to get the pure polymer.

Polyester (7): ^1H -NMR Data (CDCl_3): $\delta = 1.18$ (m, OCH_2CH_3 end group), 3.54 (m, C-11H), 3.64 (m, C-10H), 4.29 (m, C-9H), 4.60 (s, C-5H), 6.87 (m, C-3H), 7.35 (m, C-2H). ^{13}C -NMR Data (CDCl_3): $\delta = 64.75$ (C-9), 65.86 (C-5), 69.44 (C-10), 71.03 (C-11), 115.44 (C-3), 128.3 (C-2), 134.66 (C-1), 157.43 (C-4), 169.34 (C-6). M_n (GPC), 6,700 Da; PD 1.5.



Scheme 2. Biocatalytic synthesis of main-chain liquid crystalline polyesters containing diphenyl mesogens.

Polyester (8): $^1\text{H-NMR}$ Data (CDCl_3): $\delta = 1.16$ (m, OCH_2CH_3 end group), 3.68 (m, C-10H), 4.31 (m, C-9H), 4.67 (s, C-5H), 7.14 (m, C-3H), 7.51 (m, C-2H). $^{13}\text{C-NMR}$ Data (CDCl_3): $\delta = 64.35$ (C-9), 66.13 (C-5), 68.84 (C-10), 115.94 (C-3), 129.68 (C-2), 133.66 (C-1), 157.84 (C-4), 168.79 (C-6). Mn (GPC), 5,900 Da; PD 1.7.

Polyester (9): $^1\text{H-NMR}$ Data (DIOXANE): $\delta = 1.18$ (m, OCH_2CH_3 end group), 1.56 (m, C-10H), 4.12 (m, C-9H), 4.68 (s, C-5H), 7.18 (m, C-3H), 7.48 (m, C-2H). $^{13}\text{C-NMR}$ Data (DMSO): $\delta = 25.64$ (C-10), 64.14 (C-9), 66.57 (C-5), 115.74 (C-3), 129.98 (C-2), 132.76 (C-1), 157.32 (C-4), 169.10 (C-6). Mn (GPC), 4,200 Da; PD 2.6.

Polyester (10): $^1\text{H-NMR}$ Data (DIOXANE): $\delta = 1.17$ (m, OCH_2CH_3 end group), 1.38 (m, C-11H), 1.57 (m, C-10H), 4.18 (m, C-9H), 4.66 (s, C-5H), 7.14 (m, C-3H), 7.51 (m, C-2H). $^{13}\text{C-NMR}$ Data (DMSO): $\delta = 26.54$ (C-11), 31.56 (C-10), 64.21 (C-9), 66.36 (C-5), 115.54 (C-3), 129.58 (C-2), 132.56 (C-1), 157.82 (C-4), 168.98 (C-6). Mn (GPC), 4,800 Da; PD 2.2.

Polyester (11): $^1\text{H-NMR}$ Data (DIOXANE): $\delta = 1.17$ (m, OCH_2CH_3 end group), 1.28 (m, C-12H), 1.30 (m, C-11H), 1.53 (m, C-10H), 4.14 (m, C-9H), 4.68 (s, C-5H), 7.16 (m, C-3H), 7.49 (m, C-2H). $^{13}\text{C-NMR}$ Data (DMSO): $\delta = 26.18$ (C-11), 28.98 (C-12), 29.66 (C-10), 64.29 (C-9), 66.30 (C-5), 115.79 (C-3), 129.63 (C-2), 132.86 (C-1), 157.46 (C-4), 169.77 (C-6). Mn (GPC), 5,100 Da; PD 2.7.

