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# Biosynthesis of Liquid Crystalline Azo-Polyesters

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Main-chain thermotropic liquid-crystalline aromatic azobenzene polyesters containing rigid 4,4′-dihydroxyazobenzene mesogens and flexible spacers with varying lengths were synthesized using a chemo-enzymatic method. The enzyme-catalyzed approach is based on immobilized candida antarctica lipase B. The resulting polyesters were characterized by $^1$H-NMR, $^{13}$C-NMR, differential scanning calorimetry (DSC), and polarized light optical microscopy (POM).

**Keywords:** liquid-crystalline polymers; azobenzene; enzymes

## 1 Introduction

Azo polymers (azobenzene-containing polymers) are polymers that have -N=N- functional groups within the polymer structure. In the last few years, main-chain liquid-crystalline (MCLC) aromatic azo polyesters have been attracting a great deal of attention because of the numerous technological applications (1–7). Thermotropic MCLCPs are synthesized by combining the rigid mesogenic segments and flexible spacers in alternating succession (8). These polymers, when melted, exhibit mesomporphic phases of nematic or smectic order.

The first reported observations of thermotropic liquid-crystalline behavior in polymers was made by Roviello and Sirigu (8) and independently by Kuhfuss and Jackson (9). Since then, much research work has been focused on the synthesis of liquid-crystalline polymers. However, most of the synthesis is based on the conventional chemical reactions, which involve toxic catalysts and solvent. Enzymes are efficient catalysts and their activity with unnatural substrates in organic reaction media is attracting considerable attention (10). Enzymatic synthesis has been proven to have a number of advantages. These advantages include: (1) catalysis under mild reaction conditions with regard to temperature, pressure, and pH, (2) high enantio-, regio-, and chemo-selectivity; (3) nontoxic natural catalysts, avoiding the use of toxic heavy metal catalysts. Therefore, enzymatic polymerization can be regarded as an environmentally friendly "green" synthetic approach to novel polymeric materials (11–13).

The focus of this work is to utilize advances in both biochemistry and polymer science in order to synthesize and characterize the biocatalyzed main-chain liquid-crystalline polyesters with azobenzene mesogenic units.

## 2 Experimental

### 2.1 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. Dichloromethane, 4-Nitrophenol, Potassium hydroxide, 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 dimethyl ether (Mw 1,000) was purchased from Aldrich.

### 2.2 Characterization

$^1$H-NMR, $^{13}$C-NMR were recorded on a Bruker ARX-200 FT-NMR spectrometer using $CDCl_3$ as a solvent unless otherwise stated. The samples for the FT-IR measurements were made by casting thin film on a transparent potassium bromide disc from solution. The DSC measurements were carried out using a TA Instruments DSC 2910. A scan rate of $10^\circ C \cdot min^{-1}$ was used. Samples were tested under a nitrogen atmosphere and sample sizes were between 3–8 mg.

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### 2.3 *Synthesis of 4,4′-Dihydroxyazobenzene(4,4′-DHAB)*

4,4′-Dihydroxyazobenzene (DHAB) was synthesized according to the method of Willstatter and Benz (14) (Scheme 1). A mixture of KOH (50 g, 760 mmol), 4-nitrophenol (10 g, 72 mmol), and water (10 g) was heated slowly to 195–200°C for 6 h. After the reaction, the product was recrystallized from 50% (v/v) ethanol aqueous solution, and the yield was 50%. The final product is a dark red crystal powder with a melting point of 215–218°C.

$^1$H-NMR Data (DMSO): $\delta = 6.95$(m, C-2H), 7.75(m, C-3H), 10.15(s, *H*OPh). $^{13}$C-NMR Data (DMSO): $\delta = 116.67$(C-3), 125.04(C-2), 146.14(C-1), 160.87(C-4). FTIR (cm$^{-1}$), 3192 (O-H stretch), 1591, 1578 and 1503 (aromatic C═C stretch), 1251 (COC stretch), 1157(CN stretch), 846 (C-H bending).

