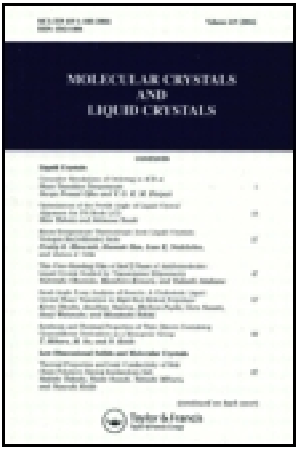

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Liquid Crystalline Polyfumarates, 1. Synthesis and Characterization of Fumarates with Two Mesogenic Groups

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Liquid Crystalline Polyfumarates, 1. Synthesis and Characterization of Fumarates with Two Mesogenic Groups

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The synthesis of fumarates with two mesogenic groups is described. The basic concept of synthesis is the coupling of phenyl benzoate derivatives containing free hydroxyl groups with fumaroyl chloride in the last step. The spacerless di-[4-(4-n-butoxybenzoyloxy)phenyl] fumarate **3** and some di-{ω[4(4-n-butoxybenzoyloxy)benzoyloxy]alkyl} fumarates **7** with increasing number of alkyl groups in the spacer, between C_2 and C_8, were synthesized. The phase behaviour of the (ω-hydroxyalkyl)-4-(4-n-butoxybenzoyloxy)-benzoates **6** and the fumarates **3** and **7** was investigated by polarizing microscopy and differential scanning calorimetry (DSC). The spacerless fumarate **3** shows a liquid crystalline (lc) phase above the melting point up to decomposition. The mesomorphism of hydroxyl-terminated precursors **6** depends on spacer length. Whereas the compounds with the shortest and the longest spacer only show a monotropic lc phase the others form an enantiotropic smectic one. Among the fumarates **7** only those with C_4 and C_6 spacer exhibit a monotropic smectic phase. The complex melting behaviour of these fumarates is discussed. The synthesized fumarates are intended for investigations on homo- and copolymerization behavior.

Keywords: Liquid crystals, fumarates, phenyl benzoates, phase behaviour, differential scanning calorimetry (DSC).

INTRODUCTION

The research on side chain liquid crystalline polymers (SCLCP) suffered an important progress during the last 15 years. A number of polymers was synthesized and characterized not only from a theoretical point of view but also for some practicable applications[1–4]. There is still a large interest to get more information about the influence of molecular structure of the polymers on the formation of lc phases. We focused our work on the synthesis and the polymerization of fumarates with two mesogenic groups. The resulting polymers are relatively rigid and have an unusual high density of mesogenic groups along the main chain. Polymers of analogous itaconates[5–7] or SCLCP with so called paired mesogens[1] show a similar density of mesogenic groups.

There are only few reports in the literature concerning with the synthesis and polymerization of lc fumarates. The fumarates listed in the standard work on liquid crystals by Demus and Zaschke[8,9] are not suitable for researches on SCLCP. These compounds were obtained by the reaction of fumaroyl chloride with substituted phenols. In such fumarates the double bond of the fumaric units is an essential constituent of the mesogenic group. Consequently, polymerization would result in the formation of products which could not exhibit lc properties.

Sugiyama *et al.*[10–18] reported on the synthesis and polymerization of some alkyl fumarates with one mesogenic group per unit. They synthesized the fumarates by the reaction of fumaroyl chloride monalkyl esters with suitable mesogens and investigated the lc properties of the compounds. The mesogens used were substituted azobenzenes, azomethines and phenylbenzonates. They found a dependence of the nature of alkyl ester group on the phase behaviour. The fumarates with unbranched alkyl ester groups showed enantiotropic nematic phases. The stability of mesophase decreased with increasing alkyl length. Branched alkyl ester groups decreased the stability of the nematic phase drastically. These fumarates did not homopolymerize which is attributed to the hindered propagation by the steric effect of bulky mesogens directly fixed at the double bond. Fumarates with an alkyl spacer (C_6 and C_{11}, respectively) between mesogenic group and fumaric unit did not show lc phases; however, SCLCP were obtained by the homopolymerization of these fumarates.