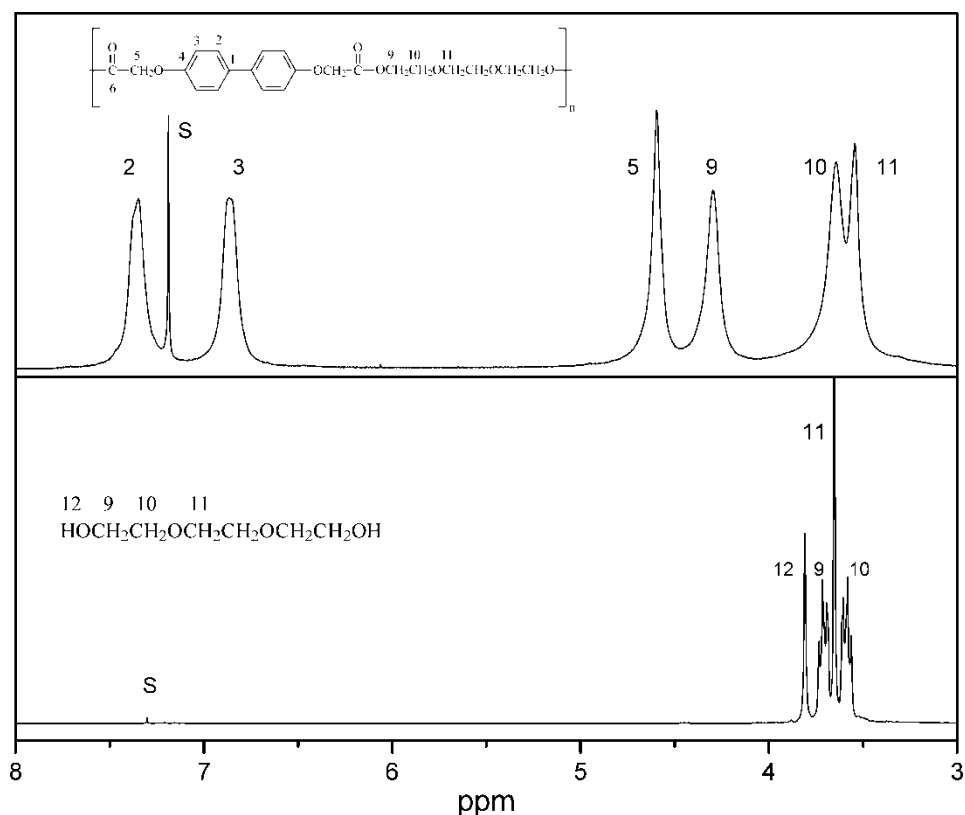


Figure 1. $^1\text{H-NMR}$ spectrum for monomer 2 and polyester 7.

Results and Discussion

The novozyme-435 catalyzed polymerization showed high regio- and chemo- selectivity. Comparison of the $^1\text{H-NMR}$ spectrum of monomer 2 and the polymer 7 showed the exclusive transesterification reaction between the ethyl ester of monomer 1 and the alcoholic hydroxyl group of monomer 2. The appearance of a new signal at $\delta = 4.29$ ppm in the polymer 7 spectra and the disappearance of the signal at $\delta = 3.72$ ppm in the monomer 2 spectra confirmed the transesterification between the CH_2OH of monomer 2 and the ethyl ester group of monomer 1. The signal at $\delta = 4.60$ ppm in the polymer 7 was assigned to the methylene protons of the COCH_2O moiety (C-5 protons in Figure 1), the signal at $\delta = 4.29$ ppm to the methylene protons of the COOCH_2 moiety (C-9 protons in Figure 1), and signal at $\delta = 3.64$ ppm to $\text{COOCH}_2\text{CH}_2$ moiety (C-10 protons in Figure 1), and signal at $\delta = 3.54$ ppm to $\text{OCH}_2\text{CH}_2\text{OCH}_2$ moiety (C-11 protons in Figure 1).

The transesterification reaction between the diethyl ester group of monomer 1 and the CH_2OH group of monomer 2 was also confirmed by the $^{13}\text{C-NMR}$ spectrum of the product polyester 7. A new peak appeared at $\delta = 69.44$ and the peak at $\delta = 73.08$ disappeared, and this confirmed the transesterification reaction (Figure 2). All the other polyesters 8–11 were also characterized as described above for polymer 7.