### 2.4 *Synthesis of Diester Monomer 2 ((1,1′-azo-4,4′-phenyleneoxy) Diacetic Acid Diethyl Acetate)*

The diester monomer 2 was prepared by the reaction of 4,4′-dihydroxyazobenzene (DHAB) with ethyl bromoacetate in 2-butanone under reflux (Scheme 1). 0.1 mol DHAB (21.4 g), 0.25 mmol ethyl bromoacetate (41.75 g), 0.25 mol potassium carbonate (34.5 g) were mixed in 200 ml 2-butanone, and the mixture was refluxed with intensive stirring for 24 h. After reaction, the product was recrystallized from 50% (v/v) ethanol aqueous solution to give yellow crystals with a 117–119°C melting point. FTIR (KBr): 3002 ($CH_2$ and $CH_3$), 1736 (C═O), 1600, 1582, and 1500 (aromatics), 1240 (C-O-C) cm$^{-1}$. $^1$H-NMR Data: $\delta = 1.33$(m, C-8H), 4.31(m, C-7H), 4.71(s, C-5H), 7.04(m, C-3H), 7.91(m, C-2H). $^{13}$C-NMR Data: $\delta = 14.57$(C-8), 61.93(C-7), 65.92(C-5), 116.67(C-3), 124.84(C-2), 145.31(C-1), 160.17(C-4), 168.92(C-6).

### 2.5 *General Procedure for the Synthesis of Main-Chain Liquid-Crystalline Polyesters*

A mixture of 1,10-decanediol (1.74 g), monomer 2 (3.86 g) and polyethylene glycol dimethyl ether (20 g) were placed in a 50 ml round-bottom flask, and to this mixture was added lipase (10 wt% of monomers). Polyethylene glycol dimethyl ether was used as solvent. The flask was then placed in a constant temperature oil bath maintained at 60–70°C under vacuum. The reaction was allowed to proceed for 48–72 h. Then the reaction was quenched by adding chloroform and filtering off the enzyme. The filtrate was concentrated and precipitated in methanol. 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 obtain the pure polymer.

DHABTEG (Polyester 7): $^1$H-NMR Data ($CDCl_3$): $\delta = 1.18$ (m, $OCH_2CH_3$ end group), 3.58 (m, C-9H), 3.66 (m, C-8H), 4.32 (m, C-7H), 4.640 (s, C-5H), 6.88 (m, C-3H), 7.37(m, C-2H). $^{13}$CNMR Data ($CDCl_3$): $\delta = 64.8$(C-7), 65.9(C-5), 69.6(C-8), 71.1(C-9), 115.6(C-3), 128.2(C-2), 134.7(C-1), 157.6(C-4), 169.4(C-6). Mn (GPC), 7200 Da; PD 1.6

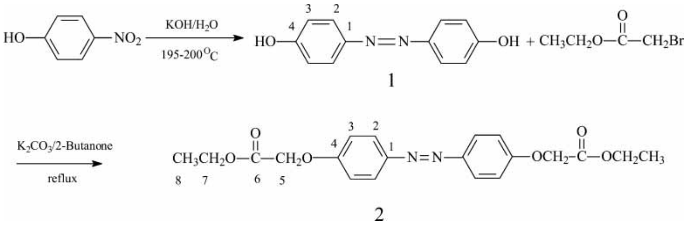
DHABC3 (Polyester 8): $^1$H-NMR Data ($CDCl_3$): $\delta = 1.18$ (m, $OCH_2CH_3$ end group), 1.95 (m, C-8H), 4.22 (m, C-7H), 4.66 (s, C-5H), 7.13 (m, C-3H), 8.04 (m, C-2H).

DHABC6 (Polyester 9): $^1$H-NMR Data ($CDCl_3$): $\delta = 1.18$ (m, $OCH_2CH_3$ end group), 1.25 (m, C-9H), 1.56 (m, C-8H), 4.12 (m, C-7H), 4.61 (s, C-5H), 6.93 (m, C-3H), 7.80 (m, C-2H).

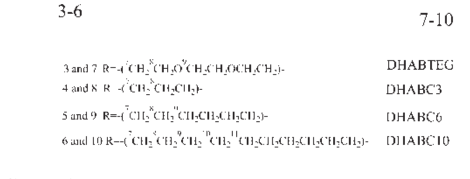
DHABC10 (Polyester 10): $^1$H-NMR Data ($CDCl_3$): $\delta = 1.19$ (m, $OCH_2CH_3$ end group), 1.33 (m, C-9H, C-10H and C-11H), 1.54 (m, C-8H), 4.14 (m, C-7H), 4.68 (s, C-5H), 7.03 (m, C-3H), 8.01 (m, C-2H).