Chiellini *et al.*[19] reported on the synthesis of unsymmetric fumarates containing an ethyl ester group and one azobenzene or phenylbenzoate derivative. Only the azobenzene containing fumarates showed a monotropic nematic phase. By copolymerization of the fumarates with mesogenic vinyl ethers they obtained SCLCP which exhibited an enantiotropic nematic phase.

It was our goal to synthesize fumarates with two phenyl benzoate groups and to investigate the influence of spacer length on the thermal properties. Additionally, the polymerization behavior of such fumarates and the properties of the obtained polymers were investigated. In this paper the synthesis and the thermal properties of the hydroxyl-terminated precursors **6** and the fumarates **3** and **7** are presented. The results of the polymerization experiments are reported elsewhere[20,21].

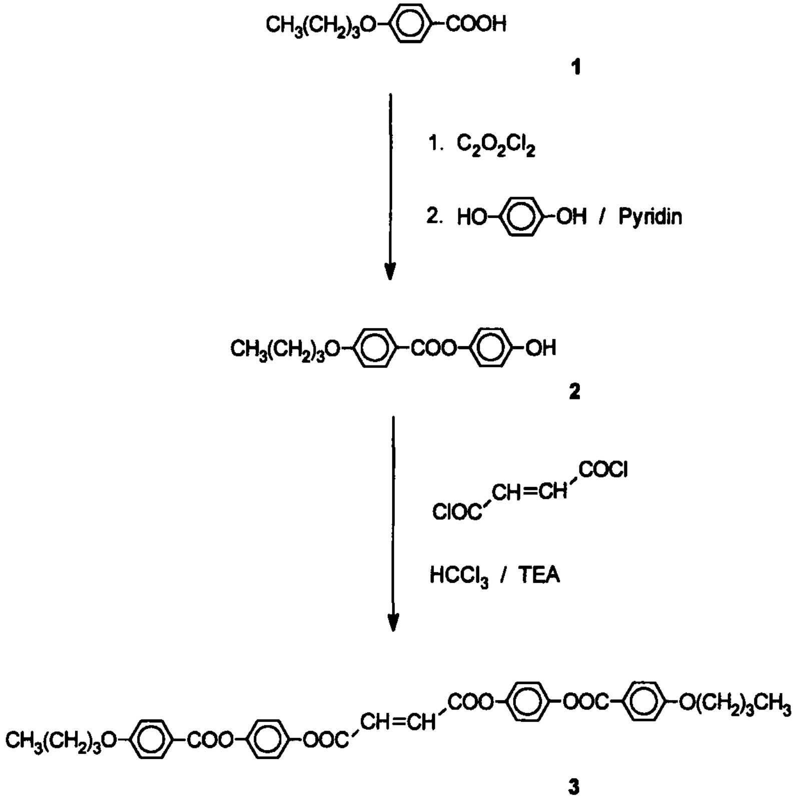
RESULTS AND DISCUSSION

Synthesis of the Fumarates

At first a spacerless fumarate was synthesized as shown in Scheme 1. The fumarate **3** is less soluble in common solvents. It has a m.p. of 209–210.5°C and shows a lc phase above that temperature. Isotropization could not be observed until decomposition at about 250 °C. The textures appeared under the microscope resemble those of a smectic phase, see Figure 1.

For further research some fumarates with a spacer between the phenylbenzoate group and the fumaric unit according to Scheme 2 were synthesized. The concept was to build up a hydroxyl-terminated mesogenic group and to couple it with fumaroyl chloride in the last step. The yields and phase transitions of the obtained compounds are listed in Table 1.

4-(4-n-butoxybenzoyloxy)-benzoic acid **5** was synthesized via aldehyde intermediate stage **4**[22] with relatively high yields. During heating the aldehyde **4** showed a nematic



SCHEME 1 Synthesis of di-[4-(4-n-butoxybenzoyloxy)phenyl] fumarate 3.

phase and decomposed without clearing. A similar behaviour was described for the analogous methoxy compound[8]. Oxidation of the aldehyde group was performed with $KMnO_4$ in pyridine/water according to ref.[23]. The resulting acid **5** formed a nematic phase after melting. However, onset of decomposition was observed before the melting point was reached.

