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Thermotropic Aromatic/Lactide Copolyesters with Lateral Methoxyethyleneoxy Substituents

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Liquid-crystalline polyesters with lateral methoxyethyleneoxy substituents and phenyl substituents were obtained by melt polycondensation of diacid dichlorides and silylated hydroquinones. Corresponding copolyesters were obtained by addition of oligolactides. The molecular structures of these polymers were verified by IR and NMR spectroscopy. Molecular weights obtained by GPC and end-group analysis proved enhanced molecular weights. All copolyesters were partially crystalline according to WAXS analysis and formed smectic melts upon heating above the melting temperature. Contact angle measurements of solution cast films showed relatively high hydrophilicity and decreasing contact angle with increasing amounts of oligolactide moieties.

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 was 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 and 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 by incorporation of oligoethylene oxide moieties in the main chain. However, a major drawback of these copolyesters for tissue engineering is that aromatic degradation products would be insoluble in an aqueous environment. To reduce this drawback, we present in this paper novel thermotropic copolyesters with lateral methoxyethyleneoxy substituents on the aromatic hydroquinone moieties, which retained their liquid crystallinity.

Experimental Section

Materials and Measurements. All chemicals were purchased from Aldrich Chemical Co. Tetrahydrofuran was distilled over calcium hydride and stored under argon. Phenylterephthaloyl chloride (**1**) was prepared following the procedure of Hatke et al.[5] A 90% aqueous solution of racemic D,L-lactic acid (purchased from Fluka) was heated stepwise to 200 °C and kept at this temperature in a vacuum for 4 h. This procedure yielded α-hydroxy-ω-carboxyoligolactide (**7**, $\overline{M}_w = 4500$, $\overline{M}_n = 1700$, $\overline{M}_w/\overline{M}_n = 2.60$, $\overline{M}_n$ calculated from ^{1}H NMR = 1100 similar to ref 6). The samples 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 $[\eta]$ ($dL \cdot g^{-1}$) 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 of 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 a cooling rate of 10 °C/min, observing the second heating run. Liquid-crystalline behavior was observed by a Leitz orthoplan polarizing microscope (OPM),

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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.

Monomer Synthesis. 2,5-Bis(methoxyethyleneoxy)-1,4-benzoquinone (4). A solution of 14 g (0.1 mol) of 2,5-dihydroxybenzoquinone in 500 mL of ethylene glycol monomethyl ether was treated with 20 mL of boron trifluoride etherate. After 5 h the solvent was distilled off. After cooling to room temperature the crude product was isolated by filtration. Recrystallization from 2-propanol gave 20 g (yield 78%) of golden yellow crystals, mp 138−139 °C. $C_{12}H_{16}O_6$ (256): Calcd. C 56.25, H 6.29, O 37.46; found C 56.49, H 6.30, O 36.90. ^{1}H NMR (300 MHz, $(CD_3)_2CO$), ppm): 3.49 (s, 6H, $2CH_3$), 4.09 (t, 4H, $2CH_2$, $J_1 = 4.6$ Hz, $J_2 = 4.2$ Hz), 4.49 (t, 4H, $2CH_2$−OAr, $J_1 = 4.4$ Hz, $J_2 = 4.4$ Hz), 6.36 (s, 2H, 2Ar−H). ^{13}C NMR (300 MHz, $(CD_3)_2CO$), ppm): 59, 70, 71, 107, 160, 199. MS (EI, 70 eV): $m/z = 256$ (M^+ 1.1%).

2,5-Bis(methoxyethyleneoxy)-1,4-hydroquinone (5). A 20 g (0.08 mol) portion of 2,5-bis(methoxy ethyleneoxy)-1,4-benzoquinone was reduced with 50 g of tin (II) chloride dihydrate and 160 mL of hydrochloric acid. After 5 h, the aqueous solution was extracted with dichloromethane. The organic phase was washed with water, dried over $MgSO_4$, and then evaporated. The remaining crystals were recrystallized from water and yielded 16 g (yield 80%) of white needles, mp 107−108 °C. $C_{12}H_{18}O_6$ (258): Calcd. C 55.81, H 7.02, O 37.17; found C 55.53, H 6.81, O 37.05. ^{1}H NMR (300 MHz, $(CD_3)_2CO$), ppm): 3.46 (s, 6H, $2CH_3$), 3.74 (t, 4H, $2CH_2$, $J_1 = 4.9$ Hz, $J_2 = 4.6$ Hz), 4.16 (t, 4H, $2CH_2$−OAr, $J_1 = 4.9$ Hz, $J_2 = 4.4$ Hz), 6.90 (s, 2H, 2Ar−H), 7.58 (s, 2H, 2OH). ^{13}C NMR (300 MHz, $(CD_3)_2CO$), ppm): 59, 71, 72, 105, 141, 199. MS (EI, 70 eV): $m/z = 258$ (M^+ 18%).

