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Thermotropic aromatic/lactide copolyesters with solubilizing side chains on aromatic rings

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Abstract

Liquid-crystalline polyesters with solubilizing side chains on aromatic rings have been synthesized by melt polycondensation of diacid dichlorides and silylated hydroquinones. Corresponding copolyesters incorporated with lactide units were obtained by addition of oligolactides. The molecular structures of these polymers were verified by spectroscopy techniques. Molecular weights were characterized by gel permeation chromatography. X-ray diffraction studies confirmed that all polyesters are partially crystalline and have self-organized ordered stacking structures. The polyesters can form smectic melts upon heating above the melting temperature. Contact angle measurements and water absorption data of solution cast films showed that the polyesters have relatively high hydrophilicity and decreasing contact angle with increasing amount of lactide moieties.

Keywords: Copolymerization; Hydrophilic polymers; Liquid-crystalline polymers (LCPs)

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1. Introduction

Aromatic polyesters have received significant attention as thermotropic liquid-crystalline polymers, which were described in several reviews [1]. The inherent insolubility, infusibility, and inprocessibility of aromatic polyesters were improved e.g. by lateral substituents, flexible spacers in the main chain, kinks in the main chain, etc. Films and fibers of processible thermotropic aromatic polyesters exhibit exceptional mechanical properties. Biodegradable polymers with exceptional mechanical properties are still a challenge for particular medical applications such as bone tissue engineering [2]. We have explored new modified aromatic polyesters with enhanced degradability under physiological conditions because aromatic polyesters are nondegradable under physiological conditions on an acceptable time scale. It has been shown that copolyesters with aromatic moieties and oligoactide moieties in the main chain are liquid-crystalline, degradable, and exhibit excellent mechanical properties [3]. Copolyesters composed of aromatic moieties, lactide moieties, and oligoethylene oxide moieties were also liquid-crystalline and showed good mechanical properties [4]. Hydrophilicity of the copolyesters, and consequently degradability, was significantly enhanced due to incorporation of oligoethylene oxide moieties in the main chain. However, a major draw back of these copolyesters for tissue engineering is that aromatic degradation products would be insoluble in aqueous environment. In order to reduce this drawback we have reported a novel thermotropic copolyesters with lateral methoxyethyleneoxy substituents on the aromatic hydroquinone moieties, which retain their liquid crystallinity and exhibit enhanced hydrophilicity [5]. In this article, we report on the synthesis and analysis of a new class of biodegradable polyesters with aromatic and lactide moieties in the main chain and solubilizing side chains on all aromatic rings. Major goal is the solubility of the corresponding low molecular weight degradation products of the polyesters under physiological conditions in order to assure proper metabolization of the polyesters in biomedical applications.

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2. Experimental section

2.1. General methods

Materials were characterized by means of elemental analysis with Elementar Vario EL, by ^{1}H (300 MHz) and ^{13}C NMR spectra (400 MHz) with $CDCl_3$ as solvent and TMS as internal standard recorded on Brucker ARX 300 and DRX 400 instruments. Gel permeation chromatography (GPC) was performed with chloroform ($CHCl_3$) as solvent and UV/RI detection versus polystyrene standards. The intrinsic viscosity $[\eta]$ (d l g^{-1}) was determined using a Schott Ubbelhode viscometer in $CHCl_3$ at 25 °C. Thermogravimetry (TG) was performed under nitrogen with a Mettler TG 851 at a heating rate of 20 °C/min and a sample size 8–10 mg. Mettler DSC 821 apparatus was used for differential scanning calorimetry (DSC) with a sample size of 8–10 mg, at a heating rate of 10 °C/min and cooling rate of 10 °C/min, observing the second heating run. Liquid-crystalline behavior was observed by a Leitz orthoplan polarizing microscope (OPM), equipped with a Mettler FP 82 hot stage. A Krüss G10 Hz was used to measure contact angles with water on polymer films. Wide-angle X-ray scattering (WAXS) was performed with a Siemens D5000 diffractometer using Cu Kα radiation. The scanning time for each measurement was 3 h.

2.2. Material synthesis: general procedure

All starting materials were purchased from Aldrich Chemical Company and used without further purification except tetrahydrofuran, which was distilled over calcium hydride and stored under argon. A 90% aqueous solution of racemic DL-lactic acid was heated stepwise to 200 °C and kept at this temperature in vacuum for 4 h. This procedure yielded α-hydroxy-ω-carboxyoligolactide ($\bar{M}_w = 4500$, $\bar{M}_n = 1700$, $\bar{M}_w/\bar{M}_n = 2.60$, $\bar{M}_n$ calculated from ^{1}H NMR $= 1100$) according to previous literature [6]. The synthetic scheme for the two monomers is shown in Scheme 1.