The next step was the reaction of the acid chloride of **5** with the alkane diols. Small amounts of the respective diester were obtained as undesirable side products. The formation of side products could be influenced by the temperature, rate of chloride addition (slowly) and vigorous stirring. A simple way for the complete removal of the side products was found. The monoesters were completely soluble in methanol, whereas the diesters were insoluble. In the last step the mesogenic group was coupled with fumaroyl chloride. The purity of all compounds was checked by size exclusion chromatography (SEC) and the structures were confirmed by ^1H and ^{13}C NMR.

Phase Behaviour

The phase behaviour was investigated by polarizing microscopy and DSC. The transition temperatures measured by DSC are listed in Table 1. The phase behaviour of the alcohols **6** depends on the spacer length. The compounds with the shortest (**6a**) and

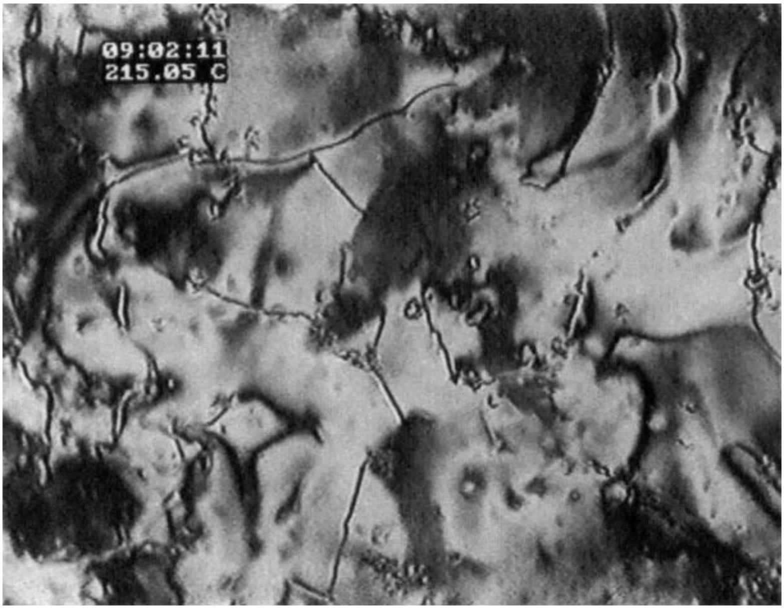


FIGURE 1 Textures of spacerless fumarate **3** at 215°C (magnification, 330x.) See Color Plate VIII.

with the longest spacer (**6d**) show a monotropic lc phase, whereas the compounds with medium spacer length (**6b** and **6c**) exhibit an enantiotropic lc phase. Cooling of the alcohol compounds from the isotropic state resulted in the development of smectic textures, see Figures 2a and 2b. The observed textures of **6c** and **6d** are similar to those of **6b**. The DSC curves confirmed the microscopic observations.

First attempts were performed to characterize the mesophases by X-ray measurements. Unoriented samples of **6b** and **6c** showed an amorphous halo at the wide-angle region and sharp reflections in the small-angle region typical of a smectic phase. It was impossible to determine the nature of the monotropic lc phases of **6a** and **6d** because they recrystallized during the measurement.

The observed phase behaviour is in keeping with the trends obtained for other homologous series of lc compounds[8,9]. The spacer group in **6** acts like a terminal group. The stability of mesophase increases with increasing length of alkyl spacer up to C_4. It seems to be an optimum. Further increase results in a decrease of the stability of mesophase. Only the products with an even number of CH_2 groups in the molecule were synthesized.

During the second heating scan compound **6c** shows some additional peaks at approximately 54 °C. We assume that there are the following simultaneously running processes. First a crystallization of some non-crystallized material occurs. By heating the material becomes more mobile and crystallization occurs. Second a partially melting of the compound takes place. This could be attributed to the existance of a metastable modification melting at this temperature. The alcohol **6d** shows an additional weak exothermic peak at 44 °C . This may also be attributed to a non-

