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Thermotropic Liquid Crystal Aromatic/Cycloaliphatic Polyesters with Flexible Spacers

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ABSTRACT: Thermotropic polyesters have been prepared from *trans*-1,4-cyclohexanedicarbonyl chloride and α,ω-alkanediyl 4-hydroxybenzoates with a variable number of methylene carbons in the alkane chain. The melt transitions generally are lower than those of the corresponding thermotropic fully aromatic triad polyesters. The presence of cycloaliphatic groups in the mesogenic triad leads to enhanced solubility which has allowed an estimation, by GPC measurements, of the molecular weights which are rather low, corresponding to degrees of polymerization of no more than 3 or 4. The inherent viscosities for the polymers, however, are comparable to values published for other thermotropic polyesters with flexible spacers. For a polyester prepared from *trans*-1,4-cyclohexanedicarbonyl chloride and 4-hydroxybenzoic acid *trans*-1,4-cyclohexanediylbis(methylene) ester no mesophase could be observed upon melting.

Introduction

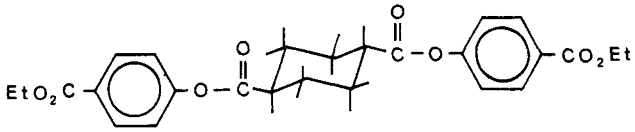
The interest in recent years in thermotropic polyesters with mesogenic units in the main chain has resulted in many papers and the major efforts have been reviewed.[1,2] Often, the structure of the polyesters consists of relatively stiff mesogenic units containing two to three aromatic units connected by suitable linking groups, and these units are separated by flexible chain segments in order to lower the melting ranges. Rather few examples on polymers having cycloaliphatic elements in mesogenic units are cited. A polymer containing a bicyclohexyl unit has been reported,[3] and attempts have been made to prepare liquid crystal block copolyesters containing a combination of cyclohexane and benzene rings.[4,5] Very recently,[6,7] studies have been reported in which polyesters have been prepared from combinations of aromatic and cyclohexanediol/dicarboxylic acid monomers.

We wish to report on the preparation of thermotropic liquid crystal polyesters with structures consisting of mesogenic units in which a central cyclohexyl unit is connected to two aromatic units and with methylene chains of variable lengths as flexible spacers. (see Figure 1.) Bis[4-(ethoxycarbonyl)phenyl] *trans*-1,4-cyclohexanedicarboxylate, 1, was prepared as a model compound. Similar polymers have been studied;[8,9] however, the details of the syntheses were not reported, and in various ways, to be discussed, these polymers prepared by interfacial techniques deviate from those reported here. Our studies include the use of 1,4-cyclohexanedimethanol as flexible spacer unit. Previously, this compound has been used in connection with random terephthalic copolyesters of methyl- and chloro-substituted hydroquinones.[10,11]

Studies of low molecular weight diester compounds in which one, two or all three of the benzene rings in mesogenic units are replaced by cyclohexane rings have been carried out.[12] For these compounds, a decrease in melting point as well as a smaller decrease in clearing point is observed. Often, however, replacement of a benzene ring in a nematic low molecular weight compound by a trans-1,4-disubstituted cyclohexane ring may actually increase the clearing temperature,[12] and this is observed unless[13] the isotropization temperature is already high ($\gtrsim$220 °C).

Results and Discussion

Model Compound. The low molecular weight model compound 1 which contains the mesogenic unit resembling that of the polyesters was prepared by reaction of *trans*-1,4-cyclohexanedicarbonyl chloride with 2 equiv of ethyl 4-hydroxybenzoate using pyridine as catalyst, HCl acceptor, and solvent. The structural proof of 1 was based on ^{1}H and ^{13}C NMR as well as IR, UV, MS, and elemental analyses and the purity was furthermore ascertained by HPLC (see Experimental Section).



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1 is a liquid crystalline material with the following phase transitions: K $\rightarrow$ N 162.5 °C; N $\rightarrow$ I 210 °C (K = crystalline, S = smectic, N = nematic, I = isotropic). The corresponding dimethyl ester has been described in the literature[14] as nematogenic with the following transitions: K $\rightarrow$ N 147 °C, N $\rightarrow$ I 162.5 °C. The triad aromatic ester analogue to model compound 1, bis[4-(ethoxycarbonyl)phenyl]terephthalate, was reported[15] to have two liquid crystal phases: K $\rightarrow$ S 196 °C, S $\rightarrow$ N 207 °C, N $\rightarrow$ I 241 °C. The increase in transition temperatures (T_m and T_i) when comparing model compound 1 with the fully aromatic ester analogue is in accordance with observations made for other compounds, where a benzene ring in the mesogenic unit has been replaced by a *trans*-1,4-cyclohexane ring.[13] In accordance with the above-cited rule by Gray, it is seen that since the isotropization temperature for the fully aromatic compound is already high, the introduction of the cyclohexyl unit does not lead to an increase in this temperature.