2.2.1. 2,5-Bis(methoxyethyleneoxy)-1,4-hydroquinone silylate (**3**)

This compound was prepared according to the procedure in previous report [5] by starting from 2,5-dihydroxy benzoquinone via the three steps as shown in Scheme 1. Mp: 50–51 °C. Calculated for $C_{18}H_{34}O_6Si_2$ (402): C, 53.70; H, 8.51. Found: C, 53.63; H, 8.99. ^{1}H NMR ($CDCl_3$, ppm) δ 0.19 (s, 18H, $6CH_3Si$), 3.21 (s, 6H, $2CH_3O$), 3.57 (t, 4H, $2CH_2$, $J_1 = 5.12$ Hz, $J_2 = 4.88$ Hz), 3.85 (t, 4H, $2CH_2$–OAr, $J_1 = 5.13$ Hz, $J_2 = 4.88$ Hz), 6.51 (s, 2H, 2Ar–H). ^{13}C NMR ($CDCl_3$, ppm) δ 0.01, 58, 70, 71, 109, 139, 144. MS (70 eV): *m/z* 402 (M^+ 78%).

2.2.2. 2-Methoxyterephthalic acid (**4**)

A mixture of 2,5-dimethylanisole (30 g, 0.22 mol), potassium permanganate (120 g, 0.76 mol) and distilled water (3000 ml) was refluxed for 5 h. The mixture was cooled to room temperature and poured into stirred cold ethanol (2000 ml). This mixture was then filtered, washed thoroughly with water, reduced under vacuum, and acidified with concentrated hydrochloric acid. The resulting white precipitate was collected by filtration, washed with water and dried. The yield was 21 g (50%). Mp: 287–288 °C. Calculated for $C_9H_8O_5$ (196): C, 55.11; H, 4.11; O, 40.78. Found: C, 55.62; H, 4.10; O, 40.02. ^{1}H NMR (Acetone-d_6, ppm) δ 4.15 (s, 3H, CH_3), 7.81 (dd, 2H, 2Ar–H), 8.01 (s, 1H, Ar–H), 11.49 (s, 2H, 2COOH).

2.2.3. 2-Hydroxyterephthalic acid (**5**)

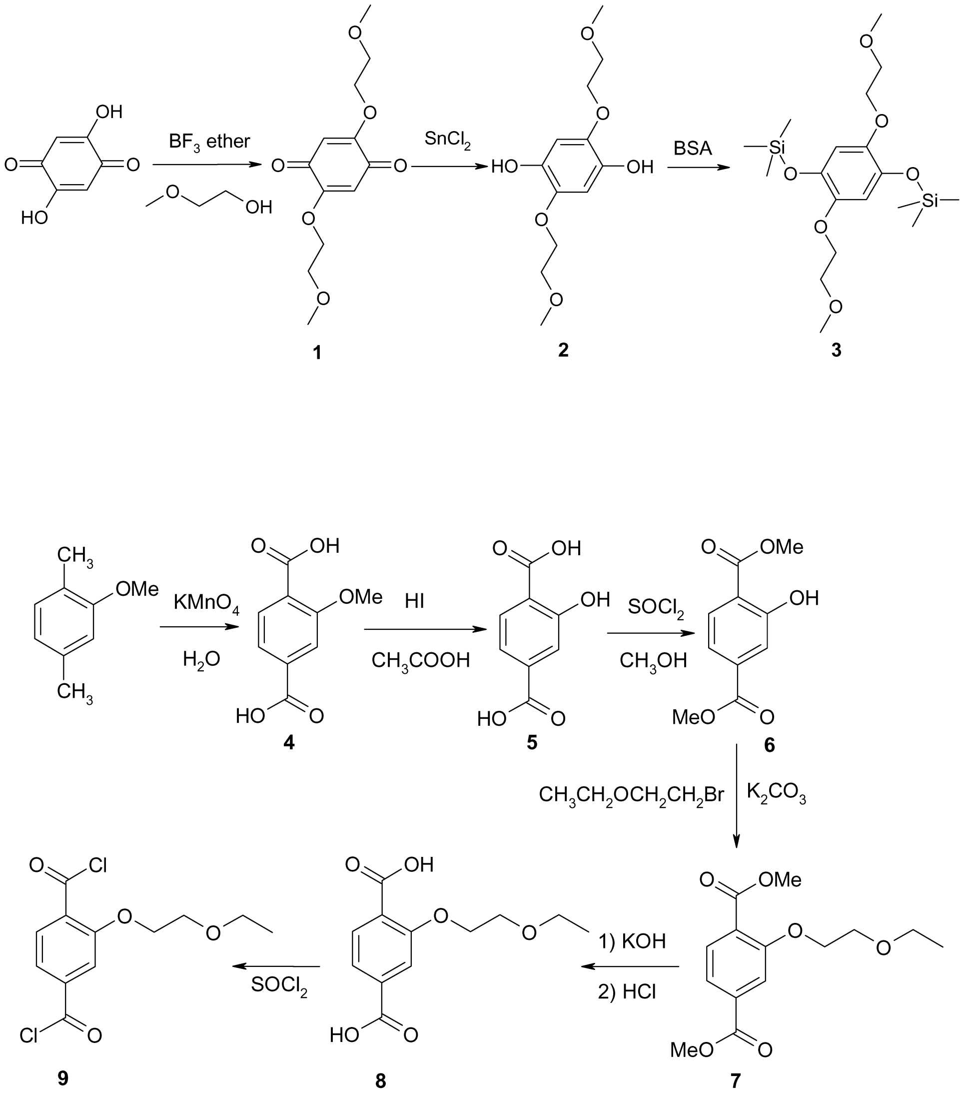
A mixture of compound **4** (19.6 g, 100 mmol), concentrated hydroiodic acid (120 ml) and acetic acid (400 ml) was refluxed for 24 h. After cooling to room temperature, the mixture was filtered, washed thoroughly with acetic acid and water, respectively. The white solid was collected and dried. The yield was 15 g (82%). Mp: 317–320 °C. Calculated for $C_8H_6O_5$ (196): C, 52.76; H, 3.32; O, 43.92. Found: C, 52.21; H, 4.00; O, 43.76. ^{1}H NMR (Acetone-d_6, ppm) δ 7.50 (d, 2H, 2Ar–H), 7.98 (s, 1H, Ar–H), 11.10 (s, 1H, OH).