Thermal properties of the polyester 7–11 were studied using a TA Instruments DSC 2910. Indium and aluminum was used for calibration of the temperature and heat of fusion

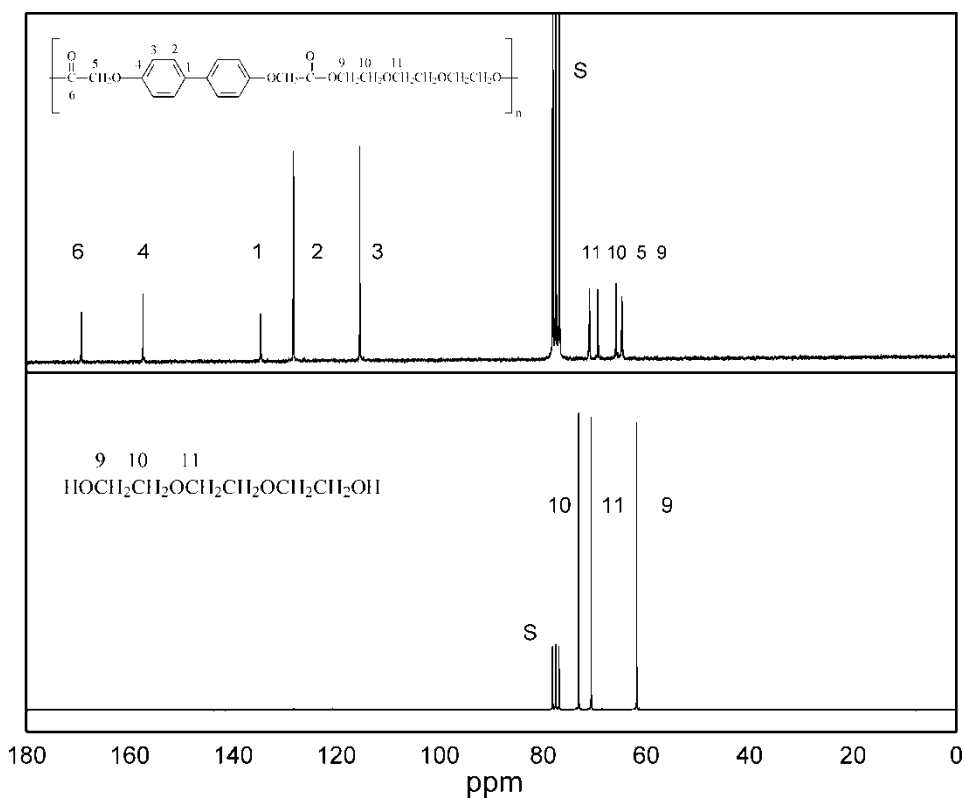


Figure 2. $^{13}\text{C-NMR}$ spectrum for monomer 2 and polyester 7.

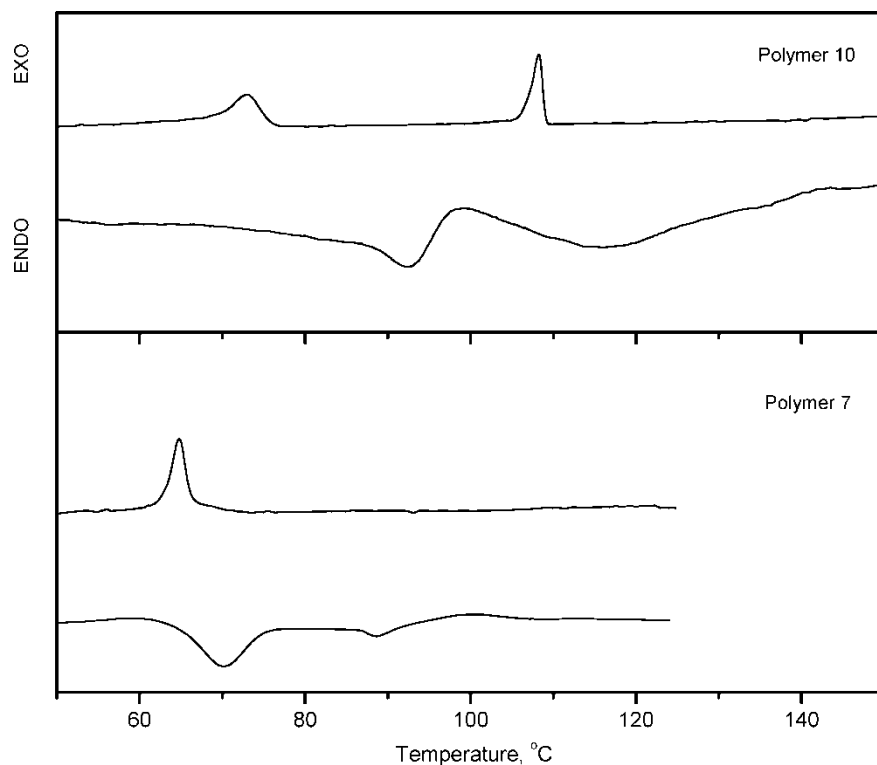


Figure 3. Differential scanning calorimetry (DSC) thermogram of polymer 7 and polymer 10 with a scan rate at $10^{\circ}\text{C min}^{-1}$.