Synthesis of Polymers. Polymers **4a–g** were prepared by the route outlined in Figure 1. The α,ω-alkanediyl 4-(phenylmethoxy)benzoates, **2a–g**, were synthesized by acylation of the aliphatic dihydroxy compounds, viz., α,ω-alkanediols and *trans*-1,4-cyclohexanedimethanol, with an excess of 4-(phenylmethoxy)benzoyl chloride using pyridine as catalyst/HCl acceptor. The structural proofs of compounds **2a–g**, which have not been described previously, were based on ^{1}H and ^{13}C NMR, IR, UV, MS, and elemental analyses (see Spectroscopic Measurements and Experimental Section). The benzyl ether protection groups of compounds **2** were removed by catalytic hydrogenation using Pd as catalyst to give the corresponding α,ω-alkanediyl 4-hydroxybenzoates, **3a–g**, in good yields. Compounds **3a–f** are known compounds, whereas **3g** has not been described previously, although a cis/trans mixture has been described in the patent literature.[16] Polymers

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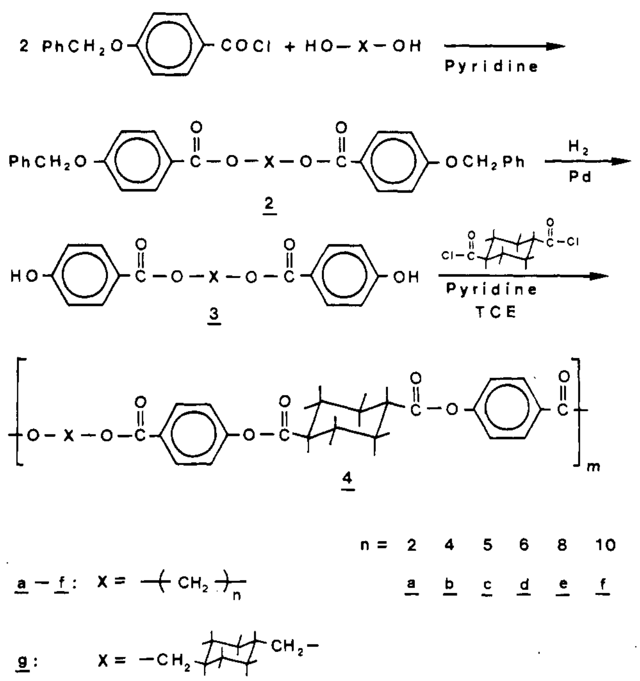

Figure 1. Syntheses of intermediates and polymers.

Table I
Molecular Weight Data for Polymers 4a–g

sample	n	polymer yield, wt %	GPC		η_{inh}[c]	
			$\overline{M}_n$ ($\overline{DP}$)	$\overline{M}_w$	whole[d] sample	$CHCl_3$[e] soluble
4a	2	95	1790 (4.1)	6590	0.34	
4b	4	97	*b*	*b*	0.32	
4c	5	78	970 (2.0)	3680	0.30	
4d	6	88	1580 (3.2)	5870	0.31	0.29
4e	8	95	1930 (3.7)	6870	0.40	0.36
4f	10	91	920 (1.7)	3430	0.27	0.25
4g	*a*	92	*b*	*b*	0.31	

[a] *trans*-1,4-Cyclohexanediylbis(methylene) spacer. [b] Insoluble in $CHCl_3$. [c] Determined in *p*-chlorophenol at 45 °C (c = 0.5 g·L^{-1}). [d] Determined on the polymers as prepared. [e] Determined on polymer recovered from filtered chloroform solutions.

Table II
Thermal Properties of the Polyesters in Comparison with Aromatic Analogues

		phase transitions, °C			
		samples **4a–g**		aromatic analogues[19,20]	
sample	n	T_m	T_i	T_m	T_i
4a	2	268	332	340	365
4b	4	255	310	285	345
4c	5	144	205	175	267
4d	6	186	279	227	290
4e	8	189	254	165	220
4f	10	188	219	221	267
4g	*a*		324		

4a–g were prepared in high yields by reaction of the α,ω-alkanediyl 4-hydroxybenzoates, **3a–g**, with equimolar amounts of *trans*-1,4-cyclohexanedicarbonyl chloride in 1,1,2,2-tetrachloroethane and with pyridine as catalyst/HCl acceptor. In all cases, the reaction mixtures stayed colorless and became more viscous during the reaction, and in some cases precipitation occurred. The reaction mixtures were worked up by precipitation in EtOH, followed by filtration and washings with EtOH and acetone.