2.2.4. Dimethyl 2-hydroxyterephthalate (**6**)

Compound **5** (14.5 g, 80 mmol) was dissolved in 400 ml of methanol. Purified thionyl chloride (54 ml, 75 mmol) was slowly added to above solution with stirring under a nitrogen atmosphere over a period of 1 h. The mixture was stirred for 15 h at room temperature. Then the reaction mixture was poured into a large excess of distilled water. To the slurry was added a 30% aqueous solution of Na_2CO_3 until the mixture became neutral. The precipitate formed was collected on a filter and washed thoroughly with distilled water. The product was recrystallized from ethanol. The yield was 15 g (89%). Mp: 94–95 °C. Calculated for $C_{10}H_{10}O_5$ (210): C, 57.14; H, 4.80; O, 38.06. Found: C, 56.85; H, 4.97; O, 37.78. ^{1}H NMR (Acetone-d_6, ppm) δ 3.91 (s, 3H, CH_3), 4.01 (s, 3H, CH_3), 7.52 (s, 1H, Ar–H), 7.54 (d, 1H, Ar–H), 7.99 (d, 1H, Ar–H), 10.76 (s, 1H, OH). MS (70 eV): *m/z* 210 (M^+ 21%).

2.2.5. Dimethyl 2-ethoxyethyleneoxyterephthalate (**7**)

Compound **6** (10.5 g, 50 mmol) and 2-bromoethyl ethyl ether (15.3 g, 100 mmol) were dissolved in 250 ml of acetone. 25 g of K_2CO_3 and 0.2 g of KI were added to above solution. The mixture was refluxed for 24 h under a nitrogen atmosphere. The solid residue was removed by filtration. Acetone in the filtrate was distilled off using a rotary evaporator followed by removal of 2-bromoethyl ethyl ether via vacuum distillation. The residue was chromatographed on a silica gel column using a mixture of *n*-hexane and ethyl acetate (6:1 by volume) as an eluent. The yield was 11.3 g (80%). Calculated for $C_{14}H_{18}O_6$ (282): C, 59.57; H, 6.43; O, 34.01. Found: C, 59.40; H, 6.54; O, 33.97. ^{1}H NMR (Acetone-d_6, ppm) δ 1.20 (t, 3H, CH_3, $J_1 = 6.83$ Hz,



Scheme 1. Synthetic route to monomers **3** and **9**.

$J_2 = 7.08$ Hz), 3.65 (q, 2H, C H_2CH_3, $J_1 = 7.08$ Hz, $J_2 = 7.08$ Hz, $J_3 = 6.84$ Hz), 3.82 (t, 2H, CH_2, $J_1 = 4.89$ Hz, $J_2 = 4.39$ Hz), δ 3.93 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 4.47 (t, 2H, CH_2, $J_1 = 4.39$ Hz, $J_2 = 4.64$ Hz), 7.55 (s, 1H, Ar–H), 7.58 (d, 1H, Ar–H), 7.99 (d, 1H, Ar–H).

2.2.6. *2-Ethoxyethyleneoxyterephthalic acid (8)*

A solution of 30% KOH in water (42 ml, 224 mmol) was added to compound **7** (8 g, 28.4 mmol). The reaction mixture was refluxed for 12 h. After cooling to room temperature the solution was poured into excess water, and then acidified with hydrochloric acid. The white solid was collect on a filter and washed thoroughly with distilled water. The product was recrystallized from ethyl acetate. The yield was 7.1 g (98%). Calculated for $C_{12}H_{14}O_6$ (254): C, 56.69; H, 5.55; O, 37.76. Found: C, 56.30; H, 5.52; O, 37.65. ^1H NMR (Acetone-d_6, ppm) δ 1.19 (t, 3H, CH_3, $J_1 =$ 6.83 Hz, $J_2 = 7.08$ Hz), 3.62 (q, 2H, C H_2CH_3, $J_1 = 7.08$ Hz, $J_2 = 7.08$ Hz, $J_3 = 6.84$ Hz), 3.89 (t, 2H, CH_2, $J_1 =$ 4.89 Hz, $J_2 = 4.39$ Hz), 4.49 (t, 2H, CH_2, $J_1 = 4.39$ Hz, $J_2 = 4.64$ Hz), 7.78 (d, 1H, Ar–H, $J = 8.06$ Hz), 7.83 (s, 1H, Ar–H), 8.01 (d, 1H, Ar–H, $J = 8.06$ Hz).