of the DSC unit, and liquid nitrogen was used as coolant. The mass of liquid crystal samples used were between 3 and 8 mg. Prior to DSC runs, each samples was heated to ca. 10°C above its melting point and held at that temperature for few minutes to ensure it complete to the isotropic phase. Consecutive cooling and heating curves were recorded at a rate of $10^{\circ}\text{C}/\text{min}$ between this temperature and -30°C . Figure 3 shows the DSC experiment result of polyester 7 and 10. Table 1 shows the summary of the thermal behavior of the polymer 7–11. From Table 1, the introduction of flexible

Table 1
Transition temperature by differential scanning calorimetry for polymer 7–11

Polymer	Cr \rightarrow Sm($^{\circ}\text{C}$)	Sm \rightarrow Iso($^{\circ}\text{C}$)
7	70	89
8	77	108
9	101	121
10	98	119
11	104	143

Note: Cr, Sm, Iso represent crystalline, smectic and isotropic phases, respectively.

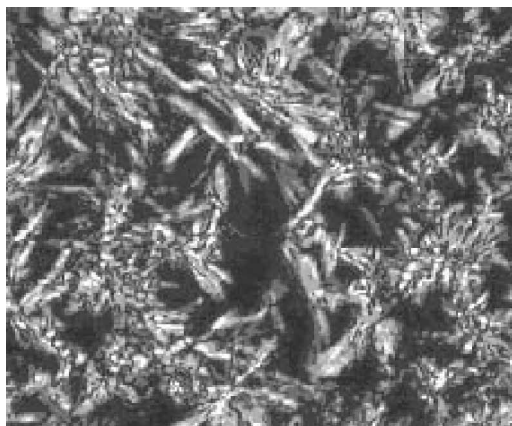


Figure 4. Polarizing optical micrograph (POM) of mesophasic texture for polymer 10 at 110°C after 1 h of annealing. magnification 400 \times .

segment into the polymer main chain decreases the transition temperature. Polymer 7 has the lowest transition temperature because of the introduction of the most flexible segment, triethylene glycol.

The DSC investigation suggests that polymer 7–11 show liquid-crystalline transitions. Thus, the phase transition of the polymers was studied using polarizing light optical micrograph (POM). For the preparation of samples, the respective polymer was heated up to isotropic state, after that, the sample was cooled down slowly to liquid crystalline temperature and annealed at that temperature for 1 h. Upon cooling from the isotropic liquid, a birefringent phase forms, and ultimately develops a fanlike texture. Figures 4 and 5 show the fanlike texture, a typical smectic texture. The fan's structure is small in all cases, as can be expected from polymers having a high molecular weight and melt viscosity.

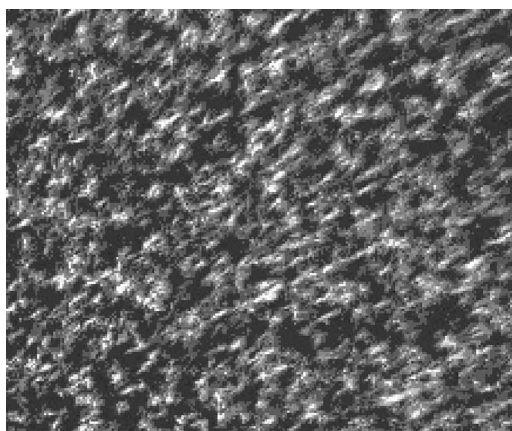


Figure 5. Polarizing optical micrographs (POM) of mesophasic texture for polymer 7 at 80°C after 1 h of annealing. magnification 100 \times .

Conclusions

Main chain liquid-crystalline polyesters containing rigid biphenyl mesogens and flexible spacers have been synthesized using chemo-enzymatic route. The enzyme catalyzed polymerization showed high region- and chemo- selectivity. The optical texture revealed by POM shows that the liquid-crystalline polymers have smectic phase.

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