Molecular Weights. The molecular weights of polymer samples **4a,c–f** were determined by GPC in $CHCl_3$ solvent, and the data are given in Table I. The calculations of the molecular weights were done on the basis of an extrapolated calibration curve based on extended chain lengths of polystyrene standard samples. The lengths of the polyester repeat units were estimated from measurements on molecular models built from the Orbit system.[17] It is obvious from Table I that the molecular weights are not very high and attain values corresponding at the most to trimer or tetramer. The determination of molecular weight values for thermotropic polyesters is, however, unusual since generally such polymers have been reported to be insoluble in common solvents used for GPC. The present polymers which have a cycloaliphatic unit in the mesogenic unit have enhanced solubility compared to the fully aromatic triad polyester with flexible spacers which have previously been studied. Some samples appeared not to be fully soluble in $CHCl_3$; however, in these cases only marginal amounts remained insoluble. The GPC analyses were of course always, as part of a standard procedure, run on filtered solutions. Inherent viscosities were determined in *p*-chlorophenol at 45 °C, see Table I, in order to be able to compare these values with those obtained for other thermotropic polyesters in this solvent, which is often used. In Table I, values are listed for polymers which were dissolved directly in *p*-chlorophenol along with values determined on polymers recovered from filtered chloroform solutions. It is seen that the inherent viscosities correlate well with the molecular weight values determined by GPC. Also, the inherent viscosities are comparable to those published for the fully aromatic triad thermotropic polyesters.[18] Samples were rerun for determination of the inherent viscosities after filtration in the same manner as the samples analyzed by GPC. These viscosity data, which are still comparable to most published values for thermotropic polyesters, clearly correlate with the low molecular weight values indicated by GPC. Thus, we propose that the molecular weights of previously published thermotropic polyesters with flexible spacers often in reality are rather low. This should have only a minor influence on the thermal properties which have been reported; however, the mechanical properties of such polyester will be markedly affected.

Phase Transitions and LC Behavior. The T_m and T_i values determined by DSC for polymers **4a–g** are presented in Table II. In all cases, except for **4g**, mesophases are observed. The transitions are not sharp but take place within a 10–20 °C range. The polymer with an uneven number of methylene groups (n = 5) melts definitively lower. The optical polarized microscopy observations were obscured in the case of polymers **4a,b,d,g** because decomposition starts before the clearing point (for **4g** the melting point) is reached. The literature T_m's and T_i's for the analogous triad aromatic ester[19,20] polymers are included in Table II as well.

Lenz[20] observed in the case of the analogous aromatic polyesters that the texture of the mesophases varied with the number of methylene groups in the spacer. Thus, nematic texture was observed in the case of even-numbered compounds up to n = 6 and smectic in all other cases. We were not able to make such a distinction for the present polymers.

It is seen from Table II that the transition temperatures for polymers **4a–f** are lower than those of the aromatic analogues, except for n = 8. In this case, the T_m and T_i values are the lowest in the fully aromatic series, and replacement of a aromatic ring with a cyclohexane ring actually increases the transition temperatures. Again, this appears to conform to the previously cited rule by Gray.[13] The transition temperatures for the similar polyesters

Table III
Experimental, Analytical, and Spectroscopic Data for Compounds 2a–g

compd	n	yield, %	mp[b]	R_t, HPLC, system 2	^{13}C NMR[c] signals of aliphatic spacer C's[d] 1	2	3	4	5	formula	analyses calcd/found C	H
2a	2	73	148	533	62.49					$C_{30}H_{26}O_6$	74.67 74.40	5.43 5.42
2b	4	71	156	568	64.14	25.57				$C_{32}H_{30}O_6$	75.28 76.82	5.92 6.22
2c	5	36	70	533	64.28	28.28	22.52			$C_{33}H_{32}O_6$	75.55 75.66	6.15 6.15
2d	6	85	119	465	64.50	28.61	25.72			$C_{34}H_{34}O_6$	75.82 75.17	6.36 6.35
2e	8	94	89.5	377	64.58	28.59[e]	25.81	28.98[e]		$C_{36}H_{38}O_6$	76.30 76.05	6.76 6.77
2f	10	90	93.5	308	64.72	28.69[e]	25.95	29.16[e]	29.32[e]	$C_{38}H_{42}O_6$	76.74 76.14	7.12 6.98
2g	*a*	95	167	377	69.44	37.25	28.94			$C_{36}H_{32}O_6$	76.57 76.92	6.43 6.51

[a] *trans*-1,4-Cyclohexanediylbis(methylene) spacer. [b] Determined by peak value in DSC. [c] 22.63 MHz, $CDCl_3$. [d] Numbering in accordance with nomenclature; for **2g** numbering starts with exo methylene. [e] Assingments arbitrary.

Table IV
Experimental, Analytical, and Spectroscopic Data for Compounds 3a–g

compd	n	yield, %	mp[c]	mp [lit.]	R_t, HPLC, system 3	^{13}C NMR[d] signals of aliphatic spacer C's[e] 1	2	3	4	5
3a	2	86	250.5	245–246[21]	799	62.47				
3b	4	63	195	194–195[21]	734	63.71	25.12			
3c	5	83	129	132–133[21]	679	63.97	28.07	22.29		
3d	6	82	183	183–184[21]	652	63.99	28.23	25.26		
3e	8	93	182.5	185[18]	585	64.02	28.26[f]	25.47	28.61[f]	
3f[a]	10	88	164	165[18]	532	63.99	28.26[f]	25.50	28.65[f]	28.85[f]
3g	*b*	45	284		652	68.71	36.78	28.40		

[a] Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29. Found: C, 68.86; H, 6.48. [b] *trans*-1,4-Cyclohexanediylbis(methylene) spacer. [c] Determined by peak value in DSC. [d] 22.63 MHz, DMSO-d_6. [e] Numbering in accordance with nomenclature; for **3g** numbering starts with exo methylene. [f] Assignments arbitrary.