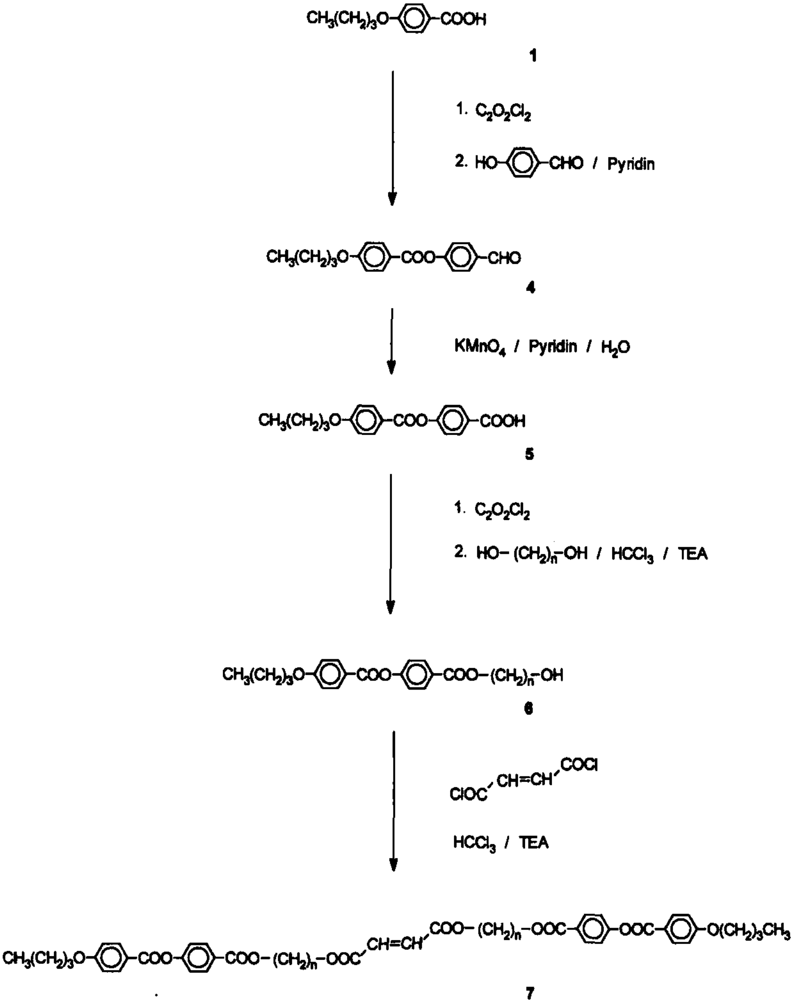
1 Phase transitions of hydroxyl-terminated mesogenic groups **6** and fumarates **7**

ound	Spacer	Yield in %	Empirical formula (molecular mass)	Phase transitions in °C (ΔH in J/g)	
				heating	cooling
	C_2	75	$C_{20}H_{23}o_6$ (359.4)	k 104,9 (80,8) i k 104,6 (75,2) i	i 96,0 (– 19,4) s_X 64,7 (– 43,6)$^{a)}$
	C_4	67	$C_{22}H_{27}O_6$ (387.45)	k 67,6 (73,8) s_X 90,3 (17,8) i k 67,3 (71,3) s_X 90,3 (17,7) i	i 86,5 (– 18,0) s_X 33,1 (– 54,2) k
	C_6	75	$C_{24}H_{31}O_6$ (415.51)	k 77,1 (121,9)$^{a)}$ s_X 79,1 i k 76,4 (118,0)$^{a)}$ s_X 78,9 i	i 74,6 (– 15,6) s_X 28,9 (– 53,9) k
	C_8	58	$C_{26}H_{35}O_6$ (443.56)	k 77,7 (138,3) i k 77,1 (135,1) i	i 65,4 (– 17,9) s_X 43,8 (– 84,4) k
	C_2	47	$C_{44}H_{44}O_{14}$ (796.82)	k 156,3 (68,6) i k 154,5 (66,0) i	i 102,1 (– 51,2) k
	C_4	51	$C_{52}H_{60}O_{14}$ (852.93)	k_1 95,7 (45) k_2 108,8 (44,4) i$^{b)}$ k 110,3 (65,1) i	i 79,6 (– 14,8) s_X 61,1 (– 45,6) k
	C_6	24	$C_{52}H_{60}O_{14}$ (909.04)	k_1 80,8 (37,5) k_2 105,5 (69,6) i$^{c)}$ k_1 104,5 (52,6) k_2 104,5 (18,7) i	i 69,4 s_X 54,5 (– 63,1) k$^{a)}$
	C_8	65	$C_{56}H_{68}O_{14}$ (965.15)	k 99,6 (103,3) i k 96,6 (97,6) i	i 83,1 (– 96) k

was only detectable for both transitions.