2,5-Bis(methoxyethyleneoxy)-1,4-hydroquinone silylate (6). Bis(trimethylsilyl) acetamide (BSA, 36 mL) was added to 15 g (0.06 mol) of 2,5-bis(methoxyethyleneoxy)hydroquinone in 120 mL of dried tetrahydrofuran. The reaction mixture was refluxed for 3 h. While the solvent was evaporated, the residues were extracted with dichloromethane. The organic phase was washed with water several times, dried over magnesium sulfate, and then evaporated. Crystals were purified by recrystallization from water to give 21 g (yield 87%) of white needles, mp 50−51 °C. $C_{18}H_{34}O_6Si_2$ (402): Calcd. C 53.70, H 8.51; found C 53.63, H 8.99. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.196 (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 (300 MHz, $CDCl_3$, ppm): 0.01, 58, 70, 71, 109, 139, 144. MS (EI, 70 eV): $m/z = 402$ (M^+ 78%).

Polymer Synthesis. All homopolyesters and copolyesters were synthesized by bulk polycondensation. A detailed procedure illustrating the preparation of a random copolymer with a 1:0.3 molar ratio (**9b**) of aromatic monomer/oligolactide is described 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 (**6**), 2791.2 mg (10 mmol) of phenylterephthaloyl chloride (**1**), and 216.2 mg (3 mmol) of oligolactide (**7**) 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. The mixture was kept at 160 °C for 6 h. Then the temperature was raised to 220 °C. After 3 h at 220 °C and normal pressure the flask was evaporated to 2 mbar for 30 min at 220 °C. The product was cooled to room temperature, dissolved in 20 mL of $CHCl_3$, and isolated by precipitation in 400 mL of methanol. The polymer was purified by redissolution/precipitation in $CHCl_3$/methanol and dried at 60 °C in vacuo.

The NMR spectra of copolyesters **9** are almost identical with that of polyesters **8** except for additional peaks caused by the oligolactide moieties. For example, copolyester **9b** spectral data are as follows.

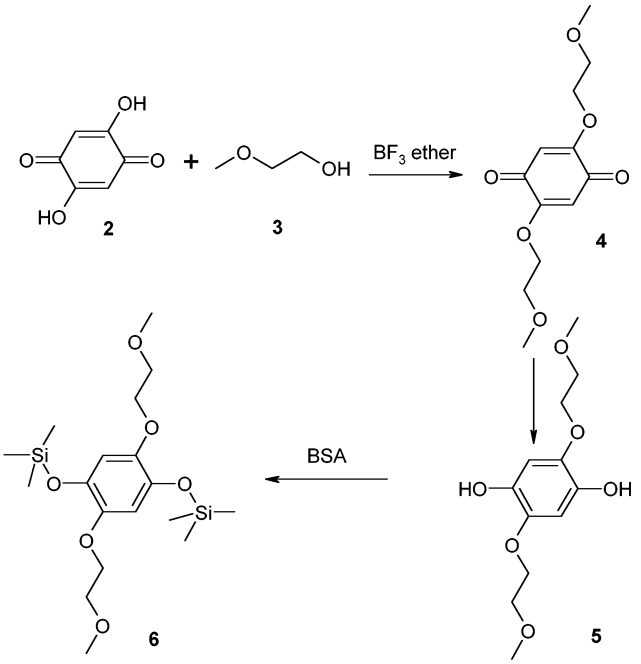
^{1}H NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 0.10-0.30$ (m, end Me_3Si), 1.25−1.50 (m, 0.9H, $0.3CH_3$ lactide), 3.10−3.30 (ss, 6H, $2CH_3O$), 3.45−3.60 (m, 4H, $2CH_2O$), 3.80−4.10 (m, 4H, $2CH_2$−OAr), 5.00−5.20 (m, 0.3H, 0.3CH lactide), 6.22−6.42 (ss, 1H, Ar−H), 6.74−6.94 (ss, 1H, Ar−H), 7.35−7.50 (m, 5H, 5Ar−H), 8.10−8.20 (m, 1H, Ar−H), 8.20−8.40 ppm (m, 2H, 2Ar−H).