2.2.7. *2-Ethoxyethyleneoxyterephthaloyl chloride (9)*

A mixture of compound **8** (5.08 g, 20 mmol) and thionyl chloride (40 ml, 544 mmol) was heated to reflux for 12 h. The excess of thionyl chloride was removed under vacuum, and the residue was recrystallized from *n*-hexane for several times in refrigerator. The yield was 5.5 g (95%). Calculated for $C_{12}H_{12}Cl_2O_4$ (291): C, 49.51; H, 4.15. Found: C, 49.66; H, 4.10. ^1H NMR ($CDCl_3$, ppm) δ 1.10 (t, 3H, CH_3, $J_1 =$ 6.83 Hz, $J_2 = 7.08$ Hz), 3.49 (q, 2H, C H_2CH_3, $J_1 = 6.84$ Hz, $J_2 = 7.08$ Hz, $J_3 = 7.08$ Hz), 3.73 (t, 2H, CH_2, $J_1 =$ 4.88 Hz, $J_2 = 4.39$ Hz), 4.19 (t, 2H, CH_2, $J_1 = 4.40$ Hz, $J_2 = 4.88$ Hz), 7.62 (s, 1H, Ar–H), 7.68 (d, 1H, Ar–H, $J = 8.30$ Hz), 7.92 (d, 1H, Ar–H, $J = 8.30$ Hz). ^{13}C NMR ($CDCl_3$, ppm) δ 15.5 (CH_3), 67.5 (C H_2CH_3), 68.9 (CH_2), 70.1 (CH$_2$), 115.9, 123.4, 129.3, 133.5, 138.8, 158.4, 164.2, 167.9. MS (70 eV): *m/z* 290 (M$^+$ 76%).

2.3. Polymer synthesis: general procedure

Since all homopolyesters and copolyesters were prepared in the same manner by bulk polycondensation, only a detailed procedure illustrating the synthesis of a random copolymer with a 1:0.3 molar ratio (**11a**) of aromatic monomer: oligolactide is given below. A two-necked flask (pretreated with dimethyl dichlorosilane) was charged with 4026.4 mg (10 mmol) of 2,5-bis(methoxyethyleneoxy)-1,4-hydroquinone silylate (**3**), 2911.3 mg (10 mmol) of 2-ethoxyethyleneoxyterephthaloyl chloride (**9**), and 216.2 mg (3 mmol) of oligolactide under a slow stream of argon. The reaction mixture was slowly heated to 160 °C until a homogeneous melt was formed which became increasingly viscous. After then this temperature was kept for 20 h, the product was cooled to room temperature, dissolved in 20 ml of CHCl$_3$ and isolated by precipitation in 400 ml of *n*-hexane. The polymer was purified by redissolution/precipitation in CHCl$_3$/*n*-hexane and dried at 60 °C in vacuo.

The NMR spectra of copolyesters **11** are almost identical with that of polyesters **10** except additional peaks caused by the oligolactide moieties. For example copolyester **11a**:

^{1}H NMR (CDCl$_3$, ppm): δ 1.20 (3H, CH_3CH$_2$), 1.55 (0.9H, 0.3CH_3 lactide), 3.35 (6H, 2CH_3), 3.60 (6H, 3CH_2), 3.90 (2H, CH_2), 4.15 (4H, 2CH_2OAr), 4.35 (2H, CH_2OAr), 5.15 (0.3H, 0.3CH lactide), 7.00 (2H, 2CH), 7.90 (2H, 2CH), 8.15 (1H, CH).

^{13}C NMR (CDCl$_3$, ppm): δ 15.4 (CH$_3$CH$_2$), 16.8 (CH$_3$ lactide), 59.3 (2CH$_3$), 67.2 (CH$_2$CH$_3$), 67.8 (CH lactide), 68.9 (CH$_2$), 69.5 (CH$_2$OAr), 70.0 (2CH$_2$), 71.1 (2CH$_2$OAr), 103.3, 110.6, 115.2, 122.4, 124.6, 132.4, 134.3, 138.4, 142.1, 144.8, 146.8, 158.9, 163.3, 163.8, 168.3 (C lactide).

Film Preparation: Films of polyesters were prepared by solution casting. Typically, a chloroform solution (30%) of the polymer was poured onto a glass plate and the solvent was slowly evaporated at room temperature. The formed film was separated from the glass plate. The residual solvent was evaporated under atmospheric pressure over 24 h at room temperature and then in vacuo for 48 h at 40 °C.

3. Results and discussion

3.1. Monomer synthesis

In order to enhance the solubility of aromatic units of the copolyesters in aqueous environment hydroquinone and terephthaloyl were synthesized with ethyleneoxy substituents as shown in Scheme 1. Detailed description of monomer **3** has been given in previous publication [5]. Monomer **9** was prepared by reaction of corresponding diacid with thionyl chloride without using DMF as a catalyst. Compound **5**, prepared from 2,5-dimethylanisole via the two steps as previously described [7], was esterified to **6** simply by reacting it at room temperature with a mixture of methanol and thionyl chloride. The diester **6**, was refluxed with excess 2-bromoethyl ethyl ether in acetone in the presence of potassium carbonate and a small amount of potassium iodide to produce **7**. The diester was then hydrolyzed to the potassium salt in presence of 30% potassium hydroxide, which was then converted to the acidic form **8** simply by acidifying the solution. The structures of all of the intermediates and the final monomers were confirmed by elemental analysis, IR and NMR spectra.