°C (– 4,6 J/g) recrystallized a small amount of molten sample.

°C (– 24.0 J/g) recrystallized a small amount of molten sample.



n	2	4	6	8
	6a	6b	6c	6d
	7a	7b	7c	7d

SCHEME 2 Synthesis of di-{ω[4-(4-n-butoxybenzoyloxy)benzoyloxy]alkyl} fumarates 7.

complete crystallization during the cooling scan as already discussed above. Further cooling and heating scans give similar results. One can observe this phenomena also by microscope.

The fumarates **7** exhibit a more complex melting behaviour. The furmarates **7b** and **7c** form monotropic lc phases. The textures developed by cooling from the isotropic state, Figure 3, are similar to those of the corresponding alcohols **6b** and **6c**. It is assumed that these fumarates form a smectic phase too. The lc phases were not detectable by X-ray measurements. The products crystallized during the measurements.

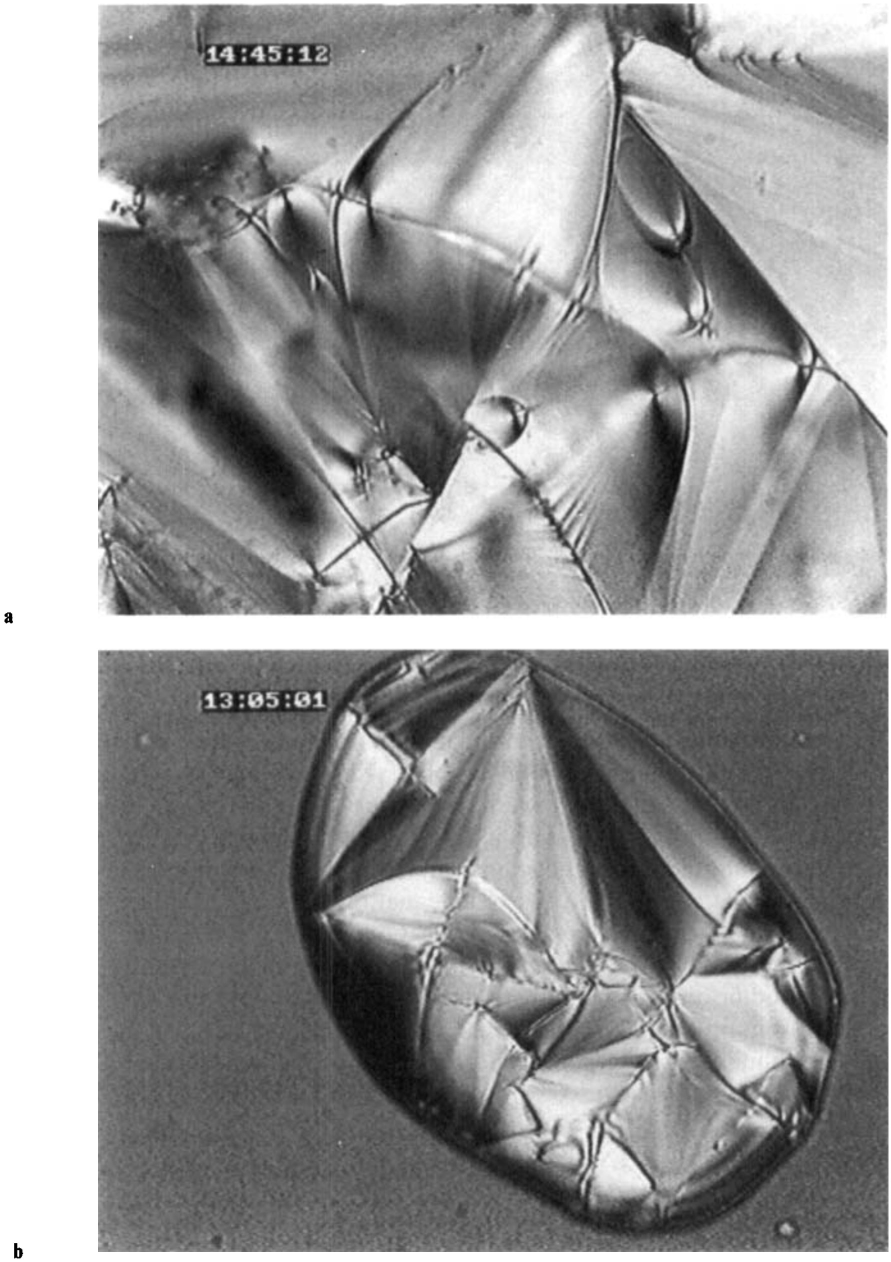


FIGURE 2 Textures of hydroxyl-terminated mesogenic groups a) compound **6a** at 85°C (cooled from 110°C, magnification: 330 x) b) compound **6c** at 80°C (cooled from 100°C, magnification: 330x). See Color Plate IX.

By first heating of **7b** a partial melting of the material at approximately 95 °C and simultaneous a crystallization of the product occurs. Sometimes only a change of the textures in the solid state was observed. The isotropization temperature was above 100 °C. On cooling a transition into a lc phase followed by crystallization was observed.

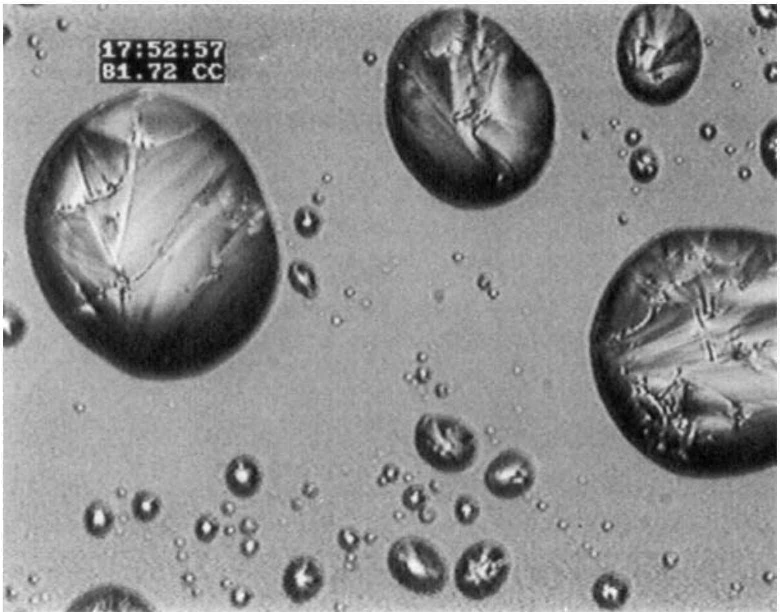


FIGURE 3 Textures of fumarate **7b** at 82°C (cooled from 115°C, magnification: 330x). See Color Plate X.