^{13}C NMR ($CDCl_3$, 400 MHz, ppm): $\delta = 16.6$ (CH_3 lactide), 59.1 (CH_3O), 68.9 (CH lactide), 69.8 (CH_2O), 70.9 (CH_2O), 109.7, 127.9, 128.4, 129.1, 130.5, 132.3, 134.8, 138.1, 139.9, 142.6, 142.9, 144.5, 144.7, 164.4, 166.8.

Results and Discussion

Monomer Synthesis. It is well-known that lateral phenyl substituents in terephthaloyl moieties of copolyesters enhance solubility and fusibility considerably. Therefore phenyl terephthaloyl dichloride (**1**) was selected here. The synthesis of **1** was described elsewhere.[5] To enhance the solubility of hydroquinione moieties of the copolyesters in aqueous environments, a hydroquinone was synthesized with lateral methoxyethyleneoxy substituents as shown in Scheme 1. However, simple polycondensation of **1** and **5** resulted in cross-linked products. Most likely, HCl that formed upon condensation of **1** and **5** caused cleavage of oligoethylene oxide substituents and formation of additional hydroxy groups. Because **1** and **5** are reactive monomers, the polycondensation reactions of **1** and **5** in methylene chloride solution with pyridine as an acid-acceptor were investigated. Low molecular weight ($\overline{M_n} = 5100$) and disadvantages on copolymerization with oligolactide for obtaining random copolymers led us to abandon this method. Therefore, compound **5** was silylated to obtain **6**, which can be polycondensated with **1** according to a previously published procedure.[7]

Scheme 1. Synthetic Route to Monomer 6



Polymer Synthesis. Polyester **8** (Scheme 2) was synthesized by melt polycondensation of **1** and **6**. Yields were between 89 and 97% and $\overline{M_n}$ was between 4300 and 24 500 g·mol^{-1}, according to ^{1}H NMR end group analysis, depending on the reaction conditions (Table

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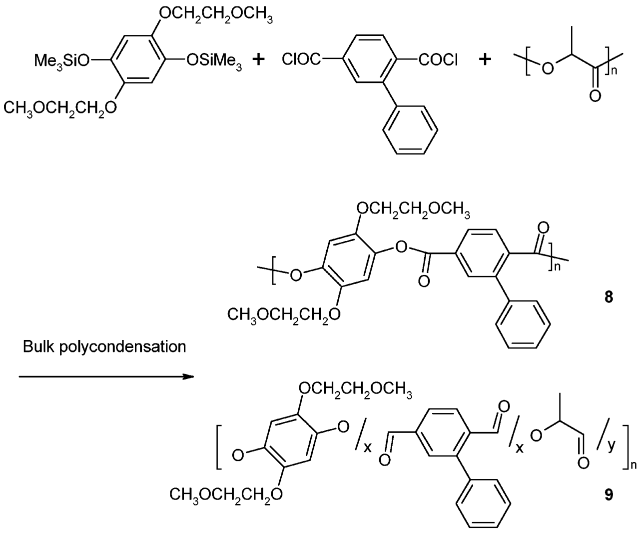
Scheme 2. Chemical Structures of Polyesters