containing the cyclohexane ring reported recently by Tani et al.[8] are much lower. In fact, the isotropization temperatures were less than 200 °C in all cases, with a number of methylene groups in the spacer $n = 5, 8, 10, 12$. Also the primary melting occurred at lower temperatures than for the polymers we report here. It appears that the polymers prepared by the interfacial technique tend to have lower thermal transitions also in the case of the aromatic triad polyesters when compared with results previously published for similar polymers by Lenz and co-workers.[18]

The melting points, determined by DSC, of compounds **2** and **3** are given in Tables III and IV along with all the pertinent data concerning these compounds. The melting points of compounds **3a–f** are all in agreement with published data.[18,21]

Spectroscopic Measurements

Compounds 2 and 3 show the expected signals in their ^{1}H NMR (60 MHz, **2** in $CDCl_3$, **3** in DMSO-d_6) spectra. Common to all the compounds are doublets ($J = 9$ Hz) at δ ~7.90 and 6.90 (1,4-disubstituted benzene). The benzyl ether protection groups of **2** give singlets of δ ~7.35 and ~5.10, and the hydroxy groups of **3** give a broad signal at ~10.5 ppm. For the polymethylene spacer, the shifts of the end methylene groups are found in the range 4.20–4.55 ppm, with the shift decreasing with increasing chain length. The interior methylene groups are found in the range 1.35–1.95 ppm. For the *trans*-1,4-cyclohexanediylbis(methylene) spacer (**2g** and **3g**) the exo methylene groups are found at ~4.10 ppm, the methine hydrogen at ~1.8 ppm, and the axial and equatorial hydrogens of the ring methylene groups at 1.1 and ~1.8 ppm, respectively. In ^{13}C NMR (22.63 MHz, **2** in $CDCl_3$, **3** in DMSO-d_6), compounds **2** and **3** have the following common shifts: ~162, ~114.5, ~131.5, ~121.5 (1,4-disubstituted benzene; C_4, C_3, C_2, C_1), and ~166 ppm (ester C=O carbon). The benzyl ether protection groups of **2** give the following signals: ~128.1, ~128.6, ~127.3, ~136.2 (aromatic C_4, C_3, C_2, C_1), and ~70.0 ppm (methylene). The shifts of the polymethylene and *trans*-1,4-cyclohexanediylbis(methylene) groups are given in Tables III and IV. IR spectroscopy shows the strong ester bands at 1710 (for **2**) and 1680 cm^{-1} (for **3**) and CH_2 bands at 2960–2850 cm^{-1}, for which the intensity is proportional to chain length. A strong broad band is observed at ~3380 cm^{-1} for **3** (H-bonded OH). The UV spectra (**2** in CH_2Cl_2, **3** in EtOH) give λ_{max} 255 nm with log ϵ 4.62–4.71 (for **2**) and 4.49–4.65 (for **3**). In the mass spectra, the molecular ion is observed in all cases. General trends for **2** are the loss from the molecular ion of 91 ($M^+ - PhCH_2$) and fragment ions 300, 211 ($PhCH_2O{-}C_6H_4{-}C{\equiv}O^+$); 181, 121 ($HO{-}C_6H_4{-}C{\equiv}O^+$); 91 ($C_7H_7^+$); and 65 ($C_5H_5^+$) and for **3** the loss from the molecular ion of 121 ($M^+{-}HO{-}C_6H_4{-}C{\equiv}O^\bullet$), 137 ($M^+\text{-}HO{-}C_6H_4{-}CO_2^\bullet$), and fragment ions 139 ($HO{-}C_6H_4{-}CO_2H_2^+$), 138 ($HO{-}C_6H_4{-}CO_2H^+$), 121 ($HO{-}C_6H_4{-}C{\equiv}O^+$), 93($HO{-}C_6H_5^+$), and 65 ($C_5H_5^+$).

The polymers **4a–g** were investigated by 500-MHz ^{1}H and 125.7-MHz ^{13}C NMR spectroscopies ($CDCl_3$ for **4a,c–e,g**, $CDCl_3$/TFA for **4b,f**). The results are listed in Table V. ^{1}H NMR spectra show the following signals common to all samples: doublets ($J = 9$ Hz) at δ 8.10 and 7.16 (1,4-disubstituted benzene), multiplets at δ 2.65, 2.32, and 1.70 (1,4-disubstituted cyclohexane; H_1, H_2 (eq.), H_2 (ax.)). The shifts of the hydrogens in the spacer groups are given at Table V. For **4b–d,f,g**, some minor (2–5% of height) extra signals at δ ~7.95 (d, $J = 9$ Hz), and ~6.85 (d, $J = 9$ Hz) corresponding to 4-hydroxybenzoate end groups are observed. In ^{13}C NMR polymers **4a–g** have the following common shifts: δ ~154.5, ~121.5, ~131.0, ~128.0 (1,4-disubstituted benzene, C_4, C_3, C_2, C_1), ~165.8 (Ar-C(O), ~173.2 (CHC(O)–) (for **4b,g**, these values are found at δ ~168 and ~178, because of added TFA), ~42.45, ~27.80 (cyclohexan; C_1, C_2). The shifts of the spacer carbons are given in Table V. 4-Hydroxybenzoate end-group signals are observed in polymer samples **4b–d,f,g** at δ ~131.6 and ~115.1. IR spectroscopy shows the strong ester bands at 1760 (CHC(O)OAr) and 1720 cm^{-1} (–$OC_6H_4C(O)O$–), and CH_2