During the second heating only a small part of material melted at 95 °C. The main part melted above 100 °C. A similar behaviour was observed for the fumarate **7c**, however, the phase transitions were shifted to lower temperatures. Sometimes these transitions could be observed only partly. It was impossible to prepare a defined state by annealing. The amount of molten and solid sample varied. It depends on the heating and cooling conditions, respectively. We assume that these behaviour is attributed to the existence of some metastable crystal modifications. Their formation depends on heating or cooling conditions. They melt during the first heating or a transition from the metastable modification into an other state occurs in the solid state.

The investigations on polymerization behaviour of these fumarates and the characterization of the obtained polymers are reported elsewhere[20,21].

EXPERIMENTAL PART

Measurements

The ^1H and ^{13}C NMR spectra were recorded on a Bruker WH-90 (^1H :90.01 Hz) and on a AMX- 300 NMR spectrometer operating at 300.13 MHz for ^1H and 75.47 MHz for ^{13}C, respectively, using $CDCl_3$ or CD_2Cl_2 as solvent and tetramethylsilane as internal standard.The purity of the reaction products was checked by SEC. The measurements were performed using a Knauer modular system equipped with Rl and UV detection and with special columns for low molecular mass substances (LiChrogel PS1, PS4, PS 40 Hibar Merck) at ambient temperature. Tetrahydrofurane was used as solvent and eluent (concentration: 0.2g/ml). The phase behaviour was investigated by polarizing microscopy and DSC. Polarizing microscopy was performed by a Carl- Zeiss microscope (magnification: 330 x) equipped with a Mettler FP84HT and a Mettler FP90 cantral processor. The samples were prepared between untreated glass slides. The thermal analyses were carried out under nitrogen using a Perkin Elmer DSC-7, heating and cooling rate 10 K/min. The transition temperatures were reported as the maxima and minima of the endothermic and exothermic peaks, respectively. For comparison of different samples the DSC curves were normalized.