1). $\overline{M_n}$ obtained by GPC in chloroform versus polystyrene standards and $\overline{M_n}$ obtained by end group analysis via ^{1}H NMR spectroscopy were in good agreement. Although polydispersity is relatively large, only monomodal GPC traces were observed for **8**. ^{1}H NMR spectroscopy showed the signals expected for polyester **8** with peaks at $\delta = 3.10-3.30$ ppm (2 CH_3O), 3.45–3.60 ppm (2 CH_2O), 3.80–4.10 ppm (2 CH_2O), 6.22–6.42 ppm (Ar–H), and 6.74–6.94 ppm (Ar–H) for the hydroquinone moieties, $\delta = 7.35-7.50$ ppm (Ar–H), 8.10–8.20 (Ar–H), and 8.20–8.40 (Ar–H) for the terephthaloyl moieties, and $\delta = 0.10-0.30$ for the trimethyl silyl endgroups. ^{13}C NMR spectroscopy verified structural composition obtained by ^{1}H NMR spectroscopy. It is noteworthy that two types of carbonyl moieties were observed which is due to the 2 and 3-position of the phenyl substituents in the terephthaloyl moieties. As shown in Table 1, the polymerization condition of 6 h at 160 °C and subsequently 3 h at 220 °C could give the high molecular weight of polyester **8** (entry no. 2). Therefore, a following copolymerization was carried out under this optimized condition. The properties of polyester **8** in this article were obtained by using entry no. 2.

Copolyester **9** was synthesized by melt polycondensation as described for **8** but with varying amounts of oligolactide (**7**) (Scheme 2). Melt polycondensation of **1**, **6**, and **7** was performed at 160 °C for 6 h followed by annealing in a vacuum at 220 °C for 3 h. Yields were in the range of 93–97% and $\overline{M_n}$, values obtained by ^{1}H NMR end group analysis were in the range of 9200–20 900 g·mol^{-1} depending on the reaction conditions (Table 2). GPC traces showed unimodal molecular weight distribution. No hints for oligolactides were found during analysis of the methanol precipitation bath, which indicated quantitative incorporation of oligolactide in copolyester **9**. ^{1}H NMR spectroscopy of copolyesters **9** showed additional peaks caused by oligolactide moieties compared to that of **8**. ^{13}C NMR spectroscopy verified structural composition obtained by ^{1}H NMR spectroscopy. Here $\delta = 1.25-1.50$ ppm (CH_3), 5.00–5.20 (CH) signals for lactide moieties were observed which indicates quantitative incorporation of oligolactide in copolyester **9** by means of integration of peaks.

As observed previously for related copolyesters with oligolactide moieties,[3] molecular weights of **9** dropped systematically with increasing amounts of oligolactide. The decrease of molecular weight of **9** with increasing amount of **7** is most likely due to the increasing amount of carboxyl end-groups of **7**. To the best of our knowledge, the reaction activity of the carboxylic group is lower than that of the carboxylic chloride group in this polymerization.

Solubility. The solubility of **8** and **9** was checked for solutions with 0.5 wt. % of polymer. Polyester **8** is soluble in chloroform and *p*-chlorophenol but only partially soluble in DMF, pyridine, and chlorobenzene, and insoluble in THF and water. In contrast, copolyesters **9** showed increasing solubility in DMF, pyridine, and THF with increasing amount of oligolactide moieties. Because **9** was designed as degradable under physiological conditions, the water solubility of the hydrolyzed aromatic moieties in water was analyzed as well. Hydroquinone **5** is water soluble at 37 °C with maximal concentration of 2.3% in water, while the phenylterephthalic acid displays solubility concentration with less than 100 ppm in water at 37 °C.

Table 1. Bulk Condensation of 6 and 1 under Various Conditions Yielding Polyester 8

8	condition							
no.	time (h)	temp. (°C)	yield^a (%)	$[\eta]^b$ (L·g^{-1})	$\overline{M_w}^c$	$\overline{M_n}^c$	$\overline{M_w}/\overline{M_n}^c$	$\overline{M_n}^d$
1	3	200	90	1.40	81800	19000	4.30	23000
2	6/3	160/220	97	1.85	164400	22100	7.40	24500
3	3	250	89	0.40	9200	3700	2.40	4300
4	6	140						
5	3/3	160/220	96	1.30	98400	12500	7.80	13500

[a] After reprecipitation from chloroform/methanol. [b] Measured in chloroform at 25 °C. [c] Gel permeation chromatography in chloroform. [d] ^{1}H NMR end group analysis after reprecipitation from methanol.