Table V
Experimental, Analytical, and Spectroscopic Data for Polymer Samples 4a–g

		^{1}H NMR[b] signals of aliphatic spacer group H's[c]					^{13}C NMR[d] signals of aliphatic spacer group C's[c]						analyses calcd/found		
sample	n	1	2	3	4	5	1	2	3	4	5	formula	C	H	O
4a	2	4.67					62.81					$(C_{24}H_{22}O_8)_n$	65.75 64.81	5.06 5.12	29.19 28.71
4b	4	4.50	2.00				66.29	25.18				$(C_{26}H_{26}O_8)_n$	66.94 65.84	5.62 5.69	
4c	5	4.35	1.86	1.61			64.84	28.36	22.61			$(C_{27}H_{28}O_8)_n$	67.49 66.06	5.87 5.88	26.64 26.46
4d	6	4.35	1.82	1.55			65.00	28.62	25.72			$(C_{28}H_{30}O_8)_n$	68.00 67.24	6.11 6.22	25.80 25.98
4e	8	4.33	1.78	1.46	1.41		65.17	28.66[e]	25.92	29.13[e]		$(C_{30}H_{34}O_8)_n$	68.95 68.27	6.56 6.52	24.49 24.58
4f	10	4.33	1.79	1.47	1.36	1.36	65.26	28.69[e]	25.98	29.21[e]	29.41[e]	$(C_{32}H_{38}O_8)_n$	69.80 68.97	6.96 7.04	
4g	*a*	4.25	1.85	1.21(ar) 1.98(eq)			71.07	37.01	28.73			$(C_{30}H_{32}O_8)_n$	69.22 68.25	6.20 6.17	

[a] *trans*-1,4-Cyclohexanediylbis(methylene) spacer. [b] 500 MHz, $CDCl_3$ (**a**,**c**–**f**), CDCl,/TFA (**b**,**g**). [c] Numbering in accordance with nomenclature; for **4g** numbering starts with exo methylene. [d] 125.7 MHz, $CDCl_3$ (**a**,**c**–**f**), $CDCl_3$/TFA (**b**,**g**). [e] Assignments arbitrary.

bands at 2960–2860 cm^{-1}, with intensities proportional to spacer length. The UV spectra of **4a**,**c**–**e** (CH_2Cl_2) (the others were insoluble in CH_2Cl_2) give λ_{max} 235 nm with log ϵ 4.46–4.49. Elemental analyses are also given in Table V.

Experimental Section

Apparatus. ^{1}H NMR spectra were recorded at 60 and 500 MHz on Varian EM 360 and Bruker AM 500 spectrometers, respectively. $SiMe_4$ was used as internal standard. ^{13}C NMR spectra were recorded at 22.63 and 125.7 MHz on Bruker WH 90 and AM 500 spectrometers, respectively. IR spectra were recorded on a Perkin-Elmer 157 G spectrophotometer using KBr disks. UV spectra were recorded on a Perkin-Elmer 320 spectrophotometer. Mass spectra were recorded on a VG 7070 F instrument operating at 70 eV using a direct inlet. Elemental analyses were carried out by NOVO Microanalytical Laboratory. HPLC analyses were performed with a Spectra Physics SP 8000 B liquid chromatograph using a Waters μ-Porasil column, 30 cm × 3.9 mm (i.d.). Operating conditions were as follows. System, 1, 80% CH_2Cl_2/heptane, flow rate 2.0 mL/min, column temperature 30 °C, UV detection 240 nm; system 2, CH_2Cl_2, flow rate 2.0 mL/min, column temperature 25 °C, UV detection 260 nm; system 3, 20% THF/heptane, flow rate 2.0 mL/min, column temperature 25 °C, UV detection 255 nm; system 4, THF/$CHCl_3$, gradient 0–10% (20 min), 10–20% (5 min), 20% (5 min), 20–0% (2 min), 0% (8 min), flow rate 2.0 mL/min, column temperature 35 °C, UV detection 270 nm. HPLC-grade solvents were purchased from Rathburn. GPC analyses were performed with a Waters Model 510 pump/R-400 refractometer/730 data module using a train of four columns, 30 × 7.8 mm (i.d.), consisting of 10^5, 10^4, 10^3, and 5×10^2 Å ultrastyragel; mobile phase $CHCl_3$, flow rate 1 mL/min, column temperature 25 °C. Transition temperatures were determined with a Du Pont 900 DTA instrument equipped with a DSC unit. Polarizing microscopy was performed on a Reichert-Jung Microstar 110 polarizing microscope, equipped with a Mettler FP 82 hot stage/FP 80 central processor and an American Optical photomicrographic camera/ExpoStar shutter control.