## 3 Results and Discussion

The enzymatic synthesis of the MCLC polyesters was performed as shown in Scheme 2. The structure of the polyesters was identified using NMR. Figure 1 shows the $^1$H-NMR spectrum of monomer 3 and the polyester 7 (Scheme 2). Comparison of the $^1$H-NMR spectra confirmed the transesterification reaction between the ethyl ester of monomer 2 and the alcoholic hydroxyl group of monomer 3. The appearance of a new signal at $\delta = 4.35$ ppm (C-7H) and the disappearance of the signal at $\delta = 3.59$ ppm in the polyester 7 spectra confirmed formation of an ester linkage between the $CH_2OH$ of monomer 3 and the ethyl ester group of monomer 2. The transesterification reaction between the ethyl ester group of monomer 2 and the $CH_2OH$ group of monomer 3 was also confirmed by the $^{13}$C-NMR spectra of the monomer 3 and polyester 7 (Figure 2). A new peak (C-1) appeared at



**Sch. 1.** Synthesis of compound 2.



**Sch. 2.** Biocatalytic synthesis of main-chain liquid crystalline polyesters containing DHAB mesogens.

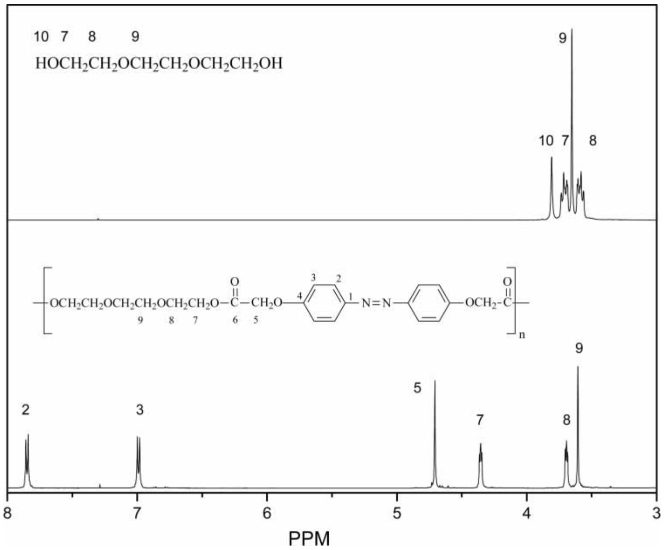


**Fig. 1.** $^1$H-NMR spectrum for monomer 3 and polyester 7.

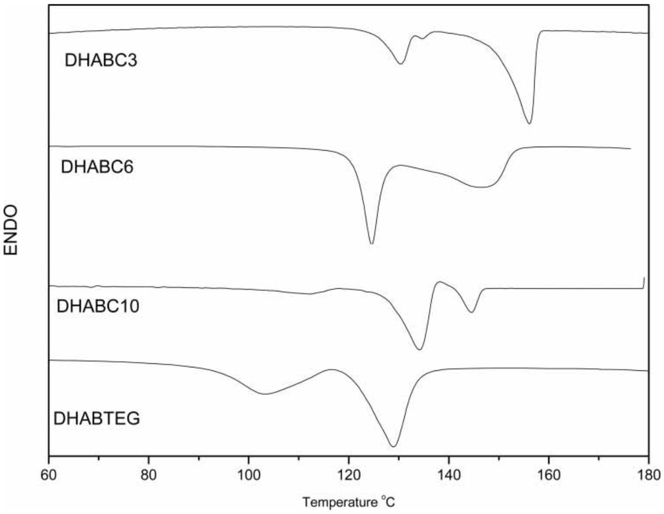


**Fig. 3.** Differential scanning calorimetry (DSC) thermograms of polymers 7–10 with a scan rate at 10°C · min$^{-1}$.

$\delta = 64.8$ ppm and the peak at $\delta = 62.7$ ppm disappeared, and also confirmed the transesterification reaction. All the other polyesters, 8–10, were also characterized as described above for polymer 7.

### 3.1 *Characterization of Mesophases of the Main-Chain Liquid-Crystalline Polyesters by DSC and POM*

Thermal properties of the synthesized polyesters were studied using a TA Instruments DSC 2910. Indium and aluminum was used for calibration of the temperature and heat of fusion of the DSC unit, and liquid nitrogen was used as the coolant. The mass of the liquid crystal samples were between 3 and 10 mg. Prior to DSC runs, each sample was heated to ca. 10°C above its melting point and held at that temperature for a few minutes to ensure complete conversion to the isotropic phase. Consecutive cooling and heating curves were recorded at a rate of 10°C/min between this temperature and 0°C. Figure 3 shows the DSC experiment result of DHABC3, DHABC6, DHABC10 and DHABTEG. Table 1 shows the summary of the thermal behavior of polymers 7–10. These results show that the introduction of a flexible segment into the polymer main-chain decreases the transition temperature of the synthesized polyesters. For the liquid-crystalline polyesters with the DHAB mesogen unit, DHABC3 has the highest LC transition temperature because of the presence of the most rigid segment into the polyester main-chain, and DHABTEG has the lowest LC transition temperature because of the presence of the most flexible segment, triethylene glycol, into the main chain.