Table 2. Yield and Molecular Weight Data of Copolyesters 9a–d

	x/y^e	$[\eta]^a$ (dL·g^{-1})	$\overline{M_w}^b$	$\overline{M_n}^b$	$\overline{M_w}/\overline{M_n}^b$	$\overline{M_n}^c$	yield^d (%)
9a	1/0.1	1.45	73900	14500	5.10	20900	93
9b	1/0.3	1.25	49400	11100	4.40	14600	96
9c	1/0.5	0.80	35800	9300	3.80	9200	96
9d	1/0.7	0.60	29000	8400	3.40	9300	95

[a] Measured in chloroform at 25 °C. [b] Gel permeation chromatography in chloroform. [c] ^{1}H NMR end group analysis after reprecipitation from methanol. [d] After reprecipitation from chloroform/methanol. [e] *x*/*y* is the molar ratio of the repeating units in polyesters, and same as the ratio in the feed.

Table 3. Thermal Properties of the Polyester 8 and Copolyesters 9a−d

	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)
8	345	368	380	403	92	207	12.7	137	270
9a	360	376	388	409	90	210	14.4	134	245
9b	356	376	389	417	71	206	13.7	133	265
9c	336	355	368	399	66	198	12.8	130	220
9d	340	364	377	406	62	195	12.4	128	210

[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.

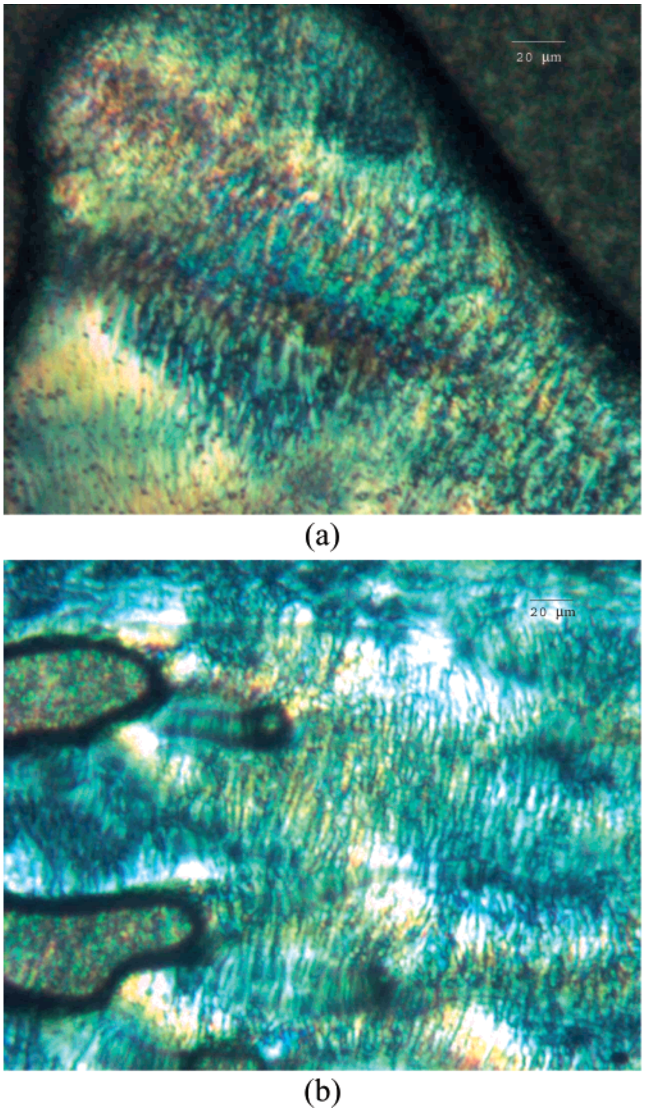


Figure 1. Optical microscopy photographs of a melt of **8** at 226 °C (a); **9b** at 221 °C (b) after annealing at 140 °C for 10 h.

Thermal Properties and Solid-State Structure. The thermogravimetrical analysis of **8** and **9** showed one-step degradation under nitrogen. The 5% weight loss was observed between 355 and 376 °C and the 10% weight loss was between 368 and 389 °C (Table 3).