Materials. The following starting materials were commercial: 1,1,2,2-tetrachloroethane (Merck), *cis*/*trans*-1,4-cyclohexanedimethanol (EGA), thionyl chloride (Merck), benzyl chloride (May and Baker), benzoyl chloride (Merck), *trans*-1,4-cyclohexanedicarboxylic acid (99% T) (EGA), ethyl 4-hydroxybenzoate (Fluka), silica 60 for column chromatography (Merck), and TLC plates (silica 60 F_{254}, 5 × 10 cm) (Merck). The 1,2-, 1,4-, and 1,5-alkanediols were distilled, and the 1,6-, 1,8-, and 1,10-alkanediols were recrystallized before use. Pyridine was distilled and kept over KOH. Palladium black was prepared according to a literature procedure[22] from palladium(II) chloride (Carl Roth KG).

***trans*-1,4-Cyclohexanedicarbonyl Chloride.** This was prepared according to Malachowski et al.:[23] mp 66–67 °C [lit.[23] mp 67 °C].

4-(Phenylmethoxy)benzoyl Chloride. This was prepared from 4-(phenylmethoxy)benzoic acid[24] according to a procedure described in the literature:[25] mp 104–107 °C [lit.[25] mp 105–106.5 °C].

***trans*-1,4-Cyclohexanedimethanol.** The commercial cis/trans mixture of 1,4-cyclohexanedimethanol was separated according to a procedure described in the literature.[23,26] 1,4-Cyclohexanedimethanol was refluxed with an excess of benzoyl chloride for 30 min. The benzoic acid *trans*-1,4-cyclohexanediylbis(methylene) ester was isolated by fractional crystallization from EtOH and Et_2O: mp 122–124 °C [lit.[23,26] mp 125 °C]. HPLC, system 1: The trans and cis esters were well separated with retention times of 317 and 448 s, respectively. The purity of the ester was (99.3% trans, 0.7% cis). Debenzoylation was effected by reflux with 20% KOH/MeOH for 50 min. Recrystallization was from anhydrous Et_2O: mp 64–67 °C [lit.[23] mp 67 °C; lit.[26] mp 66 °C].

Bis[4-(ethoxycarbonyl)phenyl] *trans*-1,4-Cyclohexanedicarboxylate, 1. Ethyl 4-hydroxybenzoate (3.32 g, 0.02 mol), *trans*-1,4-cyclohexanedicarbonyl chloride (2.09 g, 0.01 mol), and pyridine (25 mL, 0.31 mol) were stirred under reflux for 24 h. Excess pyridine was removed on a rotatory evaporator, and the residue was subjected to column chromatography on silica in 10% AcOEt/CH_2Cl_2 followed by crystallization from AcOEt (60 mL)/pentane (10 mL): yield 4.33 g (92%). Phase transitions (DSC): K → N 162.5 °C, N → I 210 °C. Phase transitions (hot stage): K → N 153.5–154.5 °C, N → I 202.5–203.0 °C. HPLC, system 4: R_t: 168 s. ^{1}H NMR (60 MHz, $CDCl_3$) δ: 8.05 (4 H, d, J = 9 Hz, Ar $H_{3,5}$), 7.15 (4 H, d, J = 9 Hz, Ar $H_{2,6}$), 4.40 (4 H, q, J = 7 Hz, CH_2), ~2.5 (2 H, m, cyclohexane $H_{1,4}$), ~2.3 (4 H, m, cyclohexane $H_{2,3,5,6}$(eq)), ~1.7 (4 H, m, cyclohexane $H_{2,3,5,6}$(ax)), 1.40 (6 H, t, J = 7 Hz, CH_3). ^{13}C NMR (22.63 MHz, $CDCl_3$), δ: 172.98 (CHC(O)O), 165.58 (ArC(O)O), 154.15 (Ar C_1), 130.94 (Ar $C_{3,5}$), 127.93 (Ar C_4), 121.30 (Ar C_2), 60.89 (CH_2), 42.27 (cyclohexane $C_{1,4}$), 27.64 (cyclohexane $C_{2,3,5,6}$), 14.15 (CH_3). IR, cm^{-1}: 1760 (s) (CHC(O)OAr), 1715 (s) (ArC(O)O). UV (CH_2Cl_2) λ_{max}, nm: 236 (log ϵ 4.48). MS m/z: 468 (M^+, 2%), 423 ($M^+ - EtO^\bullet$, 5) 303 (M^+-EtO_2C—C_6H_4—$O^\bullet$, 15), 302 (M^+-EtO_2C—C_6H_4—OH, 18), 275 (EtO_2C—C_6H_4—OC(O)—$C_6H_{11}^+$, 70), 137 (OC—$C_6H_{10}^+$—CO, 22), 121 (HO—C_6H_4—CO^+, (C_6H_{11}—CO^+, 109 (C_6H_{11}—CO^+, 60), 81 (100). Elemental analysis: Found: C, 66.66; H, 6.03; O, 27.29. Calcd for $C_{26}H_{28}O_8$: C, 66.66; H, 6.02; O, 27.32.