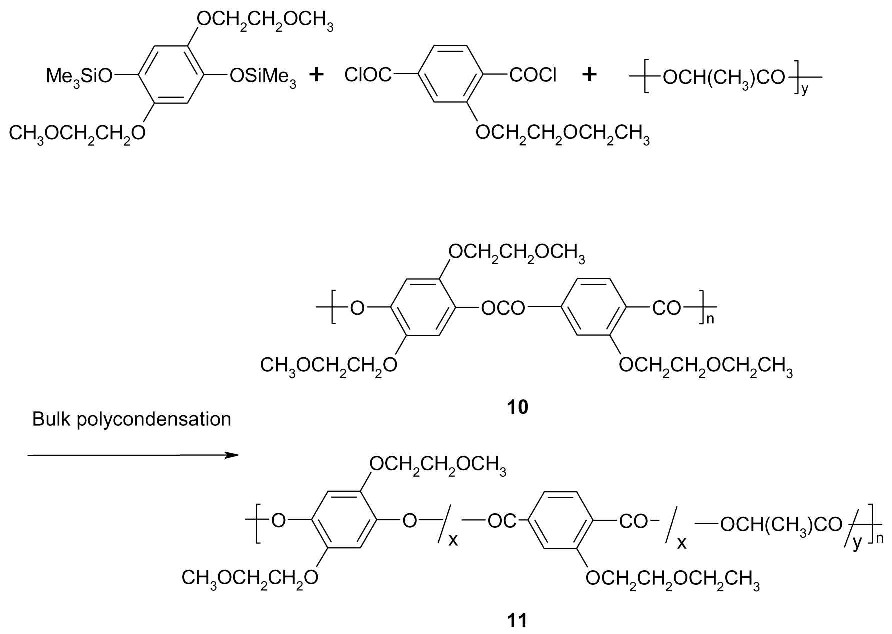
3.2. Synthesis and properties of polyesters

Monomer **3** and **9** were polymerized by melt polycondensation according to a previously published procedure [8]. The synthetic route to polyester is shown in Scheme 2. Yields are between 81–89% and $\bar{M}_w$ between 2700 and 33200 g mol^{-1}, according to GPC analysis in chloroform versus polystyrene standards, depending on the reaction conditions (Table 1). Although polydispersity is relatively large only monomodal GPC traces were observed for **10**. ^{1}H NMR spectroscopy showed the signals expected for polyester **10** with peaks at 3.35 (2CH$_3$), 3.60 (2CH$_2$), 4.15 (2CH$_2$OAr), and 7.00 (2Ar–H) for the hydroquinone moieties, and, 1.20 (CH_3CH$_2$), 3.60 (CH_2CH$_3$), 3.90 (CH$_2$), 4.35 (CH$_2$OAr), 7.90 (2Ar–H), and 8.15 (Ar–H) for the terephthaloyl moieties. ^{13}C NMR spectroscopy verified structural composition obtained by ^{1}H NMR spectroscopy. It is noteworthy that two types of carbonyl were observed which is due to the 2 and 3-position of the ethyleneoxy substituent in the terephthaloyl unit. As shown in Table 1, the polymerization conditions of 20 h at 160 °C resulted high molecular weight of polyester **10** (Entry no. 6). Therefore, copolymerizations were carried out under this optimized conditions. The properties of polyester **10** in this article were obtained by using entry no. 6.

Table 1
Bulk condensation of **3** and **9** under various conditions yielding polyester **10**

No.	Condition		Yield^a (%)	$[\eta]^b$ (dl g^{-1})	$\bar{M}_w$^{c}	$\bar{M}_n$^{c}	$\bar{M}_w/\bar{M}_n$^{c}
	Time (h)	Temperature (°C)					
1	3	140	81	0.14	4900	3600	1.30
2	3	160	85	0.13	2700	1500	1.80
3	6	160	87	0.18	7200	1900	3.60
4	10	160	86	0.36	27100	5900	4.60
5	10/3	160/200	–	–	–	–	–
6	20	160	89	0.95	33200	9800	3.40

[a] After reprecipitation from chloroform/methanol.
[b] Measured in chloroform at 25 °C.
[c] Gel permeation chromatography in chloroform.



Scheme 2. Synthetic route and chemical structures of polyesters.

Copolyesters **11** were prepared by melt polycondensation in the same manner described for **10** but with varying amounts of oligolactide as shown in Scheme 2. Melt polycondensation was performed at 160 °C for 20 h. Yields are in the range of 86–89%, and weight-averaged molecular weights are in the range of 14400–27100 g mol^{-1} depending on the content of lactide moieties, which were obtained by GPC analysis in chloroform versus polystyrene standards (Table 2). All GPC traces showed unimodal molecular weight distribution. No hints for oligolactides were found during analysis of the hexane precipitation bath, which indicate quantitative incorporation of oligolactide in copolyester **11**. ^{1}H NMR spectra of copolyesters **11** showed additional peaks caused by lactide moieties with comparing to **10**. Here peaks at 1.55 (CH_3) and 5.15 (CH) signals caused from lactide moieties were observed which also indicates quantitative incorporation of oligolactide in copolyester **11** by means of integration of peaks. ^{13}C NMR spectroscopy verified structural composition obtained by ^{1}H NMR spectroscopy. The intrinsic viscosity values of copolyesters measured at 25 °C in chloroform were between 0.46 and 0.67 dl/g. Elemental analysis of all polymers resulted in carbon contents that coincide with those expected for the theoretical composition determined by NMR techniques.