Compounds **8** and **9** formed anisotropic melts as observed by hot stage polarizing microscopy, which indicated thermotropic liquid-crystalline behavior of these polymers. The formation of smectic melts was suggested by the observed textures (Figure 1) as obtained by annealing at 140 °C for 10 h following melting at 220 °C. The smectic melt is transformed to a smectic glass on cooling below the glass transition temperature of the polymers. The glass transition temperature of **8** was observed by DSC at 92 °C but dropped systematically for **9** down to 62 °C with increasing amounts of oligolactide moieties (Table 3). Endothermal peaks (T_m) were observed in DSC heating runs of **8** and **9** between 195 and 210 °C and exothermal peaks (T_c) were observed in DSC cooling runs between 128 and 137 °C. No additional peaks such as anisotropic phase transition were found in DSC heating and cooling runs for **8** and **9** between 25 and 300 °C (Figure 2). Melting of **8** and **9** above 200 °C observed by DSC was verified by polarizing microscopy. Isotropization of anisotropic melts (T_i) was observed between 210 and 270 °C. The isotropization of the melts was reversible upon cooling below T_i.

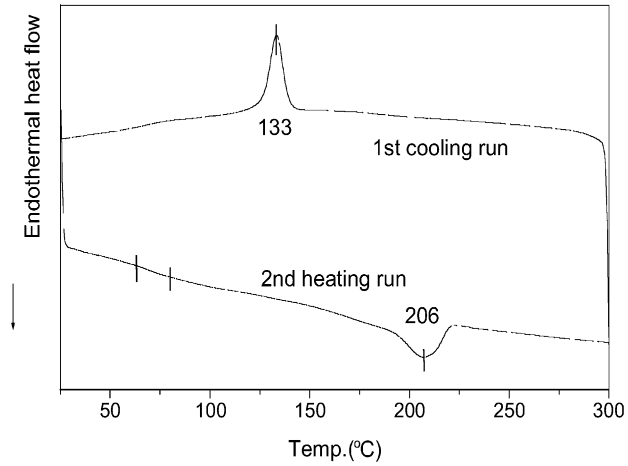


Figure 2. DSC traces of copolyester **9b** recorded in the second heating run at a rate of 10 °C/min.

The X-ray analysis revealed that the solid state structure of the polymers at room temperature was kinetically controlled and depended strongly on the thermal history. Broad halos were obtained for samples which were heated to 290 °C and subsequently quenched in the glassy state. The X-ray diagrams resembled that of amorphous polymers such as polystyrene. Solution cast films, on the other hand, displayed one relatively broad reflection at a smaller scattering angle (about $2\theta = 8°$) in addition to the halo at large scattering angles (Figure 3). Such diagrams tend to be characteristic for smectic polymers, i.e., polymers displaying a one-dimensional large structure. Yet it has to be pointed out that a disturbed hexagonal packing would lead to similar diagrams. Additional evidence for a smectic type structure came from the textures described above. The X-ray diagram observed for as-polymerized polymers, i.e., powder precipitated from solution, was characterized as a somewhat enhanced order (Figure 4a). The small angle reflection split up into a doublet and the halo showed weak indication of additional peaks. These

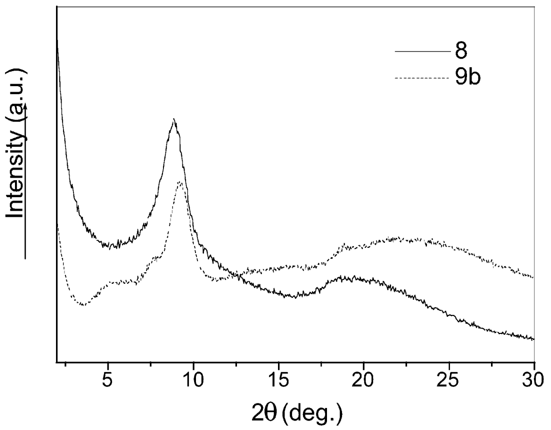


Figure 3. WAXS of the solution cast films of homopolyester **8** (solid line) and copolyester **9b** (dashed line).