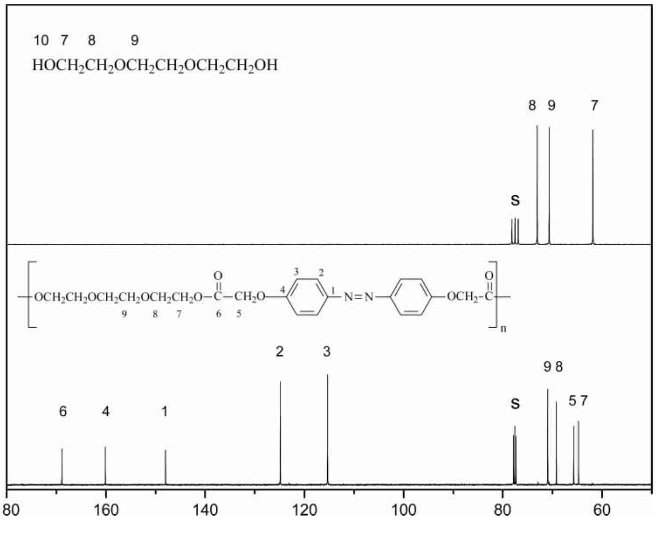
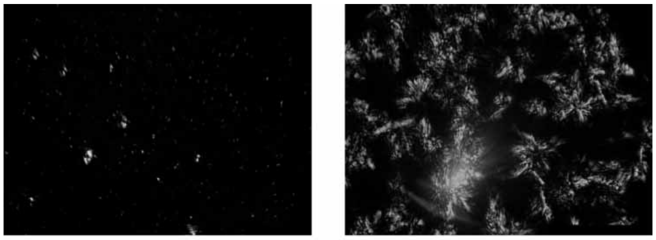


**Fig. 2.** $^{13}$C-NMR spectrum for monomer 3 and polyester 7.

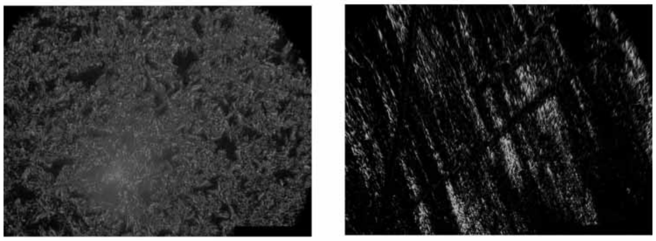
The DSC investigation suggests that polymer 7–10 show liquid-crystalline transitions. Thus the phase transition of the polymers was studied using polarized optical microscopy (POM). For the preparation of samples, the respective polymer was heated to isotropic state, then covered with cover glass. The sample was then slowly cooled down to below the Liquid-Crystalline temperature and annealed at that temperature for 1 h. Upon cooling from the isotropic

**Table 1.** DSC and optical data of liquid-crystalline polyesters

| Polyesters | Phase transitions (°C) | LC texture |
|---|---|---|
| DHABC3 | K 130.5 S 156.1 I | Smectic |
| DHABC6 | K 125.6 S 147.2 I | Smectic |
| DHABC10 | K 134.1 S 144.5 I | Smectic |
| DHABTEG | K 103.3 S 129.0 I | Smectic |



(a) 145°C 400x (b) 142.5°C 400x



(c) 138°C 400x (d) 138°C 400x

**Fig. 4.** Polarized optical micrographs of DHABC10.

liquid, a birefringent phase forms, which ultimately develops a Liquid-Crystalline texture. Figure 4 shows the polarized optical micrographs of DHABC10. Upon cooling from the isotropic liquid, a birefringent phase forms at 145°C (4a), which upon further cooling, assumes oblong shapes (batonnets) at 142.5°C (4b), and ultimately develops a fanlike texture at 138°C (4c). This behavior shows that the Liquid-Crystalline polyester is in the smectic state. Figure 4d shows a banded texture induced by mechanical shearing between the glass slide and the cover glass. The bands are perpendicular to the shear direction. Formation of these bands is due to the slight relaxation of the liquid-crystalline molecules after shearing, and the bands are composed of a small fanlike texture. The formation of the banded texture confirmed that polyesters are in a liquid crystal state at 138°C.

## 4 Conclusions

Main chain liquid-crystalline polyesters containing rigid azobenzene mesogens and flexible spacers with varying length have been synthesized using a chemo-enzymatic route. The synthesized polyesters have been characterized using $^{1}$H-NMR, $^{13}$C-NMR, differential scanning calorimetry (DSC), and polarized light optical microscopy (POM). The optical texture revealed by POM shows that the liquid-crystalline polymers have a smectic phase.

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