α,ω-Alkanediyl 4-(Phenylmethoxy)benzoates, 2a-f, and 4-(Phenylmethoxy)benzoic Acid *trans*-1,4-Cyclohexanediylbis(methylene) Ester, 2g. To a mixture of 4-(phenylmethoxy)benzoyl chloride (10.85 g, 0.044 mol) and pyridine (25 mL, 0.31 mol) was added dropwise a solution of α,ω-alkanediol (0.02 mol) in pyridine (5 mL). The reaction mixture was stirred at 80 °C. The reaction was monitored by TLC in 75% CH_2Cl_2/pentane (the diol was developed by exposure to iodine vapor). All esterifications were complete within 3–5 h. Excess pyridine was evaporated on a rotatory evaporator, and the residue was dissolved in CH_2Cl_2 (250 mL) and washed with 0.5 M HCl, 0.5 M $NaHCO_3$, and brine and then dried over $MgSO_4$ and filtered.

The CH_2Cl_2 was evaporated, and the residue subjected to column chromatography on silica in 2% $AcOEt/CH_2Cl_2$. The samples were recrystallized from $CHCl_3$/pentane. Some experimental, physical, and spectroscopic data are presented in Table III. Analytical HPLC (normal phase) gave single sharp peaks indicating that all compounds were pure. Retention times are given in Table III. As expected, the retention times decrease with increasing spacer length with a minor disturbance in the general trend for $n = 2$.

α,ω-Alkanediyl 4-Hydroxybenzoates, 3a–f, and 4-Hydroxybenzoic Acid *trans*-1,4-Cyclohexanediylbis(methylene) Ester, 3g. A 500-mL, three-necked, round-bottom flask, equipped with a magnetic stirrer, a gas inlet, a thermometer, and a gas outlet, was charged with α,ω-alkanediyl 4-(phenylmethoxy)benzoate, **2** (0.01–0.02 mol), and dioxane (250–400 mL). To the stirred solution was added 1–2 g of palladium black, and the temperature was adjusted to 35 °C. The solution was deaerated with a nitrogen stream, and then a slow stream of hydrogen was passed through the system. The reaction was monitored by TLC in 75% CH_2Cl_2/PE and in Et_2O. After some time (~2 h), two spots showed up on the TLC (Et_2O) together with the starting material, but at the end of the reaction, only one (the lower) spot remained. For reactions a–f, the reaction was completed within 24 h, but in the case of g, a reaction time of 60 h was needed. The palladium black was filtered off on a sintered glass filter and washed thoroughly with warm EtOH and stored under H_2O. The solvent as evaporated on a rotatory evaporator and the residue purified by recrystallization from EtOH/PE or EtOH/H_2O. Some experimental, physical, and spectroscopic data are presented in Table IV. Analytical HPLC (normal phase) indicated that all compounds were pure. The retention times are given in Table IV. As expected, the retention times decrease almost linearly with increasing spacer length.

Polymers of *trans*-1,4-Cyclohexanedicarboxylic Acid, 4a–f, with α,ω-Alkanediyl 4-Hydroxybenzoates and Polymer of *trans*-1,4-Cyclohexanedicarboxylic Acid, 4g, with 4-Hydroxybenzoic Acid *trans*-1,4-Cyclohexanediylbis(methylene) Ester. A 25-mL, one-necked, round-bottom flask equipped with magnetic stirring was charged with α,ω-alkanediyl 4-hydroxybenzoate, **3a–f**, or 4-hydroxybenzoic acid *trans*-1,4-cyclohexanediylbis(methylene) ester, **3g** (1.5 mmol), *trans*-1,4-cyclohexanedicarbonyl chloride (0.314 g, 1.5 mmol), 1,1,2,2-tetrachloroethane (10 mL), and pyridine (1.19 g, 15 mmol), and stoppered. The reaction was monitored by TLC in 30% $AcOEt/CH_2Cl_2$. All the reactions were completed within 24 h. When the α,ω-alkanediyl 4-hydroxybenzoate had been consumed, the rather viscous reaction mixture was added dropwise to EtOH (250 mL) with vigorous stirring for an additional 30 min. The precipitate which formed was filtered off on a sintered glass filter (G-3), applying only weak vacuum, washed with EtOH and acetone, and then dried in a vacuum desiccator. Some experimental and physical data are presented in Tables I and II, and some analytical and spectroscopic data are presented in Table V. Analytical HPLC (normal phase, system 4) gave complex chromatograms, but generally the chromatograms were composed of a low-retention time part showing sharp individual peaks together with a continuum of peaks and a high retention time part showing a broad unresolved peak. Since the separation is governered mainly by polarity, it is suggested that the first part of the chromatograms consists of polymers having 4-hydroxybenzoate end groups and the fine structure arises because of polymer length differences and the second part consists of polymers having cyclohexanecarboxylic acid end groups.