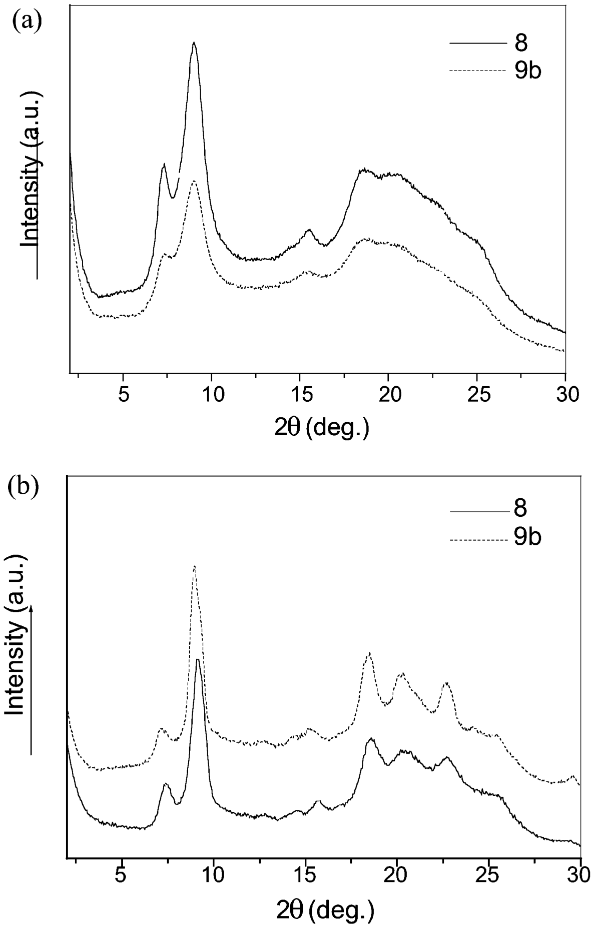


Figure 4. WAXS of homopolyester **8** (solid line) and copolyester **9b** (dashed line) as polymerized (a), and annealed at 160 °C for 10 h after melting at 220 °C (b).

features were strongly enhanced for samples annealed at 160 °C for 10 h after melting at 220 °C (Figure 4b). Several reflections were superimposed on the halo. It was evident that the polymers became partially crystalline by annealing properly. The crystallinity was calculated to be about 10%. The small number of detectable reflections did not allow for a crystal structural determination.

Surface Properties. The surface properties of solution cast films of **8** and **9** were analyzed by contact angle measurements (Table 4). The contact angle of polyester **8** is significantly smaller than the contact angles observed for corresponding polyesters without lateral methoxyethyleneoxy substituents (e.g., the contact angle of a fully aromatic polyester with phenyl substituents on each phenylene moiety is 109° against water). Further decrease of contact angle was observed by increasing the content of oligolactide moieties. From the contact angle analysis, thermodynamic parameters such as surface tension could be obtained as a function of the amount of lactide moieties of the copolyesters. According to the theory of fractional polarity, various molecular forces are linearly additive and, therefore, the surface tension (γ) can be separated into two components: the dispersion (γ^d) and the polarity (γ^p):[8]

$$\gamma = \gamma^d + \gamma^p \tag{1}$$

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[8] which is suitable for predicting the surface tension of polymers. The calculated surface tensions and their polar components of the copolyesters are listed in Table 4. There is a clear trend that the polarity, dispersion, and surface tension increase with increasing amounts of lactide moieties in the copolyesters or with modifying methoxyethyleneoxy group from side chain of the polyesters. Thus, higher polarity and surface tension usually result in better hydrophilicity.

Table 4. Contact Angles of Polyester 8 and Copolyesters 9a–d against Water and Their Surface Tension (γ), Surface Polarity (γ^p), and Dispersion (γ^d)

sample	*x*/*y*	γ^p (mN·m^{-1})	γ^d (mN·m^{-1})	γ (mN·m^{-1})	contact angle (°)
8	1/0	9.28	34.73	44.02	82
9a	1/0.1	9.42	34.70	44.12	81
9b	1/0.3	11.36	35.29	46.65	78
9c	1/0.5	11.55	36.88	48.43	76
9d	1/0.7	11.88	37.60	49.48	75

Conclusions

Thermotropic liquid-crystalline polyesters with lateral substituents were obtained by polycondensation of methoxyethyleneoxy substituted silylated hydroquinones and phenyl terephthaloyl dichlorides. Corresponding copolyesters were obtained by addition of oligolactides, which showed enhanced solubility, lower glass transition temperatures, and smaller contact angles. All copolyesters exhibited thermotropic mesophases. The enhanced hydrophilicity induced by the methoxyethyleneoxy substituted hydroquinones is of prime interest for hydrolytical degradation and makes these copolyesters promising candidates for medical applications in the area of tissue engineering. Mechanical properties, hydrolytical degradation, and biocompatability tests are presently underway and will be reported in a forthcoming paper.

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