Table 2
The yield and molecular weight data of copolyesters **11a–c**

	x/y[a]	$[\eta]$[b] (dl g^{-1})	$\bar{M}_w$[c]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	Yield[d] (%)
11a	1/0.3	0.67	27100	8600	3.20	86
11b	1/0.5	0.54	25500	7800	3.30	89
11c	1/0.7	0.46	14400	4400	3.30	87

[a] x/y is molar ratio of the repeating units in polyesters, and same as the ratio in the feed.

[b] Measured in chloroform at 25 °C.

[c] Gel permeation chromatography in chloroform.

[d] After reprecipitation from chloroform/methanol.

As observed previously for similar copolyesters containing lactide moieties [3,5] molecular weights of **11** dropped systematically with increasing amount of oligolactide. The decrease of molecular weight of **11** with increasing amount of lactide moieties is most likely due to the increasing amount of carboxyl end-groups of oligolactide. To the best our knowledge, the reaction activity of the carboxylic group is lower than that of the carboxylic chloride group in this polymerization.

3.3. Solubility of polymers and degraded products

The solubility of **10** and **11** was checked for solutions with 0.5 wt.% of polymer. The polyesters exhibit excellent solubility in a variety of polar organic solvents such as chloroform, DMF, NMP, and pyridine, but only partial solubility in THF and insolubility in water. Since **11** was designed as being degradable under physiological conditions the water solubility of the hydrolyzed aromatic moieties in water was analyzed as well. The hydrolyzed products of the copolyester are supposed to be 2,5-bis(methoxyethyleneoxy)-1,4-hydroquinone (compound **2**) and 2-ethoxy ethyleneoxy terephthalic acid (compound **8**) besides lactic acid. Compound **2** is water soluble at 37 °C with maximal concentration of 3.0% in water while compound **8** displays solubility concentration with 0.8% in water at 37 °C. By using NMR technique, the solubility of compound **2** and **8** in pH 7.4 phosphate buffer at 37 °C are estimated to be 10 and 4%, respectively.

3.4. Thermal and liquid crystalline properties of polymers

The thermal properties of polymers are summarized in Table 3. The thermogravimetrical analysis of **10** and **11** showed a one-step degradation under nitrogen. A weight loss of 5% was observed between 351–371 °C and a 10% weight loss between 365–382 °C. **10** and **11** formed anisotropic melts as observed by hot stage polarizing microscopy indicating a thermotropic liquid-crystalline behavior of these polymers. A typical optical texture obtained at 170 °C for polyester **10** is shown in Fig. 1. The observed textures suggest the formation of smectic melts. Such a phase assignment was also confirmed by the results of the X-ray evaluation discussed below. The smectic melt is transformed to a smectic glass on cooling below the glass transition temperature of the polymers. An isotropization of the anisotropic melts (T_i) was observed between 158–220 °C. The isotropization of the melts was reversible upon cooling below T_i. The glass transition temperature of **10** found by DSC analysis is 99 °C. The T_g values of **11** dropped systematically down to 90 °C with increasing amount of lactide moieties. Endothermal peaks (T_m) as observed in the second heating runs for **10** and **11** were located between 148–164 °C, and exothermal peaks (T_c) as observed in the first cooling runs between 73–108 °C by DSC. No additional peaks indicative for the occurrence of a liquid-crystalline transitions were found in DSC heating and cooling runs for **10** and **11** between 25 and 300 °C. Melting of **10** and **11** above 150 °C observed by DSC was verified by polarizing microscopy. In comparison to the corresponding oligolactide no melting transition of oligolactide (26 °C) was found in the DSC analysis of the copolyester **11**. This indicates that the lactide units are fully incorporated into the chain backbone.

The X-ray analysis revealed that the solid state structure of the polymers at room temperature is kinetically controlled and depends strongly on the thermal history. Quenching down from the melt at 250 °C leads to a completely amorphous polymer with two broad halos, one in the wide angle regime and one at smaller scattering angles as obvious from Fig. 2. X-ray diagrams resembled the one of amorphous polymers such as polystyrene. Precipitating from solution, on the other hand, leads to a powder displaying an enhanced order as also apparent from Fig. 2. The wide angle peak has no significant changes while the intensity of the small angle peak has definitely increased. All precipitated polymers considered here display similar X-ray diagrams. A further increase of order obviously takes place if films are cast from solution i.e. if the removal of the solvent takes place within a time span of several hours. Fig. 3 shows that the wide angle peak is now superimposed by a set of broad peaks indicating the formation of crystalline regions. Yet, the rather large width of these peaks and their low magnitude is a signature of a rather imperfect state of the crystals. The small angle peak resembles in the case the one found for precipitated samples. Annealing of the samples at elevated temperature leads to a strong narrowing of the small angle reflection and a slight modification of the shape of the wide angle peak (Fig. 4). It is evident that the polymers become partially crystalline by annealing the crystallinity amounting roughly to about 10%.