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Registry No. **1**, 110223-49-9; **2a**, 110223-50-2; **2b**, 110223-51-3; **2c**, 110223-52-4; **2d**, 110223-53-5; **2e**, 110223-54-6; **2f**, 110223-55-7; **2g**, 110223-56-8; **3a**, 3236-64-4; **3b**, 24293-34-3; **3c**, 24293-35-4; **3d**, 24293-32-1; **3e**, 78644-26-5; **3f**, 70187-38-1; **3g**, 110223-57-9; **4a** (copolymer), 110223-63-7; **4a** (SRU), 110223-58-0; **4b** (copolymer), 99634-87-4; **4b** (SRU), 99627-44-8; **4c** (copolymer), 110223-64-8; **4c** (SRU), 110223-59-1; **4d** (copolymer), 110223-65-9; **4d** (SRU), 110223-60-4; **4e** (copolymer), 99634-88-5; **4e** (SRU), 99627-45-9; **4f** (copolymer), 110223-66-0; **4f** (SRU), 110223-61-5; **4g** (copolymer), 110223-67-1; **4g** (SRU), 110223-62-6; 4-$HOC_6H_4CO_2CH_2CH_3$, 120-47-8; 4-$PhCH_2OC_6H_4COCl$, 1486-50-6; $HO(CH_2)_2OH$, 107-21-1; $HO(CH_2)_4OH$, 110-63-4; $HO(CH_2)_5OH$, 111-29-5; $HO(CH_2)_6OH$, 629-11-8; $HO(CH_2)_8OH$, 629-41-4; $HO(CH_2)_{10}OH$, 112-47-0; *trans*-1,4-cyclohexanedicarbonyl chloride, 19988-54-6.

References and Notes

(1) Ober, C. K.; Jin, J.-I.; Lenz, R. W. *Adv. Polym. Sci.* **1984**, *59*, 103.

(2) Lenz, R. W. *J. Polym. Sci., Polym. Symp.* **1985**, *72*, 1.

(3) Ringsdorf, H.; Schneller, A. *Br. Polym. J.* **1981**, *13*, 43.

(4) Polk, M. B.; Bota, K. B.; Akubuiro, E. C.; Phingbodhipakkiya, M. *Macromolecules* **1981**, *14*, 1626.

(5) Polk, M. B.; Bota, K. B.; Nandu, M.; Phingbodhipakkiya, M.; Edeogu, C. *Macromolecules* **1984**, *17*, 129.

(6) Kwolek, S. L.; Luise, R. R. *Macromolecules* **1986**, *19*, 1789.

(7) Osman, M. A. *Macromolecules* **1986**, *19*, 1824.

(8) Tani, K.; Koide, N.; Iimura, K. *Rep. Prog. Polym. Phys. Jpn.* **1984**, *27*, 243.

(9) Sunahara, K.; Koide, N.; Iimura, K. *Rep. Prog. Polym. Phys. Jpn.* **1986**, *29*, 241.

(10) Bhaskar, C.; Kops, J.; Marcher, B.; Spanggaard, H. In *Recent Advances in Liquid Crystalline Polymers*; Chapoy, L. L., Ed.; Elsevier: London, 1985; p 79.

(11) Onwumere, F. C.; Polk, M. B. *J. Polym. Sci. Part A.: Polym. Chem.* **1986**, *24*, 2239.

(12) Deutcher, H.-J.; Vorbrodt., H.-M.; Zaschke, H. *Z. Chem.* **1981**, *21*, 9.

(13) Gray, G. W. In *Polymer Liquid Crystals*; Ceferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic: New York, 1982; p 13.

(14) Verbit, L.; Tuggey, R. L.; Pinhas, A. R. *Mol. Cryst. Liq. Cryst.* **1975**, *30*, 201.

(15) Galli, G.; Chiellini, E.; Ober, C. K.; Lenz, R. W. *Makromol. Chem.* **1982**, *183*, 2693.

(16) Mark, V. U.S. Patent 4 476 294, 1984; U.S. Patent 4 504 649, 1985.

(17) Lowrie, R. S. *Cochranes of Oxford molecular models*; Cochranes of Oxford: Oxford 1973.

(18) Ober, C.; Jin, J.-I.; Lenz, R. W. *Polym. J.* **1982**, *14*, 9.

(19) Lenz, R. W.; Jin, J.-I. *Liq. Cryst. Ordered Fluids* **1984**, *4*, 347.

(20) Lenz, R. W. *Polym. J.* **1985**, *17*, 105.

(21) Wilkinson, J. H.; Sprott, W. E.; MacLagan, N. F. *Biochem. J.* **1953**, *54*, 16.

(22) Greenstein, J. P.; Winitz, M. *Chemistry of the Amino Acids*; Wiley: New York, 1961; Vol. 2, p 1233.

(23) Małachowski, R.; Wasowska, J. J.; Jőźkiewicz, S. *Ber* **1938**, *71*, 759.

(24) Schroeder, D. C.; Schroeder, J. P. *J. Org. Chem.* **1976**, *41*, 2566.

(25) Braue, E. H.; Alexander, V. T.; Burton, L. L.; Crowell, T. I.; Devlin, C. P. *J. Am. Chem. Soc.* **1979**, *101*, 5303.

(26) Haggis, G. A.; Owen, L. N. *J. Chem. Soc.* **1953**, 404.