Reagents

4-n-Butoxybenzoic acid (Aldrich), hydroquinone, 4-hydroxybenzaldehyde, oxalyl chloride (Merck) and the solvents were used in commercial p.a. quality without further purification. Chloroform was distilled over P_4O_{10}. Fumaroyl chloride was distilled in vacuum. Pyridine and triethylamine were refluxed over CaH_2 and freshly distilled prior to use. The diols were distilled over K_2CO_3.

Materials

4-n-Butoxybenzoyl chloride: 29.1 g (0.15 mol) 4-n-butoxybenzoic acid **1** and 50 ml oxalyl chloride were mixed and refluxed for 30 min after evolution of gas. The unreacted oxalyl chloride was removed and the residue distilled under reduced pressure. Yield 90%,

b.p. 172–173 °C(15 Torr) $C_{11}H_{13}O_2Cl$ 212.68 g/mol

(4'-Hydroxyphenyl)-4-n-butoxybenzoate **2**: it was synthesized according to the literature[24,25]. Yield 50%,

m.p. 142–143.5 °C $C_{17}H_{18}O_4$ 286.33 g/mol

^{1}H-NMR (90 MHz, $CDCl_3$): $\delta = 0.99$(t); 1.20–2.00(m); 4.04(t); 5.71 (s); 6.71(d); 6.75(d); 6.99(d); 8.12(d) ppm.

Di-[4-(4-n-butoxybenzoyloxy)phenyl] fumarate **3**: 2.86 g(10 mmol) **2** and 1.42 ml (10.5 mmol) TEA were dissolved in 200 ml $CHCl_3$ and cooled to 5 °C. 0.795 g (5.2 mmol) freshly distilled fumaroyl chloride in 5 ml $CHCl_3$ was added dropwise to this solution. The mixture was stirred for 4 h at this temperature and then for 6 h at room temperature. After washing with aqueous solution of $NaHCO_3$ and finally with water the $HCCl_3$ was evaporated. The crude product was purified by repeated recrystallization from benzene. Yield 1.4 g (40%),

phase transitions: k 209–210.5 lc, clearing point above dec.p.

$C_{38}H_{36}O_{10}$ 652.27g/mol

^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.00$ (t); 1.54 (m); 1.82 (quintet); 4.06 (t); 6.98 (d); 7.252 (s); 7.254 (d); 7.26 (d); 8.14 (d) ppm.

^{13}C-NMR(75.47 MHz, $CDCl_3$): $\delta = 13.8$; 19.3; 31.2; 68.2; 114.5; 121.5; 122.1; 122.9; 132.4; 132.5; 147.7; 149.0; 163.0; 163.8; 164.6 ppm.

4-(4-n-Butoxybenzoyloxy) benzoic acid **5**: A modified synthesis according to ref.[26] was used. 23.4g (0.11 mol) 4-n-butoxybenzoyl chloride were added to a solution of 12.21 g (0.1 mol) 4-hydroxybenzaldehyde in 280 ml pyridine at temperatures between 0 and −5°C. The mixture was stirred for 5h and then the product was precipitated into

HCl/ice water. The crude product was dissolved in ether and extracted with aqueous solution of $NaHCO_3$ and finally with water. After evaporation of ether the aldehyde **4** was recrystallized from hexane. The following oxidation was carried out according to ref.[27]. 5.93g (37.5 mmol) $KMnO_4$ in 50 ml pyridine and 100 ml water were dropped to a vigorously stirred solution of 14.92 g (50 mmol) **4** in 350 ml pyridine at 0 °C. Stirring was continued for 5 h. After standing over night the product was precipitated into an excess of HCl/ice water containing oxalic acid. The isolated substituted benzoic acid **5** was purified by repeated recrystallization from toluene.