The small number of reflections and their large width do not allow to draw detailed conclusions with respect to structure formation in the polymers. Yet it is obvious that crystallization is strongly hindered and that some kinds of

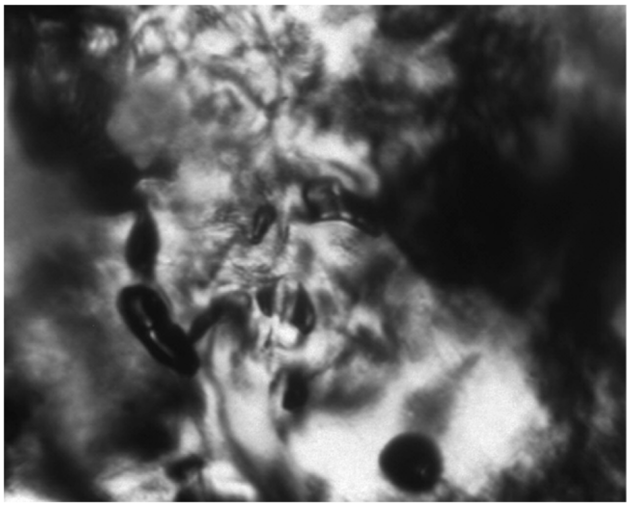


Fig. 1. Optical microscopy photographs of a melt of polyester **10** at 170 °C.

Table 3
Thermal properties of the polyester **10** and copolyesters **11a–c**

	TG[a]				DSC[b]				OPM
	Onset (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	$T_c{}^c$ (°C)	$T_i{}^d$ (°C)
10	346	371	382	402	99	164	6.2	108	220
11a	342	364	373	389	95	156	4.8	90	170
11b	336	362	375	401	93	154	5.6	89	165
11c	331	351	365	394	90	148	5.4	73	158

[a] Under nitrogen at heating rate of 20 °C min^{-1}.
[b] Transition temperatures and enthalpy of melting were taken from the second heating run (heating rate 10 °C min^{-1}).
[c] Crystallization temperatures were taken from the first cooling run (cooling rate 10 °C min^{-1}).
[d] T_i from polarizing microscopy.

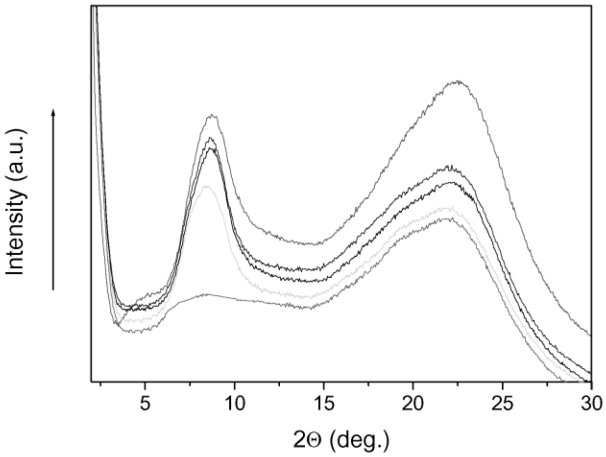


Fig. 2. WAXS of the polyesters **10**, **11a**, **11b**, and **11c** (as indicated from up to down in figure) as polymerized, the bottom curve indicates a typical amorphous WAXS of polyester **11b** while the sample was quenched in glassy state after melt at 250 °C.

layer structure seems to exist. The X-ray diffraction patterns of powdered samples shows a strong first-order reflection at 2Θ angle of 8.2° corresponding to a layer spacing of 10.7 Å for the polyesters. The tentative interpretation is that the layers are formed by parallel rigid-rod main chains spaced by the alkoxy side chains (Fig. 5). A roughly calculated length of the alkoxy side chains based on an *trans* conformation turns out to be about 10 Å, which matches the repeat distance obtained from the X-ray evaluation.

3.5. Surface properties and water absorption of polymers

The surface properties of solution cast films of **10** and **11** were analyzed by contact angle measurements (Table 4). The contact angle of polyester **10** is significantly smaller than the contact angles observed for corresponding polyesters without lateral ethyleneoxy substituents (e. g. the contact angle of an fully aromatic polyester with phenyl substituents on each phenylene moiety is 109° against water). A further decrease of contact angle was observed with an increasing content of oligolactide moieties. From the contact angle analysis, thermodynamic parameters such as surface tension was obtained as a function of the amount of lactide moieties of the copolyesters. According to the theory of fractional polarity [9], various molecular forces are linearly additive and, therefore, the surface tension (γ) can be separated into two components: the dispersion (γ^d) and polarity (γ^p), with the equation $\gamma = \gamma^d + \gamma^p$. The values of γ^d and γ^p of a given surface can then be calculated from the contact angles of two liquids of known surface tensions, such as water and methylene iodide, using a harmonic-mean equation [9] which is suitable for predicting the surface tension of polymers. The calculated surface tensions and their polar components of the polyesters are also listed in

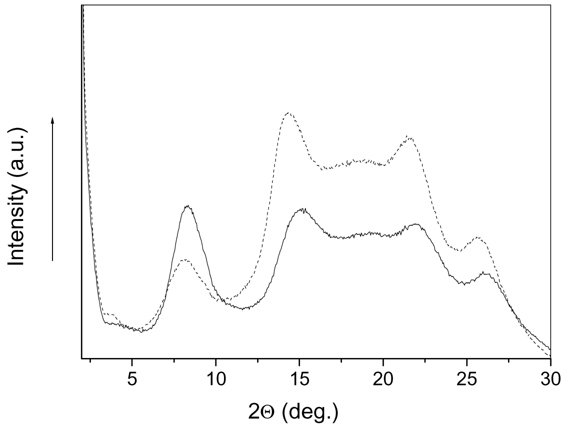


Fig. 3. WAXS of the solution cast films of homopolyester **10** (solid line) and copolyester **11b** (dash line).

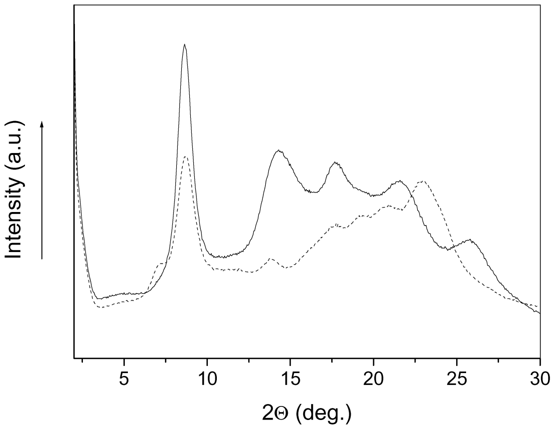


Fig. 4. WAXS of powder sample (dash line) and solution cast film (solid line) of the copolyester **11b** annealed at 80 °C for 10 h.

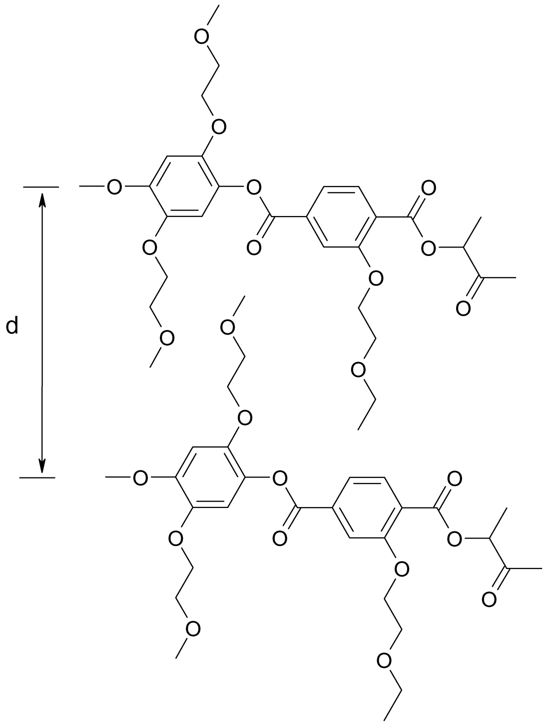


Fig. 5. Schematic of π–π stacking structure of polyesters.

Table 4
Contact angles of polyester **10** and copolyesters **11a–c** against water, their surface tension (γ), surface polarity (γ^p), and dispersion (γ^d), and water absorption data after 78 h of immersion

Sample	*x*/*y*	γ^p (mN/m)	γ^d (mN/m)	γ (mN/m)	Contact angle (°)	Water absorption (wt%)
10	1/0	11.75	37.59	49.34	75	2.4
11a	1/0.3	12.01	38.20	50.21	72	3.0
11b	1/0.5	12.43	40.02	52.45	70	3.7
11c	1/0.7	12.78	41.58	54.36	68	4.5

Table 4. There is a clear trend that the polarity, dispersion, and surface tension increases with increasing amount of lactide moieties in the copolyesters or with an increasing concentration of the side chain ethyleneoxy groups of the polyesters. Higher polarity and surface tension usually result in better hydrophilicity.

The hydrophilicity of the obtained films was also evaluated by immersion in a pH = 7.0 phosphate buffer. Table 4 shows the water absorption data of the four polymers after 78 h of immersion. These data confirmed that the polyesters are hydrophilic polymers with 2.4–4.5 wt% of water absorption ratio in comparison to a very hydrophobic poly(ϵ-caprolactone) with only 0.2% water absorption ratio. With increasing amount of lactide moieties, the polyesters exhibit higher water absorption ratio which indicates more hydrophilicity.

4. Conclusions

Thermotropic liquid-crystalline polyesters with solubilizing side chains were obtained by polycondensation of lateral methoxyethyleneoxy substituted silylated hydroquinones and ethoxyethyleneoxy substituted terephthaloyl dichlorides. Corresponding copolyesters were obtained by addition of oligolactides, which showed enhanced solubility, certain higher water absorption ratio, and smaller contact angles. All copolyesters exhibited thermotropic mesophases. The enhanced hydrophilicity induced by the solubilizing side chains is of prime interest for hydrolytical degradation and makes these copolyesters promising candidates for medical applications in the area of tissue engineering. Further experiments such as hydrolytical degradation, enzymatic degradation, and biocompatability tests are presently under way and will be reported in a forthcoming paper.

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