Yield 70% (both steps)

phase transitions: k 199–200.5 n (dec.), clearing point above dec.p.

$C_{18}H_{18}O_5$ 314.34 g/mol

^{1}H-NMR (90 MHz, $CDCl_3$): $\delta = 1.00$(t); 1.13–2.0(m); 4.07(t); 6.99(d); 7.35(d); 8.16(d) ppm.

(ω-Hydroxyalkyl)-4-(4-n-butoxybenzoyloxy)-benzoates **6**: 6.29 g(20 mmol) **5** and 25 ml oxalyl chloride were mixed and refluxed for 30 min after evolution of gas. The unreacted oxalyl chloride was completely removed under reduced pressure. The residue was dissolved in 50 ml $CHCl_3$ and then dropped to a vigorously stirred solution of 176 mmol alkane diol in 290 ml $CHCl_3$ and 2.07 g (20.5 mmol) TEA at 28–45 °C depending on diol. The mixture was stirred for additional 4 h. The solvent was distilled off and the crude product was washed with warm water for removing unreacted diol. The remaining solid was dissolved in ether and extracted with aqueous solution of $NaHCO_3$ and finally with water. The ether was evaporated and the solid was washed with small amounts of warm methanol for removing side products like diester. The insoluble diester was separated from the solution. After evaporation of methanol the residue was recrystallized from hexane or cyclohexane. Sometimes it was necessary to repeat this procedure till the product was free from impurities. The purity was > 99.5% (checked by SEC). The yields, empirical formulas and phase transitions of the alcohols **6** are listed in Table 1. The ^{1}H-NMR spectra of **6a**, **6b** and **6d** (90 MHz, CD_2Cl_2) are similar to that of **6c**.

(6-Hydroxyhexyl)-4-(4-n-butoxybenzoyloxy)-benzoate **6c**:

^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 1.00$ (t); 1.33–1.55 (m); 1.80 (m); 3.66 (t); 4.06 (t); 4.33 (t); 6.97 (d); 7.29 (d); 8.11 (d), 8.13 (d) ppm.

Di-{ω[4(4-n-butoxybenzoyloxy)benzoyloxy]alkyl} fumarates **7**:

0.76 g (5 mmol) freshly distilled fumaroyl chloride in 10ml $CHCl_3$ was dropped (about 1 h) to a solution of 10.4 mmol alcohol **6** in 50 ml dried $HCCl_3$ at temperature between -3 and -10 °C. Then a mixture of 1.03 g (10.2 mmol) freshly distilled TEA and 10 ml $CHCl_3$ was added dropwise (about 2 h) at the same temperature. After stirring for 2 h the solution was allowed to warm to ambient temperature and stirring was continued for additional 5 h. The solvent was evaporated and the residue was dissolved in ether (**7b**, **7c**) or benzene (**7a**, **7d**). The mixture was extracted with aqueous solution of $NaHCO_3$ and finally with water. Subsequently the solvent was evaported. The obtained product was washed with little amount of methanol for removing unreacted **6**. Then it was recrystallized from cyclohexane. The purification was repeated till the product was free from impurities. The purity was > 99.5% (checked by SEC). The yields, empirical formulas and phase transitions of the fumarates **7** are listed in Tab. 1. The ^{1}H-NMR spectra of **7a**, **7b** and **7d** (90 MHz, CD_2CL_2) are similar to that of **7c**.

Di-{6[4(4-n-butoxybenzoyloxy) benzoyloxy]hexyl} fumarate (**7c**):

^{1}H-NMR (300 MHz, CD_2CL_2) $\delta = 1.00$(t); 1.42–1.55(m); 1.73(m); 1.81(m); 4.06(t); 4.21(t); 4.33(t); 6.85(s); 6.97(d); 7.29(d); 8.11(d); 8.13(d) ppm.
^{13}C-NMR (75.47 MHz, $CDCl_3$):$\delta = 13.8$; 19.2; 25.6; 25.7; 28.5; 28.7; 31.1; 64.9; 65.3; 68.1; 114.1; 121.1; 121.8; 127.9; 131.1; 132.4; 133.6; 154.8; 163.6; 164.4; 165.0; 165.9 ppm.

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